A metallurgical investigation of the formation of silver beads during cupellation of a 925 ‰ silver alloy

Otto Lohne and Pål Ulseth

Department of Materials Science and Engineering, NTNU, Trondheim, Norway

Abstract

In the late 15th century and first half of 16th century, the moneyer in the Archbishop's Palace in Nidaros (present-day Trondheim) struck coins for the last three Norwegian archbishops of Nidaros in the period AD 1475–1537. In his profession he would have had to master how to make bullion with the correct silver content for the coins. This raises the question of to what degree of accuracy could be achieved in the measurement of the silver content with the use of bone-ash cupels at that time. To address this question the authors made replica bone-ash cupels from scratch and performed cupellation experiments on a silver alloy with known composition. Both the annealing time at 900°C and the cooling rate were varied. The results of the experiments were used to create a model of the metallurgical processes that took place during annealing and cooling. One important result was that the silver bead, which resulted from the cupellation process, was not pure silver once the 'flash' had been observed. However, the authors suggest that with prolonged annealing and slow cooling, the bead may become close to having a content of pure silver, depending upon type of impurities in the silver.

Introduction

The main sources of income of the last three archbishops of Nidaros (present-day Trondheim), Gaute Ivarsson (1475–1510), Erik Valkendorf (1510–1522) and Olav Engelbrektssson (1523–1537), were tithes, land rents and royal revenues which were collected as *lensherre* (suzerain) in Trøndelag (including land rent, fines, and *leidang*[1]), as well as trade surplus on trading, especially stockfish from the north of Norway. Almost all income from land rents and tithes were paid in kind, such as corn, malt, meat, fish, and furs (Nissen, 1998). However, most fines were paid in money or silver. To evaluate the value of the precious materials paid as fines it was important to have knowledge and the necessary tools for measuring the quality of precious metals.

In the Halmstad-recess of 1483, the protocol conditioning King Hans' election as king of Norway, one of several concessions was the King's reconfirmation and reinstatement of the privilege of the archbishop of Nidaros to strike coins of the same quality as the coins issued by the King. As a consequence, the last three archbishops had the privilege to issue coins. During the archaeological excavations of the Archbishop's Palace in 1991–1995, three mint complexes were found, one above the other (McLees, 1996; Saunders, 2001; Nordeide, 2003; Lohne et al., 2010). The mints have been documented as having been in operation from about AD 1500–1537 (Olsson, 2000). Among a large number of metalworking debris, 174 used

---

[1] The *leidang* (Old Norse: *leiðangr*) was the organization of the coastal defense, which included ships, crews and provision for a certain amount of time. Around AD 1200m the *leidang* was converted into a fixed tax and by the mid-1300s the *leidang* was a fixed tax on properties in both urban and rural areas.

bone-ash cupels and cupel fragments were found (Sunders 2001).[2] The total has since been increased to 186 (Risvaag et al., 2021, this volume). The finds show that fire assay by cupellation was quite common at the Mint in the first half of the 16th century. Therefore, it can be assumed that the moneyer had the ability to make cupels and measure the silver content of the coins produced in the Mint (Lohne et al., 2021).

Furthermore, we know that in 1532 the archbishop's moneyer in Nidaros, Jacob Schult, was commissioned by King Christian II to assay the silver being used for mountings on St. Halvard's shrine, possibly because the King needed silver to pay his soldiers. In a letter written in Nidaros on 6 November 1532, Jacob Schult presented the results of his assaying as follows: 'The Mark to contain 15 Lod and 6 gren' (our translation) (DN, X No. 640). If we use 1 mark = 16 lots and 1 lot = 18 grains (Ercker (1951 (1574) p.37) it follows that the metal assayed by Jacob Schult was 958 ‰ silver. Thus, the moneyer had the ability to measure the silver content of silver alloys and enjoyed a high reputation, given that he was commissioned by the King to carry out the analysis. To what degree of accuracy could the silver content in silver alloys be measured in the medieval times?

The main steps in the cupellation process are described by Lohne et al. (2021, this volume), whose main finding is that the melting of a silver alloy together with about ten times as much lead in a bone-ash cupel may end up with a bead of almost pure silver after annealing at 900°C. The percentage of silver in the starting material can be found by dividing the weight of the final bead, assuming it is pure silver, by the weight of the starting material, and multiplying the sum by 100. However, the surface appearance and internal microstructure of the bead will vary according to the chemistry of the tested material, the annealing time and the cooling rate. We investigated the external shape and internal microstructure of the beads in order to reveal the metallurgical processes that take place during the annealing and cooling, and thus to evaluate the parameters that determine the fineness (i.e. purity) of the silver in the beads.

Experiments

Replica bone-ash cupels (Lohne et al., 2021, this volume) were used in several experiments to investigate the external shape and the internal microstructure of the silver beads after cupellation of a 925 ‰ silver alloy. The material used comprised cut-offs from gating systems after casting silver jewellery in a silversmith's workshop. Fig. 1 shows a pair of replica bone-ash cupels. The outer upper rim diameters are c.35 mm and the bowls have a fine-grained surface layer – 'facing'.

Figure 1. Replica bone-ash cupels. Dimensions of paper squares: 5 × 5 mm (Lohne et al., 2021, this volume).

---

[2] S. Bergstøl and S.W. Nordeide pers. comm. 1993

A piece of thin lead plate was folded around pieces of the silver alloy, in which the silver weighed 0.15–0.38 g and the lead weighed about nine times the weight of the silver (i.e. c.1.35–3.42 g). The object was put into a pre-heated cupel, which was placed in a ceramic vessel in a furnace operating at 900°C (Fig. 2a). The annealing temperature was selected according to the ASTM proposal for gold in bullion in *ASTM E1335 - 08(2017): Standard Test Methods for Determination of Gold in Bullion by Fire Assay Cupellation Analysis* (ASTM International). The effect of annealing at other temperatures than 900°C was not investigated.

Annealing time in the experiments varied from a few minutes to 30 minutes. After annealing, the cupels were cooled at various rates: rapid cooling by taking the vessel with the cupel straight out of the furnace and let it cool down on a table at room temperature or slow cooling by turning off the heating in the furnace and later partially opening the furnace door. The cooling rate of the beads was not recorded. However, the cooling rate of the air when slowly cooled was measured with a thermocouple in the vicinity of the vessel and was of the order of 10°C per minute down to 800°C and thereafter slower until the temperature was the same as room temperature.

Silver beads (Fig. 2b) were removed from the cupels and investigated by using a scanning electron microscope (SEM) equipped with energy dispersive x-ray spectrometer (EDS). Some beads were cast in EpoFix resin and the cast was cut by a saw with a diamond-bound cutting wheel and cut surface was ground and polished. The specimens were carbon coated before being investigated using the SEM and an electron probe microanalyser (EPMA) equipped with wavelength dispersive x-ray-spectrometers (WDS). EDS and WDS were used to measure the chemical compositions of small areas (e.g. microscopic particles) on the surface of the specimens.

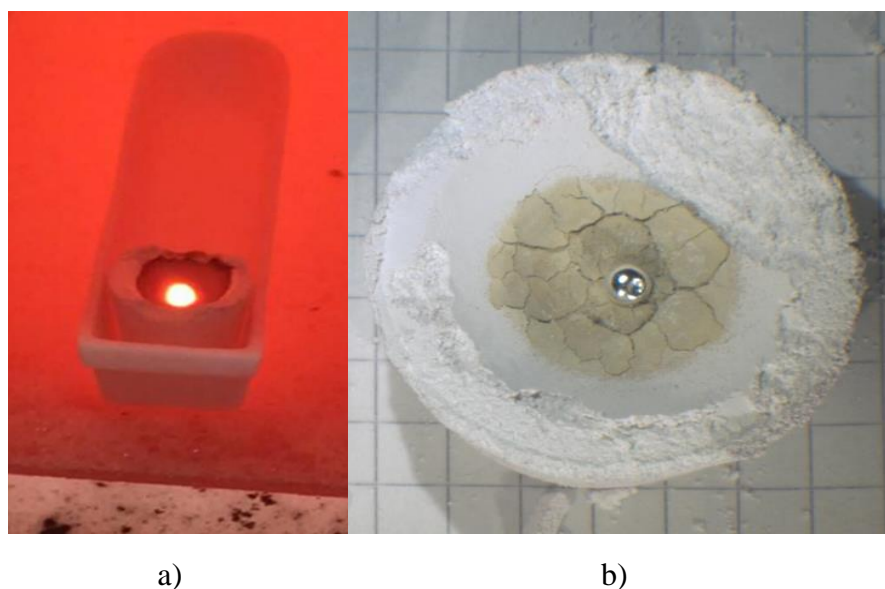a)   b)

Figure 2. a) The cupel in a ceramic vessel is viewed through a quartz glass window in the furnace door. The yellowish white pool is the melt of lead and silver. b) The cupellation process results in a shiny silver bead at the bottom of the cupel. The cracks in the facing layer appeared during the cooling. Dimensions of paper squares: 5 × 5 mm.

