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Silver coated lead coins: An appraisal of ancient technology

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Abstract

In this paper we report some experimental archaeology research consisting in applying a two-step electrochemical displacement procedure in order to simulate the fabrication route which could have been used by coin counterfeiters of the 3rd century BC for the silvering of a Pb substrate. A material characterisation of a relevant archaeological item [5] has revealed a bi-layer coating, with a Cu interlayer and an Ag top layer. SEM morphology and XRD textures of the Cu and Ag layers cannot be explained with thermal or mechanical procedures and exhibit typical features of electrochemical displacement processes. We replicated a coating process with materials that are documented for the historical period of interest and that lead to the formation of a bi-layer coating exhibiting essentially the same morphological and structural properties of the archaeological object. The direct displacement coating of Pb with Ag has been shown not to be feasible with period chemicals, whilst the duplex coating could be achieved by sequential use of a Cu(II)-acetate solution, displacing Pb, and of a Ag(I) solution obtained by dissolving AgCl in dilute ammonia. The coatings obtained have been characterised by SEM; XRD and colorimetry. The double displacement process yields a cauliflower-like agglomerate structure, showing close similarities with the morphology of residual white-metal coating of the coin. Cu and Ag displacement layers exhibit a typical (111) texture that cannot be reconciled with that obtained by thermal or mechanical plating techniques and that matches the texture found in the counterfeit coin. The spectral reflectivity and colorimetric parameters of the final Ag layer perfectly match those of bulk Ag.

1. Introduction

Solution chemistry processes are paid much less attention in ongoing archaeometric research than are ancient metallurgical and ceramic pyrotechnologies, notwithstanding the fact that some wet chemical manufacturing processes (such as precipitation, filtration and dissolution) have been in standard use ([1] and references therein contained) from the distant past for the production of dyes, paints and cosmetics.

Wet chemical processes that were practised in ancient times are indeed especially difficult to trace, despite the relative abundance of written records, mainly because of the lack of protochemical texts of both the modern linguistic representations (formula, reactions and equations) and the syntactic rules of the chemical symbolism [2] – a terminological scatter and a semantic distortion which seriously hinder deciphering the "alchemic" documentary evidence.

Researches in experimental archaeology, particularly the controlled replication of recovered artifacts, can help us in coping with this inadequacy to reconstruct the solution chemistry technologies of the ancient world from contemporary scholarly compendia, through the establishment of reasoned conclusions [3] against an initial hypothesis.

This research program has replicated, by using experimental archaeology techniques, a two-step electrochemical displacement procedure which could have been used by coin counterfeiters of the 3rd century BC for the silvering of a Pb substrate. The artifact (Figure 1) concerned with the replication experiments is a Pb coin, now on display at the National Archaeological Museum of Taranto (Italy), which resulted from a monetary hoard unearthed in 1948 near Parabita (province of Lecce, Italy). The hoard consisted of more than one thousand Western Greek coins stored in a sealed pottery vessel and exhibited no evidence of modern intrusion. Quite surprisingly the elemental composition of this artifact, went undetected through numerous examinations *and consequently* it was regarded for many years as a regular coin in the series of the silver didrachms minted in Southern Italy in the course of the 4th and 3rd centuries BC [4].

A material characterisation of this artifact, which has been assigned the number 13 in the inventory list for the

Fig. 1. Item Parabita #13 (counterfeit didrachm); Rider crowning horse walking right; dolphin below/Young man on dolphin right holding phrigian helmet, stars on either side, waves below.

Parabita hoard, is described in detail elsewhere [5] and only a brief account of the main results of interest for the present work will be given here. The data collected have disclosed a contemporary counterfeiting procedure based on a metal coating process onto a Pb substrate. This coating has been identified as a bi-layer with a Cu innermost and an Ag outermost visible layer. As far as the coating application technique is concerned, the gathered evidence has clearly indicated that the original appearance of this artifact cannot be explained in terms of established methods [6, 7], all of pyrometallurgical nature, for the growth of an artificially silvered coating in classical antiquity; SEM morphology and XRD textures suggested the achievement of the observed microstructure by an electrochemical displacement process.

There is no written record showing positive use of electrochemical displacement reactions in classical antiquity, either in hydrometallurgical processes or in base metal coating treatments. While it is claimed [8] that the use of metal iron to recover Cu from sulphate solutions was current practice in ancient China and Arabic Spain, the first citation in the literature to this reaction is found in the works of Paracelsus [9] who mentioned the process to support his alchemic belief on metal transmutation.

