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Experimental investigation of silvering in late Roman coinage

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ABSTRACT

Roman Coinage suffered from severe debasement during the 3rd century AD. By 250 AD., the production of complex copper alloy (Cu-Sn-Pb-Ag) coins with a silvered surface, became common practice. The same method continued to be applied during the 4th century AD for the production of a new denomination introduced by Diocletian in 293/4 AD. Previous analyses of these coins did not solve key technological issues and in particular, the silvering process. The British Museum kindly allowed further research at Bradford to examine coins from Cope's Archive in more detail, utilizing XRF, SEM-EDS metallography, LA-ICP-MS and EPMA. Metallographic and SEM examination of 128 coins, revealed that the silver layer was very difficult to trace because its thickness was a few microns and in some cases it was present under the corrosion layer. Results derived from the LA-ICP-MS and EPMA analyses have demonstrated, for the first time, the presence of Hg in the surface layers of these coins. A review of ancient sources and historic literature indicated possible methods which might have been used for the production of the plating. A programme of plating experiments was undertaken to examine a number of variables in the process, such as amalgam preparation, and heating cycles. Results from the experimental work are presented.

ITRODUCTION

Coinage in the Late Roman Period suffered from severe debasement. By 250 AD the fineness of the silver denomination had been reduced to just 5% Ag. For the production of these "silver" coins, copper based quaternary copper-tin-lead-silver alloys were used. Their surface was covered by thin silver plating which was worn off easily during the circulation and use of the coins. Later, the same method was used for a new coin, the *nummus*, introduced by Diocletian, in his monetary reform (AD 293/4). The *nummus* was meant to have been coined to the same standard in all the Imperial mints. It was the first time that a uniform coinage circulated throughout the Roman world and huge numbers of new coins had to be produced to cover the needs of its estimated 60 million people[1].

For a few years the economic system was quite stable, but by Constantius Chlorus' death in Britain (July 306 AD), serious political problems had arisen which caused considerable tensions between the East and the West. These political problems had an immediate impact on the monetary system. *Nummi's* weight was gradually reduced from 10 gr. to only 3 gr. and during the rest of the 4th century A.D., *nummi* continued to circulate in very debased form [2].

The main aim of this research is to investigate the method used for almost 100 years (250 – 350 AD) for the production of Roman coins. These data will contribute to:

- characterise the plating technology used in large scale production of coins
- assess the uniformity of manufacturing technology of an Empire-wide coinage

- understand the Monetary System of this turbulent Period and
- improve our knowledge of ancient coinage technology
- contribute to the development of early plating technology

METHODS OF EXAMINATION

The British Museum kindly allowed further examination of coins from Cope's archive [3]. In this study 128 coins were examined and cover the period from 260 A.D. to 350 A.D [4]. The coin denominations are *antoniniani*, tetrarchic *nummi* and debased *nummi*. Their weights vary from 2 grams to 11 grams and their diameters from 17 mm to 30 mm.

Optical microscopy and SEM examination of the surface of the coins revealed that silver plating partially existed on 57 out of 128 and had the same characteristics. In metallographic examination of cut sections though, the plating was found to survive in 43, because it was difficult to trace. Its thickness was approximately a few microns. In some cases, the plating was present under the corrosion layer or in others, there were traces in the corrosion products. Although there were small quantities of silver as inclusions in the bulk, there was no metallurgical evidence that surface enrichment had been used (Figure 1).

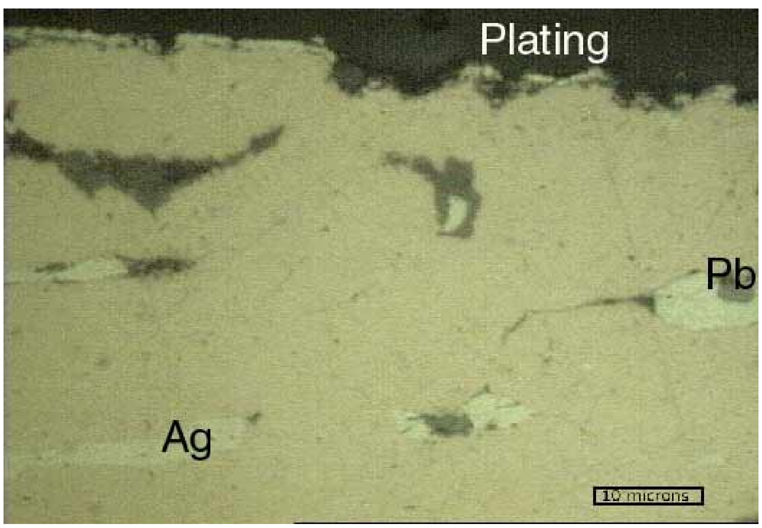

Figure 1: A characteristic example of the metallographic structure of the coins (coin BM259).