We conducted three tests:

1) Short annealing at 900°C (a few minutes) and rapid cooling (as described above in this section)
2) Short annealing at 900°C (after c.5 minutes, when a 'flash' was observed) and cooling (slower than rapid, but not slow).
3) Long annealing, 30 minutes at 900°C, and slow cooling. The vessel was lightly tapped at the end of the annealing and twice during cooling, as suggested in the ASTM Standard E1335 – 08(2017) (ASTM International). Weight of material at the start of the test: 0.3808 g. Weight of the bead: 0.3486 g (without cleaning off lead oxide). Diameter of bead: c.4 mm.

Results

Surface appearance

Short annealing at 900°C and rapid cooling: *SEM image of the bead is shown in Fig. 3.*
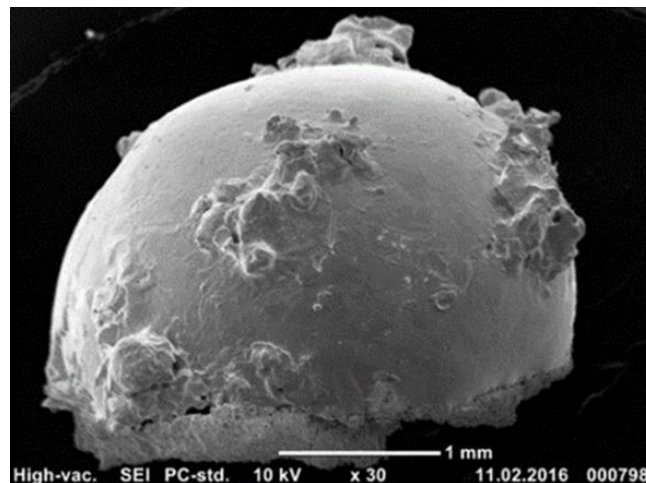
Figure 3. SEM image of the hemispherical bead after annealing for a few minutes at 900°C and rapid cooling. Exhaled melt from the inside of the bead has solidified on the surface. Spitting is a well-known effect when pure silver solidifies, as liquid silver contains much more oxygen than solid silver at equilibrium. Oxygen must therefore be rejected during solidification.

Long annealing at 900°C and slow cooling: Figures 4–8 show how lead oxide was squeezed out onto the surface at grain boundaries. The lead oxide contained some copper.
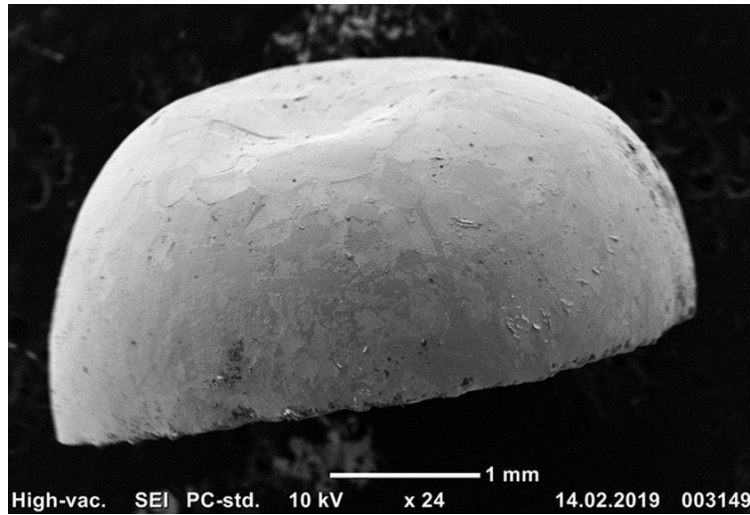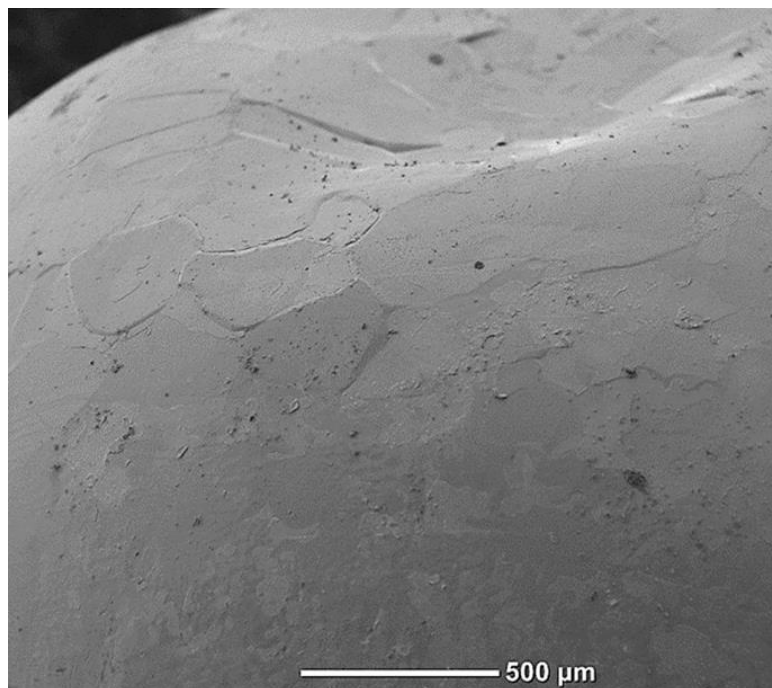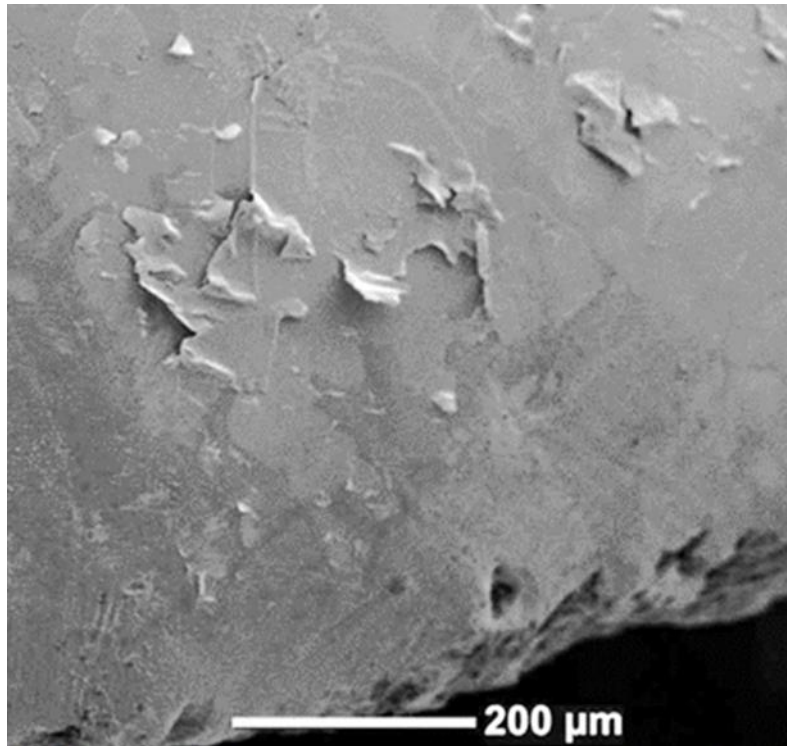
4

Figure 4. SEM image of the hemispherical silver bead after annealing for 30 minutes at 900°C and slow cooling. No 'volcanoes' are visible but there is a shrinkage cavity at the top. The surface is partially covered with flakes of lead oxide.

a)

b)

Figure 5. SEM images. a) The top of the bead in Figure 4 at a higher magnification. Lead oxide flakes are clearly visible on the rim of the shrinkage cavity. b) The 'steeper' side of the bead where some lead oxide flakes have burst.
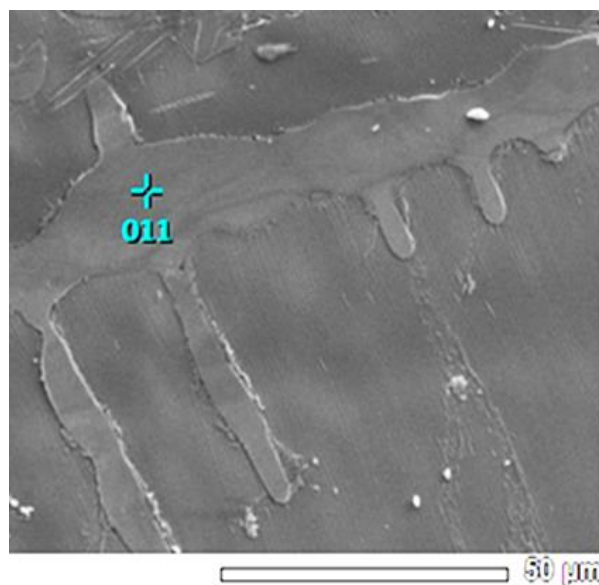