As far as the intriguing question of a duplex cementation process strategy (instead of a direct Ag plating process) is concerned, the following must be said. Direct Ag cementation onto a Pb substrate is scarcely practised in modern technology. The kinetics of this process have been studied [10, 11] in neutral nitrate and chloride solutions by the rotating disc electrode technique; in both cases the rate determining step was found to be mass transfer with low activation energy barriers. The aim of these studies was the recovery of the cemented Ag from the leach liquor and no attempts were made to obtain adherent deposits. We would anticipate here in this regard that, in our experiments, any attempt at the direct plating of an adherent Ag layer onto a Pb substrate from simple salt solutions by conventional dipping was unsuccessful, resulting in the formation of a blackish powdery deposit on the Pb surface.

2. Materials and methods

2.1. *Chemicals available to ancient coin counterfeiters*

In the following subsections we shall discuss the solutions employed in our replica experiments in terms of the availability of the relevant material in ancient times.

2.1.1. *Copper solutions*

The production of Cu(II) acetate with different states of hydration (verdigris, a green/blue pigment used by painters) by the action of vinegar on metal Cu is well documented in classical antiquity by authors such as Theophrastus, Dioscorides and Vitruvius [12]. We can list:

(a) Theophrastus of Eresus (371–286 BC [13] presented a definitive study of the use of vinegar in the production of white lead and verdigris manufacture;
(b) the Herbal (also known as “de Materia Medica”) of Dioscorides [14] (which is thought to have been written about 55AD) describes a method of preparing verdigris $(CH_3COO)_2 \cdot Cu(OH)_2$, a green/blue pigment used by painters;
(c) Vitruvius [15], who lived in first century AD, describes the production of white lead and verdigris.

Moreover, recent studies [16] on colours and inks from an Egyptian Papyri dated from the 19th dynasty revealed the presence of verdigris among the pigments used for the vignette.

2.1.2. *Silver solutions*

Solubilisation of metallic Ag requires nitric acid, whose production by distillation started in the 13th century [17] and no conclusive textual and material evidence is found in the literature on the availability in ancient times of Ag salts that can be easily converted into a water-soluble Ag(I) compound other than chlorides, before the late medieval period [8]. Mineral chlorargirite, AgCl which forms on top of Ag ore veins that have been subjected to weathering, was mined since the early stages of metallurgy [17] and, moreover, fresh evidence is now available [18] regarding a solid state process on stream by the 6th century BC for separating Au and Ag, during which much of the Ag was bound into silver chloride. Chlorargirite is largely soluble in dilute ammonia and can be dissolved in stale urine that has degraded to ammonia [19] without resorting to distillation.

2.2. *Chemicals*

The substrate used in this research was a Pb disc (diameter 12.7 mm) of 99.9% purity, metallographically polished with 320 grit silicon carbide paper. An iron wire (diameter 0.2 mm, purity > 98%) was brought in contact with the Pb disc in order to enhance the rate of displacement reactions. The analytic-grade chemicals employed for the preparation of the solutions were: Cu(II) acetate monohydrate $(CH_3COO)_2Cu \cdot H_2O$, citric acid monohydrate, ammonium hydroxide solution 28% in water. AgCl was produced by scraping the corrosion products formed on an Ag rod (diameter 7 mm, purity 99.5%), corroded galvanostatically at 5 mA cm^{-2} in a NaCl solution acidified to pH 2 by HCl [20].

2.3. *Analytical methods*

2.3.1. *Morphological characterisation*

The morphology of the samples was studied with a Cambridge Stereoscan 360 SEM. The electron source was LaB_6. Electron detection was carried out with a scintillation photodetector. The typical working pressure was 10^{-7} mbar.

2.3.2. *Structural characterisation*

Structural characterisation was performed by XRD, using a Philips PW 1830 diffractometer equipped with a Philips PW 1820 vertical Bragg-Brentano powder goniometer and a Philips 1710 control unit. The scan rate adopted was 1 deg s^{-1}. The radiation was unmonochromated Cu Kα.