To overcome the instrumental limitations of XRF and SEM-EDS analyses, a more sensitive technique was required for the examination of these thin and corroded plating layers. LA-ICP-MS, a highly sensitive method which produces analytical data for a wide range of elements, is available in the Department of Archaeological Sciences. A PlasmaQuad 3, equipped with a Microprobe II laser ablation system was used and for the first time, the presence of mercury in the surface layers of these coins has been demonstrated. It was traced in 23 sections where the plating was well preserved. In the other 20 cases, although the layer was observable it was not satisfactorily analysed because of corrosion. The coins were in circulation for many years and suffered from degradation during burial. Therefore, the composition of their surface, let alone the plating itself, had been affected severely by wear and corrosion. In these analyses, there is little possibility of contamination because mercury was present only in the areas where the silver layer survived. However, it was possible that mercury was impurity in the silver ore, or it might have been used in the refining process.

The application of another method to provide data to confirm or refute the use of mercury was crucial. The NERC Manchester Electron Microprobe Facility, in the Department of Earth Sciences, University of Manchester, became available for this purpose. Results of these analyses also confirmed that mercury was present only on the surface of the coins and in association with the silver plating (0.112 – 0.803 % Hg). These data provided conclusive evidence for the use of mercury in the plating process.

POSSIBLE METHODS FOR THE PRODUCTION OF THE PLATING

The production of the thin silver plating on the surface of the coins in the late Roman period has been subject to extensive research. Cope, in his work on the late Roman coinage, suggested that the plating was produced by dipping the blanks in molten silver chloride [5-7]. Silver chloride, was available in antiquity as hornsilver (kerargyrite). But there is no reference to this method in the ancient literature. Furthermore, hot-dipping methods were not really suitable for mass production [8,9].

Another possible method is the use of silvering pastes [10]. This method is based upon an electrochemical reaction between the paste and the metal to be plated. The basic component of these pastes is freshly precipitated silver chloride. Other additives might be sodium chloride, ammonium chloride, potassium hydrogen tartrate, mercuric chloride and chalk as thickener. The operation takes place after striking. The components were available in antiquity but the earliest references of the method were in 18th century AD. Lechtman in her research on the gilded and silvered copper objects made by the metalsmiths of Andean cultures suggested that electrochemical replacement was used [11]. However, it is uncertain when electrochemical silvering was introduced to Europe. There is only one known example where silvering paste was used for the silvering of a Sardinian horse-head coin overstruck as a Carthaginian silver coin (3rd century AD, if the plating produced during the overstriking) [9].

Amalgam plating is another method which can produce very thin plating. After the application of an Ag-Hg amalgam on the surface of the object to be plated, Hg is evaporated by heating and Ag remains forming a thin layer (Hg boiling point: 357 °C). Mercury was available in quantity in antiquity (e.g. it was used for refining metals in mines). The amalgam method is very well known mainly for gilding with mercury – gold amalgam. Amalgam gilding was used extensively in the Roman period [12]. There are many references to gilding with amalgam in early texts whereas the use of amalgam silvering is rarely cited. Theophilus (12th century AD), in his work gave different proportions for the preparation of the amalgam with silver than that with gold [13]. Also, Biringuccio (16th century AD) suggested a different treatment after heating: "*If it is gold, it is quenched in urine; and if it is silver on brass or copper, it is thrown in oil and heated with bran flames"* [14]. Amalgam silvering is also mentioned in a Byzantine manuscript with recipes for the treatment of metals where olive oil is suggested again in the finishing process [15].

However, previous works suggested that when using silver amalgam it is harder to achieve a good finished surface compared to amalgam gilding. Furthermore, it is common belief that residual mercury can be traced by XRF. Consequently, there is an absence of analytical data to prove that the method was used to any extent [9,10]. Amalgam silvering was a common method in plating counterfeit coins [16,17]. Recently, examination of four Iranian forgeries dirhams dating from 9th or 10th century AD from Cope's archive, found that they were plated with amalgam silvering (10.8 – 12.7% Hg) [18]. These coins belong to a hoard of approximately, 1200 forgeries which according to Morton, were made in the same workshop by the same method [19].

EXPERIMENTAL RESULTS

A series of experiments were designed to examine the application of plating with silver – mercury amalgam. Safety precautions were taken and special apparatus was designed. A tube furnace was used for the heating process and the evaporated mercury was collected in zinc traps (Figure 2).