Figure 6. SEM image of the melt flow pattern. Lead oxide has flowed from a boundary between silver grains and solidified. Point 011 marks lead oxide. Beyond the edges of the lead oxide flakes the metal is silver. Scale mark: 50 μm.
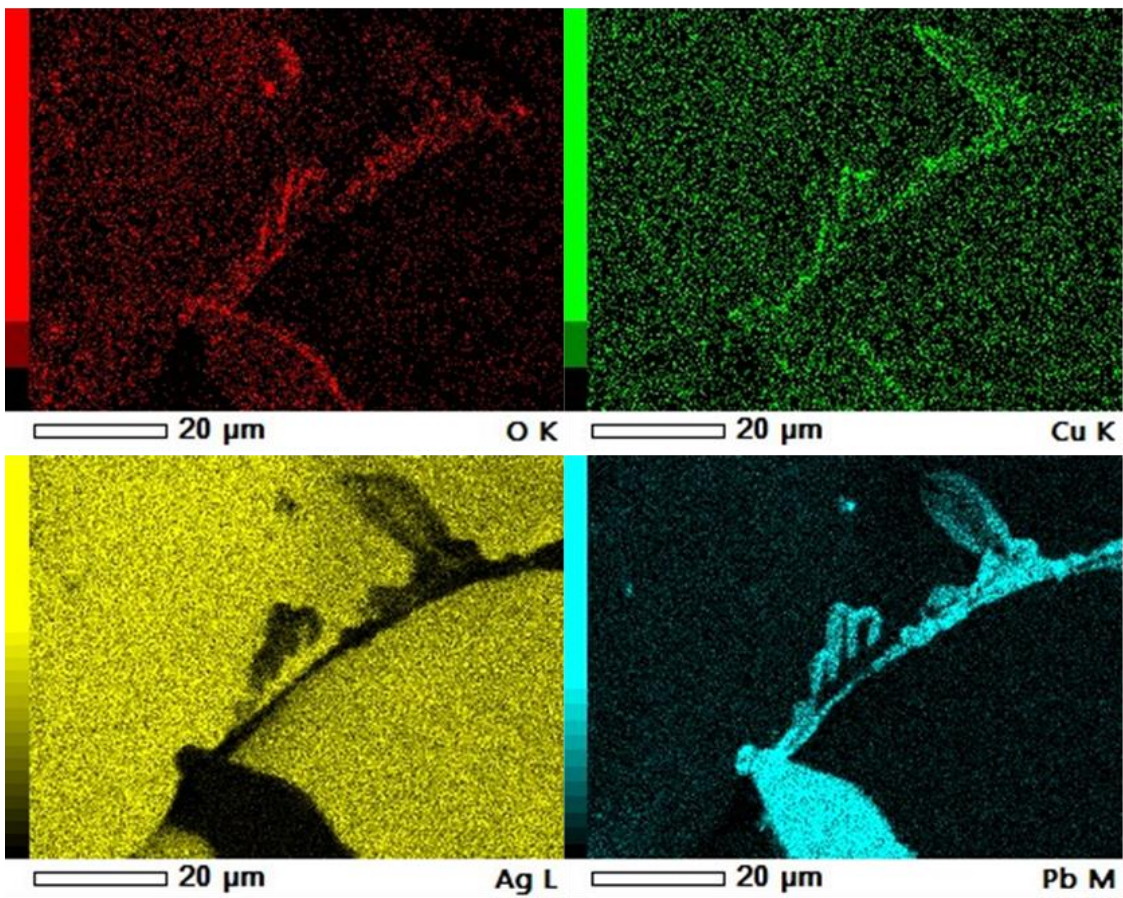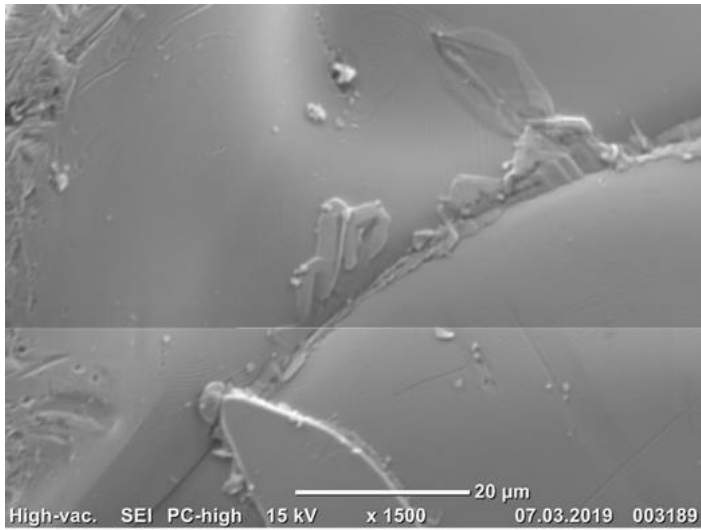
Figure 7. SEM image and EDS maps showing the distribution of oxygen (red), copper (green), silver(yellow), and lead (blue) on the surface. (An electronical fault in the lower part of the SEM image has resulted in a small change in the grey tone.)
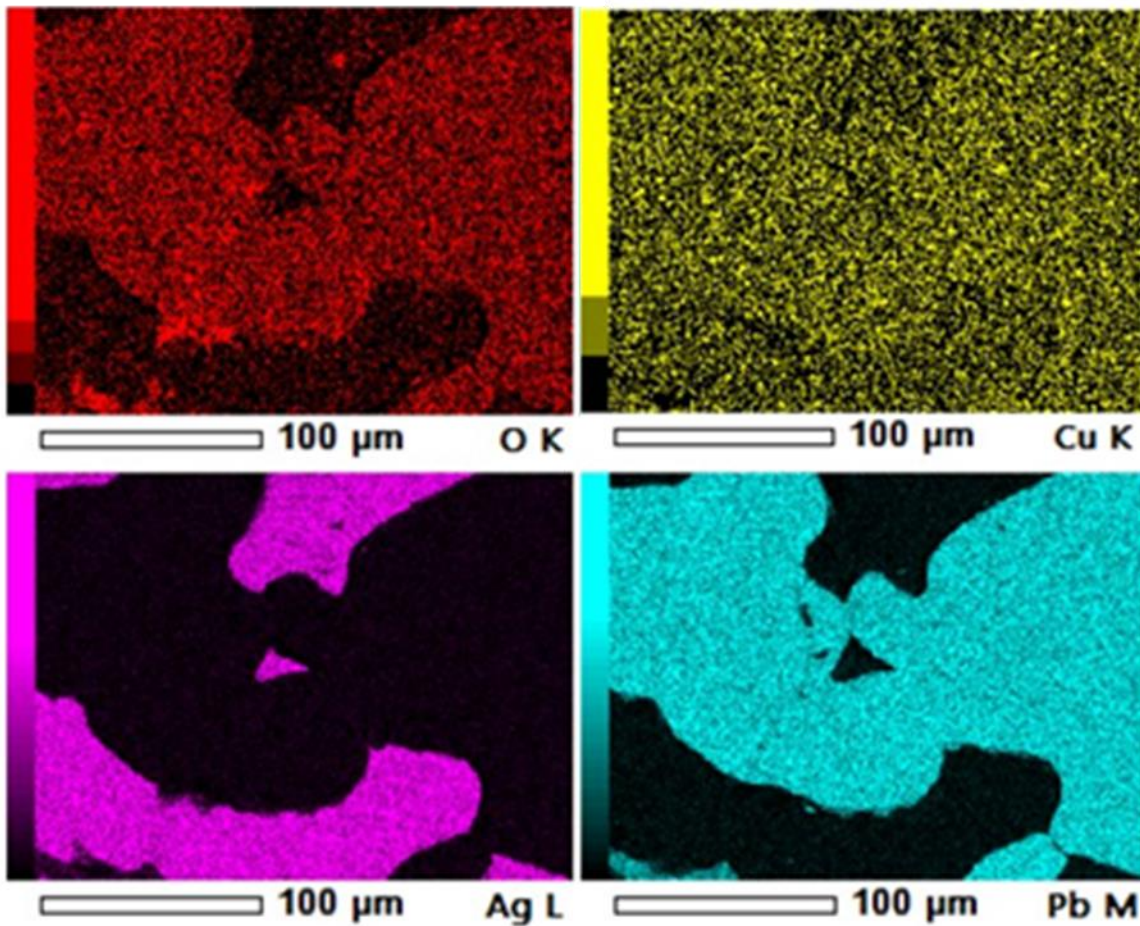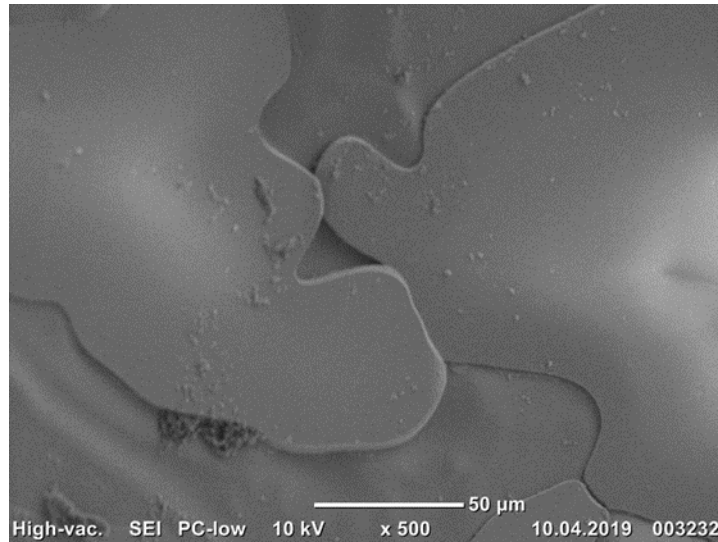
Figure 8. An SEM image and EDS maps showing the lead oxide flakes (red and turquoise), with some copper that has flowed over the silver surface (purple).