2.3.3. *Optical characterisation*

Measurements of the colour of the replicated coating was performed by measuring the CieLab coordinates with a X-Rite SP62 colorimeter. The CieLab system [21] describes colour as three-dimensional coordinates L, a and b which are obtained as direct readings from a spectrophotometer. The CieLab coordinates L, a and b are claimed to quantify the human perception of the factors affecting the perception of colour: "hue" H (the colour proper, in terms of spectral adsorption of visible light), "lightness" L (i.e. brightness) and "chromaticity" C (i.e., the distance from the pure hue). L directly quantifies the lightness, a is the red/green axis, b is the yellow/blue axis. The values of a and b define the hue H, while the chromaticity C is defined as $C = (a^2 + b^2)^{\frac{1}{2}}$. By calculating the cartesian distance between two points in the CieLab system, differences in colour between two different objects 1 and 2, can be numerically described as: [22]

$$\Delta E = [(a_1 - a_2)^2 + (b_1 - b_2)^2 + (L_1 - L_2)^2]^{\frac{1}{2}}. \qquad (2)$$

2.4. *Simulation of the fabrication process*

2.4.1. *Direct Ag plating onto a Pb substrate*

In alkaline (including ammoniacal) or neutral (pH > 6) solutions the cementation-by-dipping reaction is inhibited by the formation of an insoluble layer of $Pb(OH)_2$ on the surface of the Pb metal. This process is also strongly hindered in chloride-containing solutions, owing to the precipitation of $PbCl_2$. In $AgNO_3$ (of various concentrations) solutions no adherent deposits were obtained.

2.4.2. *Cu plating onto a Pb substrate*

Smooth, adherent deposits were obtained by dipping polished Pb discs in a dilute solution (20 g l^{-1}) of Cu(II) acetate monohydrate, $(CH_3COO)_2Cu \cdot H_2O$) for 5 min. Even better results were obtained from a solution obtained by adding 3 g l^{-1} citric acid to the cementing solution. In this latter case a bright Cu layer was detected, possibly due to the well known reducing action of the citrate ions in aerated Cu(II) solutions [23]. Quite surprisingly, only a limited amount of information is found describing the cementation of Cu on Pb [24]. Relevant results on anion effects can be derived from papers on the self-displacement of Pb [25, 26]. The thickness of the Cu deposit was regulated by contacting the coppered flan with an iron wire, thereby denobling the mixed potential.

2.4.3. *Ag plating onto the Cu surface*

The Ag–Cu displacement reaction has been extensively covered in the literature due to its possible applications in industry for solution concentration and purification [27]. The initial rate of this reaction is controlled by the rate of diffusion of the more noble metal ions to the reacting surface and is independent of the presence or absence of oxygen in solution; after the initial period of Ag deposition, rate enhancement is observed, mainly associated with an increase in the effective surface area, due to the dendritic growth of the deposit [27].

The reaction was conducted in a solution obtained by dissolving AgCl in dilute ammonia until a final Ag^+ concentration of 50 g l^{-1} was attained. A smooth, uniform and semi-bright deposit was obtained for vanishing concentrations of free ammonia and dipping times of 1–5 s. With the shortest deposition times, the Cu layer was not entirely dissolved and a bi-layer structure was obtained. If the Ag deposition reaction went to completion, no Cu would be detected by the analytical procedures described above. The rather dull aspect of the deposit was improved by polishing with 10 μm γ-alumina powder, in order to obtain a bright metal finishing.

3. Results and discussion

3.1. *Morphology*

The SEM morphologies of the deposits resulting from first and cumulative plating treatment are shown in Figures 2, 3, respectively. As expected for the first stage of the electrochemical deposition reaction on Pb cathodes [28, 29], a partial coverage is obtained consisting of nodular crystallites (Figure 2). In the case of the double displacement process (i.e. displacement of Pb with Cu followed by displacement of Cu with Ag), a cauliflower-like agglomerate structure is grown (Figure 3), showing close similarities with the morphology of residual white-metal coating of the Parabita 13 coin [5].