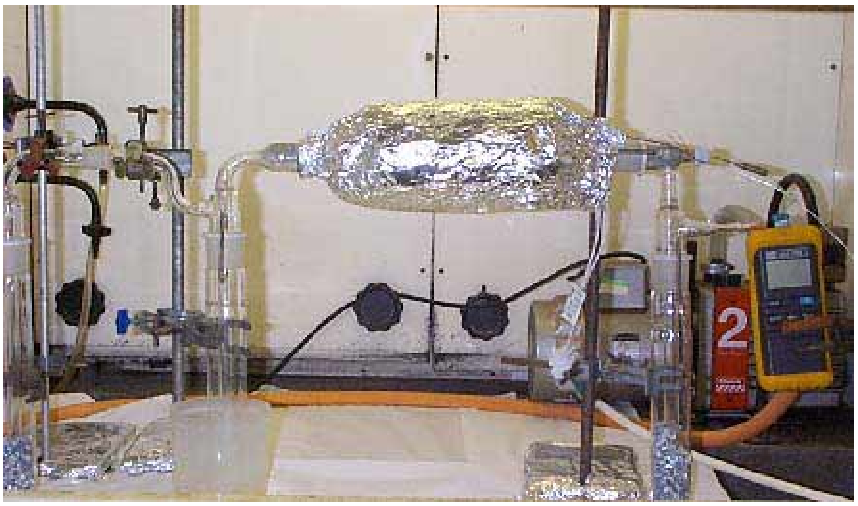

Figure 2: The experimental set up.

Anheuser's methodology was used in the first instance (Series A) [20]. An amalgam, containing 80% mercury and 20% silver, was produced by grinding the two metals together in a mortar. The resulting paste was applied on the surface of copper sheet with a stainless steel spatula and 5% nitric acid in distilled water was used as wetting agent.

The coupon was put on a metal tray and inserted into the furnace. After heating the sample for 10 min in 250°C the plating was dark coloured and it flaked from the surface. The same procedure was repeated with quaternary alloys as substrate metals (Series B). Alloys similar to those used in Roman coins were produced in the laboratory (Table I).

Table I: Experimental alloy concentrations for Series B

Alloy code	**Cu %**	**Ag %**	**Sn %**	**Pb %**
Alloy 1-3-3	93	1	3	3
Alloy 1-5-5	89	1	5	5
Alloy 1-7-7	85	1	7	7
Alloy 1-9-9	81	1	9	9
Alloy 2-3-3	92	2	3	3
Alloy 2-5-5	88	2	5	5
Alloy 2-7-7	84	2	7	7

Alloy 2-9-9	80	2	9	9

The results from these experiments were significantly different from those obtained from Series A. The plating was the same on both sides, it could withstand higher temperature (450°C) and longer times of exposure (1h), but the mercury concentration was still quite high on the coupons' surface (approximately 80% Hg).

Plating with an amalgam is a quite straightforward procedure but there are many parameters which could influence the formation of the final layer. First, is the actual amalgam concentration. Theophilus suggests that a silver – mercury amalgam should have five parts of mercury to one of silver, by weight in contrast with amalgam for gilding which have eight parts of mercury to one part of gold [13]. There are also many ways to mix the two metals by heating or grinding them together[13,21]. Finally, recipes suggest squeezing the amalgam in a cloth or leather in order for excess mercury to be removed [22]. There is also lengthy discussion on the influence of the substrate metal in the plating results mainly in the gilding process. According to Theophilus, it was very important that the copper alloys were lead free otherwise, gilding would not be that successful [13]. Based on analyses of Greek and Roman statues, Craddock and Oddy argued that in amalgam gilding cases the alloys which had been used for casting the statues were usually low in tin and lead [12,23,24]. On the other hand, Jett's work on Chinese bronzes showed that gilding with amalgam could be produced irespective of their high tin and lead concentrations [25,26].

Taking the above into account, a new series of experiments were designed (Series C). The amalgam was produced, according to Theophilus, by five parts of mercury mixing together with one part of silver and heated to 100°C for five days. Then the amalgam was squeezed in a linen cloth and ground again in a mortar to get the consistency of a paste. Three different alloys were used for substrate metals to check possible influence in the plating results. Alloy 1 represented the composition of a late Roman coin (Cu 88%, Ag 2%, Sn 5%, Pb 5%) , Alloy 2 was a binary copper – tin alloy (Cu 95%, Sn 5%) whereas, Alloy 3 also contained Pb (Cu 90%, Sn 5%, Pb 5%). The amalgam was spread on both surfaces of the coupons with a stainless steel spatula and 5% nitric acid in distilled water was used as a wetting agent (Figure 3).