Bead shape

After short annealing at 900°C and cooling after an observed flash

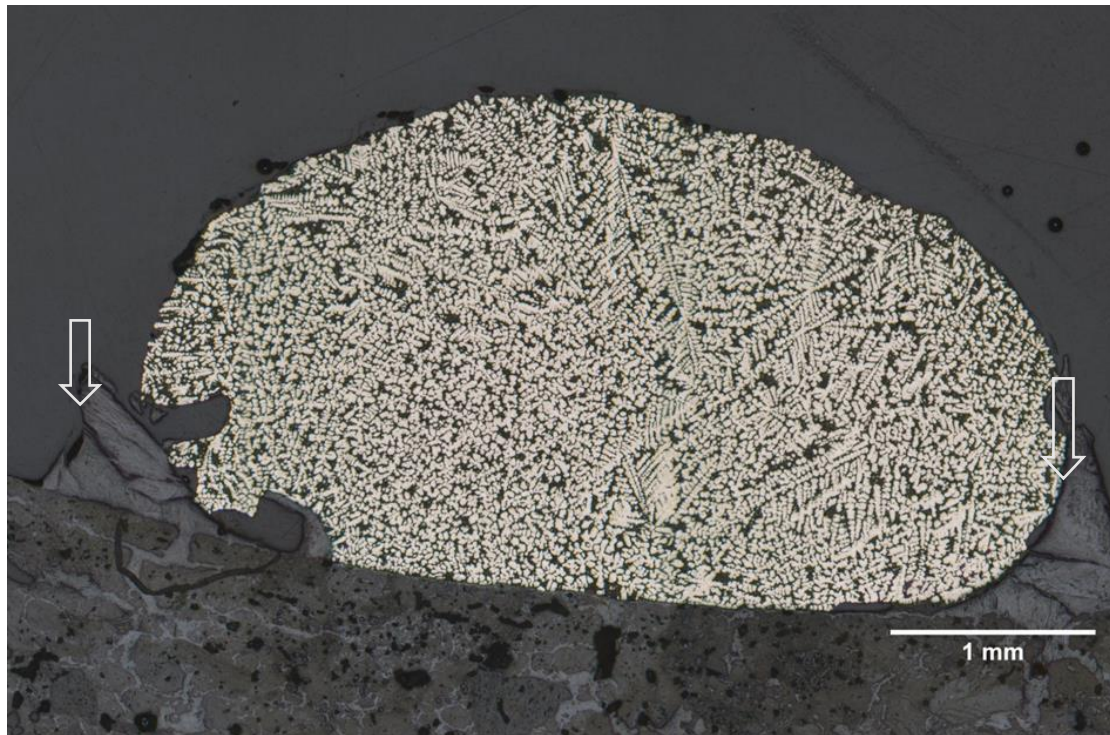The microstructure of the cross section of the bead is shown in Fig. 9.

Figure 9. Light microscope (LM) image. The cross-section shows the shape of a bead when the annealing at 900°C was stopped before all lead oxide had soaked into the cupel and then cooled fairly rapidly. Inside the bead, silver dendrites (white) are surrounded by solidified melt of silver, lead and/or lead oxide and copper and/or copper oxide. Outside lead oxide is creeping under the bead, see arrows, and into the cupel (Some small pieces of the bead have been pulled out during preparation).

After long annealing at 900°C and slow cooling

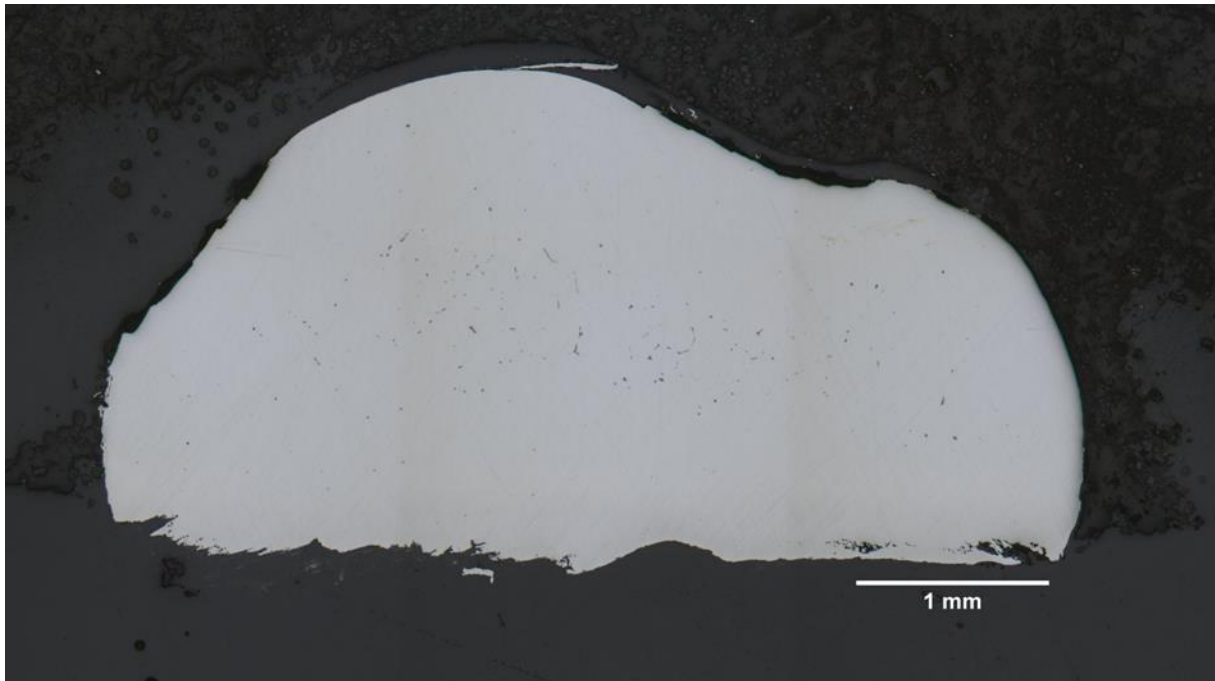A cross section of the bead after slow cooling is shown in Fig. 10.

Figure 10. Light microscope (LM) image of a cross-section of the bead after long annealing at 900°C and slow cooling. No dendrites are visible. The faint spots are precipitates of copper, silver and lead (see Figure 14 for details).

The bead shown in Fig. 11 was cast in EpoFix resin and cut. After grinding, a layer of lead oxide spalled off the silver because the bonding between the silver and lead oxide was rather weak, thus indicating that molten lead oxide does not wet solid silver very well.
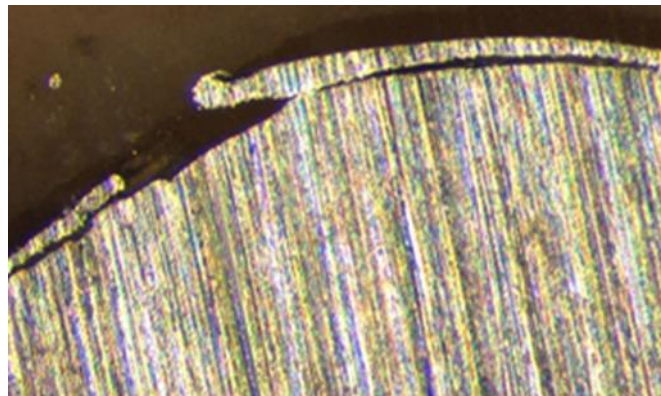

Figure 11. Light microscope (LM) image of a cross-section of a bead annealed for 30 minutes at 900°C and slowly cooled (see Figure 4). A layer of lead oxide loosened from the bead during grinding. Width of original image: 1 mm. Thickness of the loosened lead oxide layer at the surface: 50–100 μm.
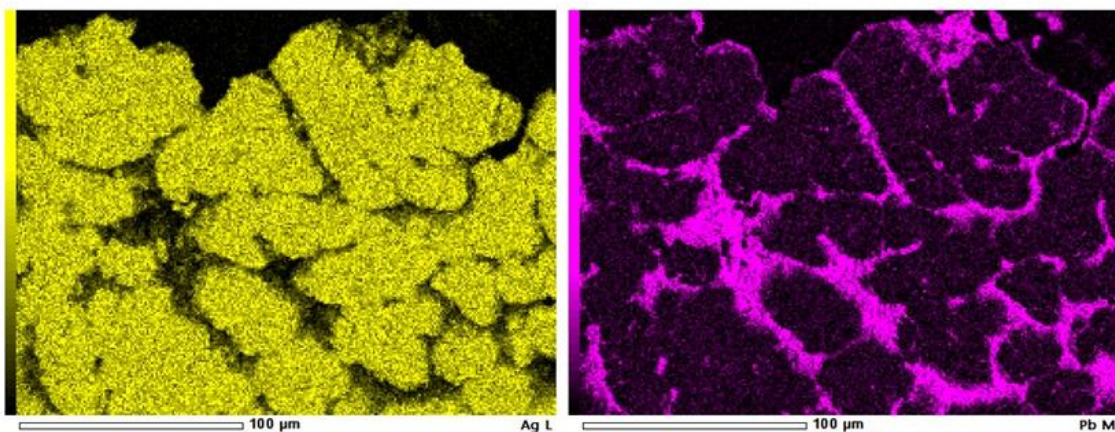
Internal structures

After short annealing at 900°C and cooling after an observed flash

Figure 12 shows how lead oxide filled the voids between the silver dendrites. There was no continuous film of lead and/or lead oxide on the surface of the bead.
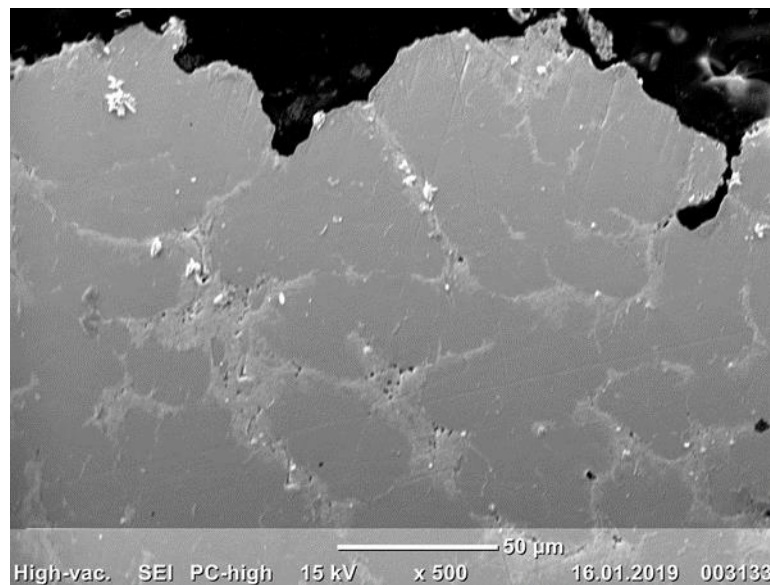
a)

b)   c)

Figure 12. SEM image (a) and two EDS maps (b and c). Cross-section near the upper surface of the bead seen in Figure 9. Lead and/or lead oxide (red) in c) lies in between the dendritic branches of silver (yellow) seen in b). Black spots in a) are pores between the silver dendrites. (Some white spots are dust particles.)

Fig. 13 shows silver dendrites surrounded by lead and/or lead oxide. With the use of an image analysing program, the silver dendrites in Fig. 13 were measured as covering an area fraction of about 67% of the area. The results of chemical analysis performed using a microprobe showed that of the material between the dendrites was 1–2% silver, 98% lead and/or lead oxide, and a small amount of copper and/or copper oxide. This corresponded to the silver content of a pure lead oxide-silver alloy annealed at 900°C (Fig. 18), where 10 mol % corresponded to c. 2.0 wt% silver. The dendrites contained more than 95% silver, and both lead and copper were present. However, when the chemical composition of the dendrites and

the material in between the dendrites were analysed, the results were uncertain because it was difficult to avoid soft lead being smeared over the entire surface during grinding and/or mechanical polishing.

Figure 13. Enlarged light microscope (LM) image of a ground and polished cross-section of an inner part of the bead shown Figure 9. Dendrites of silver (white) are surrounded by solidified melt of lead and/or lead oxide, silver, and copper and/or copper oxide.

After long annealing at 900°C and slow cooling

After annealing for 30 minutes at 900°C and slow cooling, the microstructure of the bead was multicrystalline. Elongated precipitates were found on the grain boundaries (Fig. 14a). The precipitates consisted of particles of copper, lead and silver. Smaller, spherical shaped precipitates were found in the interior of the grains. The composition of the precipitates was in accordance with known phase diagrams with no intermediate phases in either the binary or ternary systems of silver-copper-lead. Thus, the precipitates, either on grain boundaries or in the silver matrix, were a mixture of copper, silver and lead particles, as shown in Fig. 14b. The area fraction of precipitates was c.2%. From visual inspection of photographs from the outer regions of the bead there appeared a somewhat lower density of precipitates than in the central region. When measured by a microprobe, it was found that the silver content in the interior of the grains was c.99.5% silver and higher outside the particles.
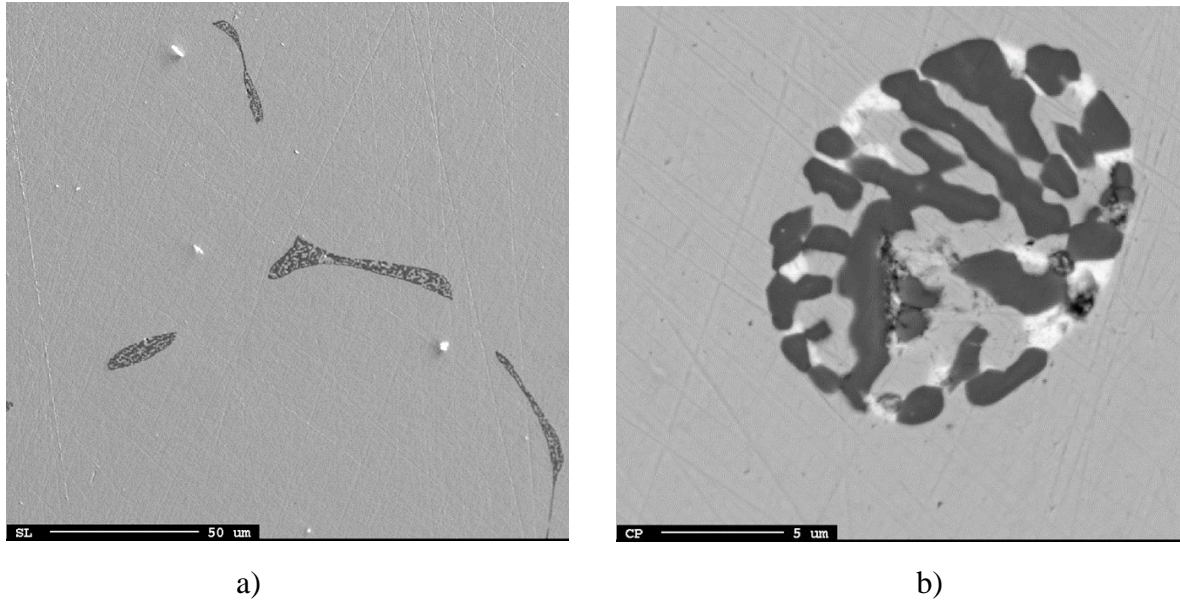
a)   b)

Figure 14. Microprobe image of a ground and polished cross-section of the bead shown in Figure 4. a) Copper-silver-lead particles along grain boundaries (the three white spots are dust particles). b) A precipitate in the interior of a silver grain. Copper (dark grey), lead (white), silver (pale grey), pores (black).