Figure 3: The coupons after the application of the amalgam

Heating temperatures were increased from 200°C to 600°C at 50°C intervals. The samples remained in the furnace for 20 minutes each. After heating, the coupons were cleaned with 5% nitric acid in distilled water and burnished. The results from these experiments are summarised in Table II.

Table II: Summary of the Series C results. (√: successful plating, ≈: partially oxidised, —: failure of plating)

	360°C	400°C	450°C	500°C	550°C	600°C

Alloy 1	√	√	√	√	√	≈
Alloy 2	√	√	≈	—	—	—
Alloy 3	√	√	√	√	√	—

Alloy 2 underperformed in the experiments compared to the other two alloys. It's plating could not survive heating at 500°C (Figure 4). At higher temperatures, differences between the other two alloys started to appear. The plating in Alloy 3 could withstand the heating to 500°C but not to 550°C. It was only plating of Alloy 1 which could survive after heating to 600°C. Overall, Alloy 1 had the best resistance to high temperatures. Furthermore, the concentration of mercury on the surface of the samples varied considerably. At 360°C, just above Hg boiling point, the plating on Alloy 2 contained only 45% Hg, whereas, Alloy 1 contained 62% Hg and Alloy 3, 69% Hg. The surface of the Alloy 1 after heating in 600°C for 20 minutes contained 12 – 13% Hg.

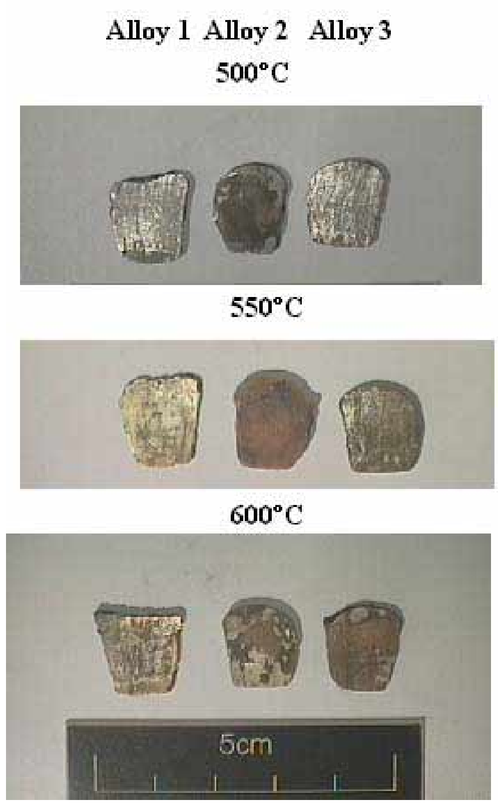

Figure 4: The coupons after heating for 20 min in 500°C, 550°C and 600°C.

DISCUSSION

Previous authors have not considered the use of amalgam silvering for plating objects and had presented data that seemed to exclude this possibility [5,10]. However, EPMA and LA-ICP-MS analyses clearly demonstrated the use of mercury in the silvering of late Roman coins. A series of experiments were conducted to investigate factors that influence the amalgam plating. The investigation into the importance of alloy composition proved to be the most crucial. The results showed that the composition is important in facilitating successful plating. Quaternary alloys, similar to the Roman coins, are essential for successful plating, enabling the alloy to be heated to sufficient temperature and to achieve volatilisation of mercury.

The use of quaternary alloys for the production of the coins and their contribution to the plating process is a new evidence for the technological knowledge of the workers in the Roman mints. This information is crucial because it provides an alternative theory as to why there were low silver concentrations (1 - 5%) in the coins although it did not affect the alloy colour. Numismatists believed that these small quantities of silver gave intrinsic value in the coins but the results from this work showed that there were also key technological issues for the silver content.

The experiments also demonstrated that the preparation of the amalgam was crucial in producing a successful layer. Previous experiments had prepared the amalgam very simply [10]. However, utilising description in early texts a more prolonged preparation was undertaken. This proved successful. The results of the experiments to-date demonstrate that a layer much lower in mercury than previously achieved, was prepared, with a thinness comparable to those observed in the coin alloys. However, further work is required to clarify further issues, e.g. the role of the Ag/Pb in the alloy producing a better layer, the application of the plating before the striking of the coin to reduce the length of the process, the use of higher temperature in less heating time to reduce mercury on the surface.

The importance in this research not only lies in numismatic technology, but also in the wider analysis of silver plating. Silver amalgam plating must be considered a possibility for all other archaeological and historical artefacts plated with silver.

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