Testing the silver alloy used in the experiment

As mentioned at the beginning of the section headed 'Experiment', the material used comprised 925 ‰ silver alloy cut-offs from gating systems from casting silver jewellery. A cross-section of the gating material is shown in Fig. 15. The black spots are evenly distributed precipitates mainly of copper, which show that the alloy used was homogeneous. EDS analysis performed over an area of 2 mm × 2 mm gave a mean result of several measurements (in wt %) for the main elements as follows:

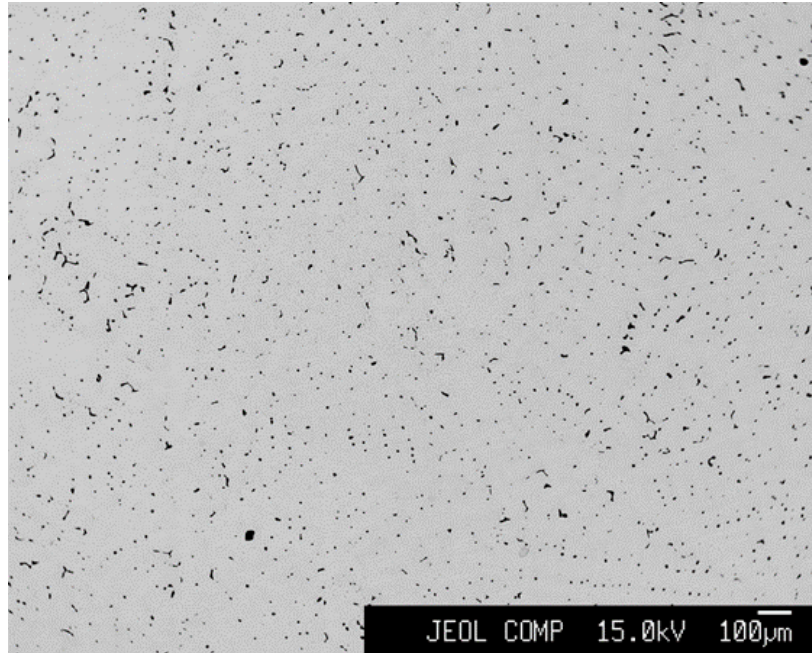91.5% Ag + 4.6% Cu + 2.4% Zn + 1.0% Pb + 0.2% O

Figure 15. Microprobe image of a cross-section of the staring silver material used for the cupellation experiments. The black spots are precipitates mainly of copper.

Discussion

The cupellation process

In this section we discuss the results of the experiments with reference to a model illustrated in Fig. 16 and further extends the description in more detail in 12 steps. In Fig. 16a the concentration of lead in the melt button has been reduced to c.10% by transforming lead to lead oxide, which is evaporating or being sucked into the cupel wall. Thus, the alloy concentration has passed the liquidus line in the phase diagram of the silver-lead system (Fig. 17). If we disregard the presence of copper and zinc, the melt now consists of c.90% silver and 10% lead. Dendrites of solid silver are nucleated, probably near the surface where the silver concentration may be higher than in the lower part. A liquid of lead oxide covers the surface of the melt button. Lead oxide wets the cupel surface and 'creeps' under the button and into the cupel. Dendrites of solid silver are heavier than the melt and will sink.

Fig. 16b shows that more lead has been transformed to lead oxide. Dendrites grow and impinge, and new dendrites are nucleated. Molten lead oxide covers the surface of the button. The melt consists of silver, lead and/or lead oxide, and copper and/or copper oxide. Lead oxide and copper oxide may form in the melt due to oxygen being rejected from the silver during solidification because the concentration of oxygen in liquid silver is higher than in solid silver at equilibrium.

Fig. 16c shows how the dendrites grow together and form grains with melt on some grain boundaries. On the surface, the molten lead oxide has broken, leaving a ring around the bottom of the bead. A shrinkage cavity appears on the top.

Fig. 16d shows the silver when it has solidified, and liquid lead oxide is being squeezed out onto the surface. During cooling the lead oxide may be liquid down to c.825°C (Fig. 18) in a pure mixture of lead oxide and silver. However, due to impurities, in this case copper, the eutectic point may be further lowered, even to 750°C (Ulseth et al., 2015). Lead oxide will be

14

squeezed out and solidify on the surface due to the contraction of silver both during solidification and linear contraction during cooling down. Elements in solid solution in silver may precipitate, preferentially at grain boundaries.
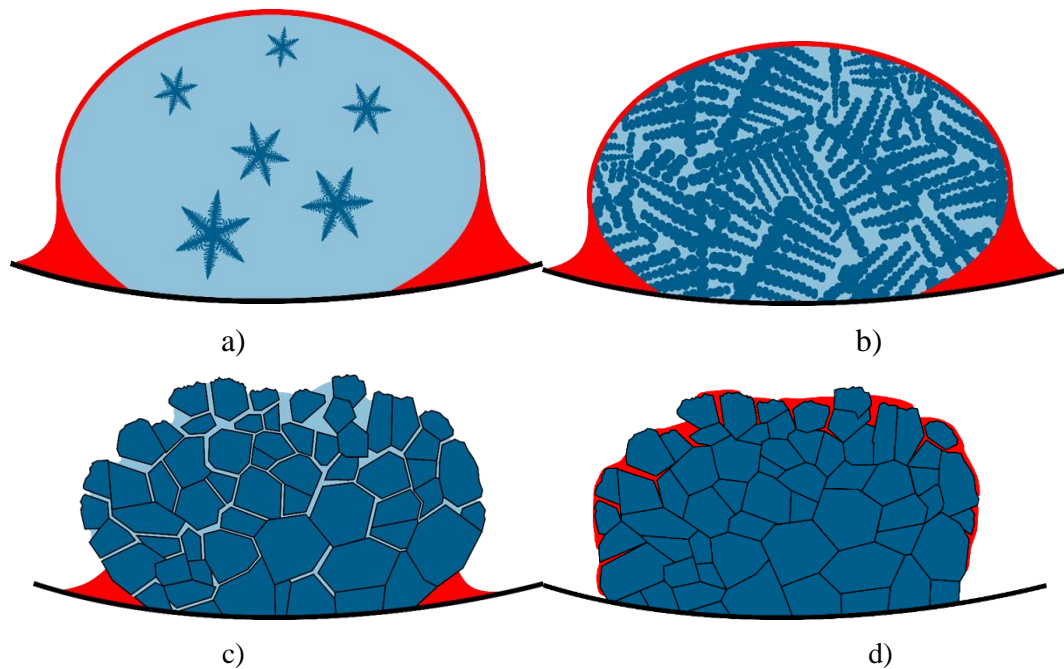

Figure 16. Model of the cupellation process. A melt button is lying at the bottom of the cupel. Red – molten lead oxide (with some copper), dark blue – solid silver, and pale blue – melt of silver, lead and/or lead oxide and copper and/or copper oxide (The flow of lead oxide into the cupel wall is not shown.

Twelve steps in a model of the cupellation process

Twelve steps in the cupellation process are outlined in the following list, where steps 1–3 represent heating, 4–10 annealing at 900°C, and 11–12 cooling. These steps are based on the phase diagrams in Fig. 17 (Ag-Pb) and Fig. 18 (PbO-Ag), and that the concentration of oxygen is much higher in liquid silver (0.32%) than in solid silver (0.006%) (Massalski, 1986, p. 49) at equilibrium, and that molten lead oxide, but not lead or silver, is wetting the bone-ash cupel:

1) During heating lead melts at 327.5°C. The silver alloy to be investigated is dissolved in the lead melt. The shape of the melt is a flattened sphere covered by solid lead oxide (PbO) on the surface. The chemistry of the melt is c.90% Pb, 9.2% Ag, 0.5% Cu, and 0.2% Zn at the starting of the annealing process (zinc is omitted in the following steps).
2) Just below the annealing temperature, 900°C, PbO melts (Fig. 18). During annealing, lead oxide vapourizes and some is sucked into the wall of the cupel. New lead oxide is formed by reactions between the molten lead and the air above the melt.
3) Copper and other impurities in the silver alloy are dissolved in the molten lead oxide and are either vaporized with the lead oxide or sucked into the wall of the cupel.

4) During annealing at 900°C the amount of lead in the melt will be reduced due to the continuous formation of lead oxide; the same applies to copper, but not silver (Fig. 17). In this way, the melt will be enriched with silver over time.

5) When the concentration of lead in the melt has been lowered to c.10% (the liquidus concentration of Ag-Pb at 900°C is 90% Ag + 10% Pb), solid silver, with c.1.5% of lead and some copper in solid solution, starts to precipitate in the melt as dendrites, probably near to the surface. The volume of the melt has now been reduced by c.90% since the start of annealing.

6) During further annealing, the amount of silver in the melt is reduced (but the concentration is constant) as solid silver dendrites grow (Fig. 9) and new dendrites are formed. The silver dendrites are heavier than the melt and will sink, impinge on each other and grow together. There will be a reduction by volume when silver solidifies by 4–5%.

7) During solidification of silver, oxygen will be rejected and either form pores between the silver dendrites (Fig. 12a)) or react with lead to form lead oxide or with copper to form copper oxide (CuO). Thus, between the dendrite arms the melt contains lead and/or lead oxide, some copper and/or copper oxide, and silver.

8) The rejection of oxygen from the silver melt, the transformation of lead into lead oxide (and copper to copper oxide) will increase the volume of the melt, which will then be squeezed out at the surface (Fig. 4-8).

9) As the annealing proceeds, the dendrite arms at the surface 'puncture' the continuous layer of molten lead oxide due to roughness and a reduced area of lead in contact with air (Fig. 12). As the liquid of lead oxide poorly wets solid silver (Fig. 11), the lead oxide layer will, at a certain stage, burst and leave a bright silver surface. This process may be observed as a flash. The liquid lead oxide may contract to form a ring around the bottom of the bead and disappear as it is sucked into the cupel. There may still be melt between the dendrites, which upon contact coalesce and form grains.

10) When the silver in the melt has solidified, the contact area between grains increases and the remaining melt of lead oxide, with some copper and/or copper oxide, is squeezed out onto the surface, slides down (Fig. 5b) and is sucked into the cupel.

11) During cooling from 900°C the lead oxide may still be in a liquid state to temperatures far below 900°C (see Fig. 18, which shows a eutecticum at 825°C or lower due to the presence of impurities, in this case mainly copper). Liquid lead oxide that is still present between grains of silver may be squeezed out due to the contraction of the solid silver and then solidify on the surface of the silver bead.

12) During cooling, impurities in solid solution in silver at 900°C may precipitate. Preferred sites for the precipitation will be grain boundaries and/or grain boundary nodes (Fig.14).
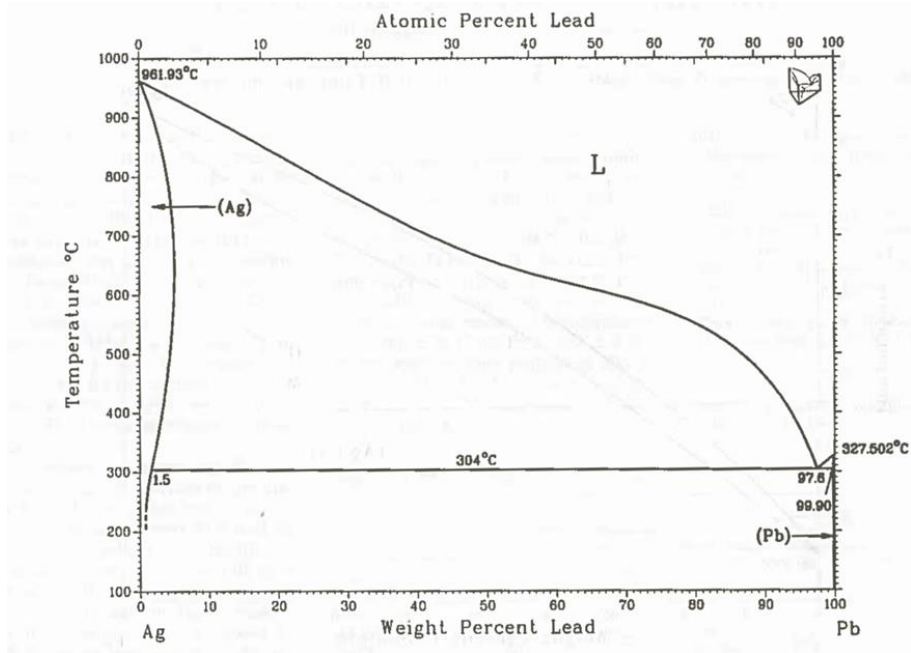
Figure 17. Phase diagram of silver–lead (AG and Pb respectively) system (Massalski, 1986, p. 53).
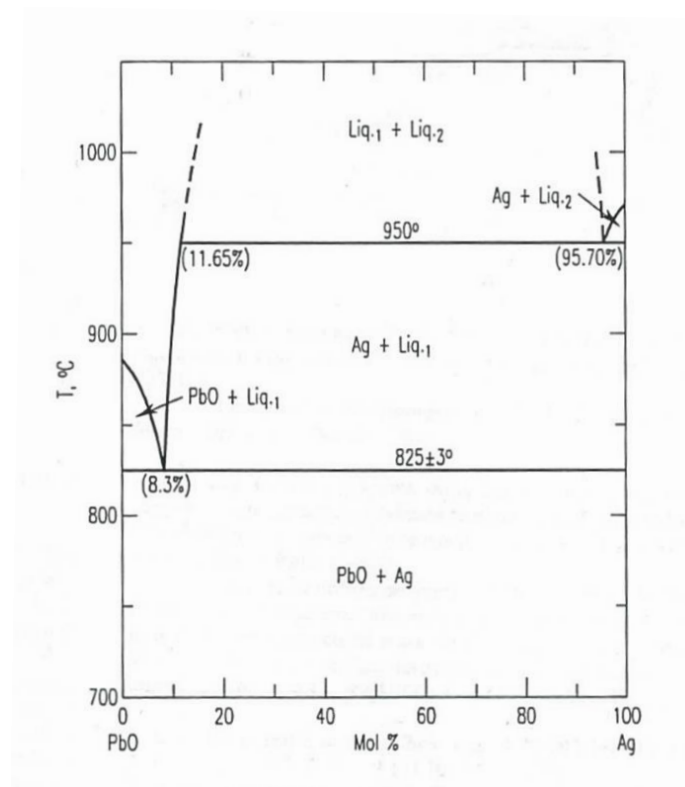

Figure 18. The phase diagram of lead oxide-silver (PbO-Ag) – Silver (Ag) (Roth, 2001).

How to clean the bead

With the exception of impurities on the surface, earlier assayers assumed that after brushing the beads were pure silver (Sieblist, 2008; Mongiatti et al., 2009; White, 2010). Ercker (1951 [1574], p. 60)[3] recommended that the beads should be prised from the cupels while still warm:

> Then they will come cleanly off the cupel facing. If something should stick to the beads, they should be squeezed with pliers or flat-nosed tongs, and the dirt will spall off. Then brush them with a small hard brush made from bristles.

During our experiments we experienced that material from the facing could stick to the lower side of the bead, but could be brushed away. We also observed that the lead oxide spalled off the silver surface during grinding (Fig. 11). As a consequence, lead oxide on the surface could break away from the surface when the bead was squeezed. Thus, after brushing, the surface of the bead may be quite clean.

The purity of the beads

In addition to melt of lead and/or lead oxide and copper and/or copper oxide being trapped between solid silver grains, impurities in solid solution in silver grains inside the bead will still remain. Correct annealing will keep such impurities to a minimum. When annealed at 900°C' the bead will contain c.1–1.5 w% of lead. At room temperature, copper will be found both as precipitates on grain boundaries and in solid solution in the silver. The concentration of elements in solid solution will depend also on the cooling conditions.

What about other alloying elements that were normally found in silver alloys from the Archbishops Palace? S. Bergstøl and S.W. Nordeide (pers. comm. 1993) tested five bone-ash cupels by using XRF (X-rays fluorescence) on the cupel surface. In addition to silver, they found lead, copper, and small amounts of zinc (Zn). In one of the cupels they registered some tin (Sn) and in three cupels small amounts of nickel (Ni). Zinc might have been present due to the use of brass (Cu-Zn) instead of pure copper when making bullion for coins produced in this 16th century mint, which normally contained c.70% copper. The presence of zinc reduces the tendency of pore formation during casting and might have been added at will. The zinc would have been in solid solution in the silver. The presence of tin could have resulted from bronze (Cu-Sn) being used instead of copper in bullions for coins. The solid solubility of tin in silver is high (c.10%).

The solid solubility of nickel in silver is low. However, in a binary lead-nickel alloy c.2–3%, nickel may be dissolved in liquid lead at 900°C and at the surface form a high-temperature stable oxide that is not dissolved in lead oxide (Moesta and Franke, 1995, p. 66). Therefore, nickel would not have been sucked into the cupel wall but would rather be found on the surface of the cupel.

A small amount of silver would have been lost to the lead oxide during annealing and ultimately sucked into the cupel or solidified on the surface. However, some silver might have come from the lead material (the lead used contained c.0.5% Ag). Ercker underlined that both the silver lost to the lead oxide and silver gained from the lead had to be taken into account when evaluating the results after cupellation.

---

[3] See also: *Katalog for Sølvverksmuseet, Kongsberg*, 1942. Handwritten, possibly by a secretary under dictation of the foreman of miners Bjarne Sanness.

Ercker (1951 [1574], p. 60) recommended that 'When the beads […] have just blicked (flashed) clearly, lift the cupels from the furnace and pry the beads out while the crucibles are still hot'. However, as shown in Fig. 13, a substantial amount of lead and/or lead oxide and copper and/or copper oxide may be locked between the silver dendrites if the cooling starts just after a flash. Fig. 13 shows dendrites with a concentration of more than 95% silver covering about 67% of the cross-section. The melt covers about 33% and has a concentration of c.1–2% silver. Together, these results show that the fineness of the bead in the image might have been c.70% silver. If the weight of the bead was supposed to constitute pure silver, a mistake or overestimation of c.30% was made.

Furthermore, Ercker (1951 [1574]) recommended that two cupellations with the same amount of material should be done. Then, if the weight of the resulting beads is equal, the cupellation has been done correctly.

Estimation of fineness in the starting material after long annealing and slow cooling

If, after long annealing and slow cooling, the bead was well cleaned before being weighed the uncertainties of the fineness would have to be estimated from several parameters: How much silver followed the lead oxide into vapour or into the cupel or solidified on the surface of the bead? How much silver was gained from the lead applied in the process? What are the contributions of impurity elements present as precipitates on the grain boundaries or in solid solution? If we assume that silver lost balances silver gained, the effect of precipitates and elements in solid solution may be evaluated as follows: the area fraction of precipitates was measured as c.2%, of which silver might have constituted c.50% of the precipitates; the purity of the interior of the grains was measured as higher than 99.5% silver. Together, the two evaluations give the fineness of the bead as between 98–99% silver, not 100% (Téreygeol and Thomas, 2003).

Other contributions to the uncertainties of the estimated fineness of the starting material in our case may be calculated as follows:

1) The silver bead after long annealing and slow cooling was not cleaned for lead oxide. Using the weight of the starting material, 0.3808 g, and the final weight, 0.3486 g, without cleaning for lead oxide on the surface, a fineness of 91.5% is obtained, which is the same percentage as found in the EDS analysis of the gating material. However, we know that this is an overestimate because the bead was not clean.

2) If we suppose that a 50 µm thick layer of lead oxide covers c.25% of the bead surface, the weight of the oxide layer will be c.0.005 g. Then, the fineness will be about 90.2% Ag, which is a deviation of 1.3% and an overestimate.

3) If we also correct for precipitates and elements in solid solution and use a value of 98.5% silver in the bead, the estimated fineness of the starting material will be 88.9%, which is a deviation of 2.6%.

The right annealing temperature

The active part in the cupellation process is liquid lead oxide (PbO). In the experiments, the annealing temperature was kept constant at 900°C. However, pure lead oxide (PbO) melts at 888°C (Fig. 18) and may be kept molten at lower temperatures if other elements, such as

copper, are absorbed (Ulseth et al., 2015). The phase diagram of silver and lead in Fig. 17 shows that at 900°C solid silver will contain c.1.5% of lead in solid solution at equilibrium. At higher temperatures, the concentration of lead in silver will be lower. The same will apply for copper. However, by increasing the temperature, the loss of silver by evaporation may become a problem. Ercker discussed the problem of regulation of temperature during cupellation of copper containing silver alloys and considered it 'a master's assay'. Essentially, the assaying temperature should not be too high during the start of annealing but increased towards the end of the annealing process. The phase diagram in Fig. 17 shows that if the temperature is raised to the melting temperature of pure silver, 961.93°C, it will be possible to remove lead and copper if done correctly. However, it is not possible for beginners to master such temperature regulations.

Conclusions

The processes that take place during cupellation (i.e. heating, annealing and cooling) may be understood as sequences of the metallurgical processes: melting, melt enrichment, dendrite nucleation, dendrite growth and dendrite impingement, internal and surface oxidation, and metal shrinkage.

Due to the dendrite and/or grain structure there may be some lead and/or lead oxide locked inside the silver bead. The amount will vary with impurity content, annealing temperature and time, and cooling conditions. Therefore, merely measuring the weight of the bead after the surface has been cleaned well will give results that have some errors. We found an error of about +30% when the cupellation process was terminated just after a flash was observed. The results may be better than 3% or 1–3% after long annealing at 900°C and slow cooling, and even better if the assayer manages to follow Ercker's advice to increase the annealing temperature to the right level at the end of the annealing. Without knowing how the moneyer performed the assaying process in detail, the uncertainties may lie somewhere in between the above given percentages.

Acknowledgements

References

Diplomatarium Norvegicum. Oldbreve til kundskab om Norges indre og ydre forhold, sprog, slaegter, saeder, lovgivning og rettergang i middelalderen, X (1), 1878, C.R. Unger and H.J. Huitfeld-Kaas, Christiania. [in text referred to as: DN]

Ercker, L., 1951 [1574]. *Treatise on Ores and Assaying*, Transl. A.G. Sisco and C.S. Smith. University of Chicago Press, Chicago.

Lohne, O. Risvaag, J.A., Ulseth, P., Lohne, J., 2010. *The Mint in the Nidaros Archbishop's Palace: Coin Production under Archbishop Gaute Ivarsson (1475–1510)*, Transactions of the Royal Norwegian Society of Sciences and Letters 2010:1. Trondheim.

Lohne, O., Ulseth, P. and Risvaag, J.A., 2021. From calves' sculls to finished bone-ash cupels and testing of precious metals: An investigation of the cupellation practised in the Mint in the Archbishop's Palace in Trondheim in medieval times [This volume].

Massalski, T.B., 1986. *Binary Alloy Phase Diagrams*, Vol. 1. American Society for Metals, Materials Park, OH.

McLees, C., 1996. Itinerant craftsmen, permanent smithies and the archbishop's mint: The character and context of metalworking in medieval Trondheim, *Historical Metallurgy*, 30(2), pp. 121–135.

Moesta, H. and Franke, P.R., 1995. *Antike Metallurgie und Münzprägung*, Birkhäuser Verlag, Basel.

Mongiatti, A., Martinòn-Torrres, M. and Rehren, T., 2009. Testing ores for gold and silver in Renaissance Austria: New techniques, new discoveries. In: Moreau, J.F., Auger, R., Chabot, J. and Herzog, A. (eds.) *Proceedings of the 36th international Symposium on Archaeometry*, pp. 444–447. CELAT, Université Laval, Quebec.

Nissen, H.A., 1998. *Utgravingene i Erkebispegården i Trondheim. Arbeidsstyrke og lønnsforhold ved erkesetet i 1530-årene*. NIKU Temahefte 14. NIKU, Trondheim.

Nordeide, S.W., 2003. *Erkebispegården i Trondheim: Beste tomta i by'n*. PhD thesis, University of Oslo, Oslo.

Roth, R.S. (ed.), 2001. *Phase Equilibria Diagrams, Vol. XIII: Oxides*. American Ceramic Society, Westerville, OH.

Risvaag, J.A., Lohne, O. and Ulseth, P., 2021. A catalogue of bone-ash cupels dating from AD 1500–1537 found in the Mint in the Archbishop's Palace, Trondheim, during archaeological excavations in 1991–1995 [This volume].

Saunders, T., 2001. *The Archbishop's Palace: A Social Analysis of the Power Centre in the Late Medieval Period – Money, Warfare and Charity*. NIKU Temahefte 18. NIKU, Trondheim.

Sieblist, U., 2008. Interdisziplinäre Tagung zur Geschichte der neuzeitlichen Metallgeldproduktion, «Die «trockene» Silberprobe», pp. 391–398. Beiträge zur Tagung in Stolberg (Harz) im April 2006. Braunschweig 2008. ISBN 978-3-87707-752-8.

Téreygeol, F. and Thomas, N., 2003. La coupellation des alliages cuivre-argent: Approche expérimentale de l'essai d'argent par voie sèche. *Revue d'Archéométrie* 27(1), pp. 171–181.

Ulseth, P., Lohne, O., Risvaag, J.A., Lohne, J. and Ervik, T., 2015. Late medieval bone-ash cupels from the archbishop's mint in Trondheim, *Fornvännen* 4, pp. 26–279.

White, H., 2010. *Legge's Mount, The Tower of London, London: Scientific Examination of the Cupels*. Technology report. Research Department Report Series, no. 57-2010. Archaeological Science, English Heritage, Portsmouth.