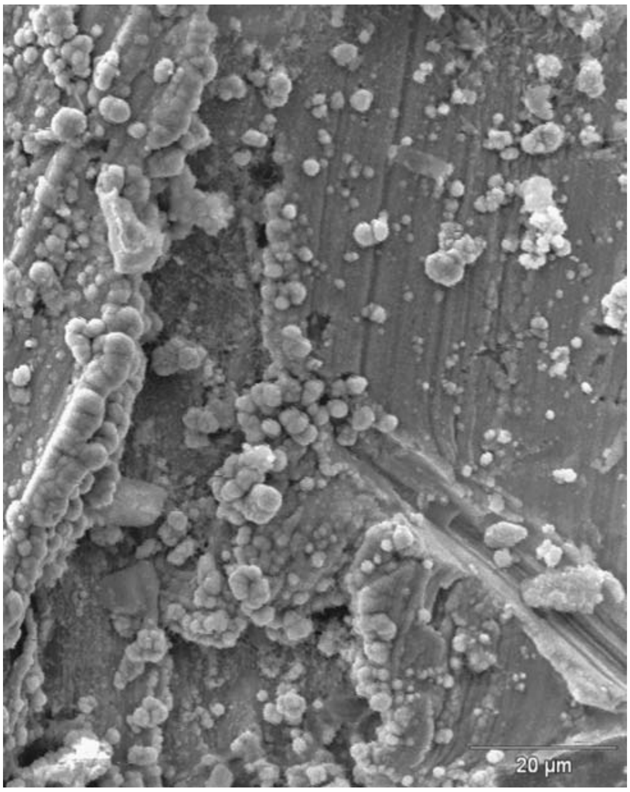

Fig. 2. SEM micrograph exhibiting the morphology of a Cu displacement deposit onto Pb.

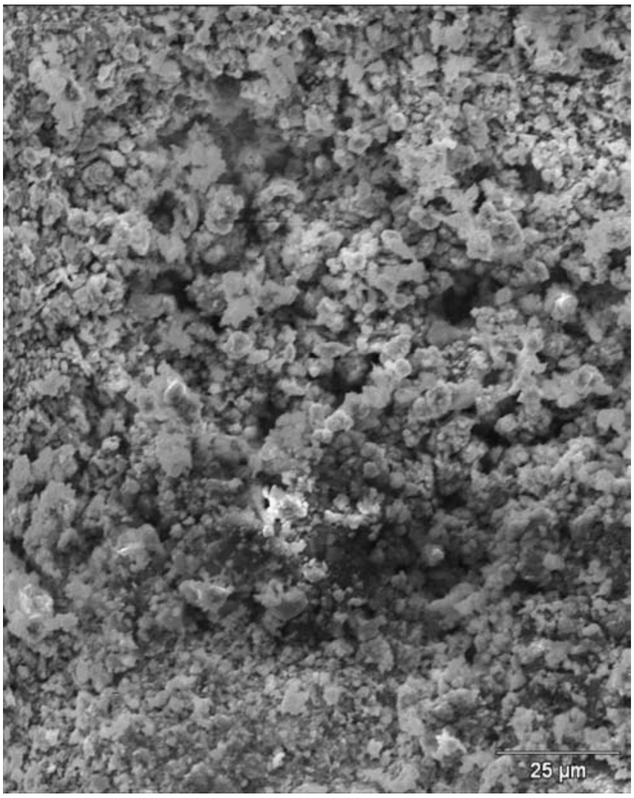

Fig. 3. SEM micrograph exhibiting the morphology of a double displacement deposit obtained by displacing Pb with Cu first and then Cu by Ag.

3.2. *X-ray diffractometry and texture analysis*

Figure 4 shows an X-ray diffractogram of a Pb disc cemented with Cu. Figure 5 shows an X-ray diffractogram of a Pb disc that underwent two subsequent cementation treatments (displacement of Pb with Cu followed by displacement of Cu with Ag), without achieving the complete dissolution of the intermediate Cu layer. Figure 6 shows a diffractogram pertaining to a duplex cementation process in which the Ag deposition reaction was given completion: the diffraction peaks of Cu are almost undetectable. In this latter case a thick Ag layer is revealed. Quantitative analysis of the relative diffractometric peak intensities of the substrate and coating [30] allow estimation of coating thickness of Cu displacing Pb and Ag displacing Cu plated onto Pb. Cu and Ag thicknesses of 4.43 ± 0.25 and 3.23 ± 0.66 μm are found. The preferred orientations of both Cu and Ag deposited layers are invariably $\{111\}$. These results substantially match those of the texture analysis reported in [5].

3.3. *Colour measurements*

Colour data collected by the CieLab method on the replicated duplex electrode are compared to the measurements taken on two genuine Ag Tarentine didrachms from the same hoard. All the investigated items show similar spectral reflectivity curves (Figure 7) and CieLab parameters (Table 1), typical for Ag metal. Moreover, vanishing values of the difference in colour, ΔE, are observed between the laboratory-made specimens and the coins taken as a standard.

4. Conclusions

As indicated in the foregoing discussion, any attempt, carried out in this work, to plate an adherent Ag layer

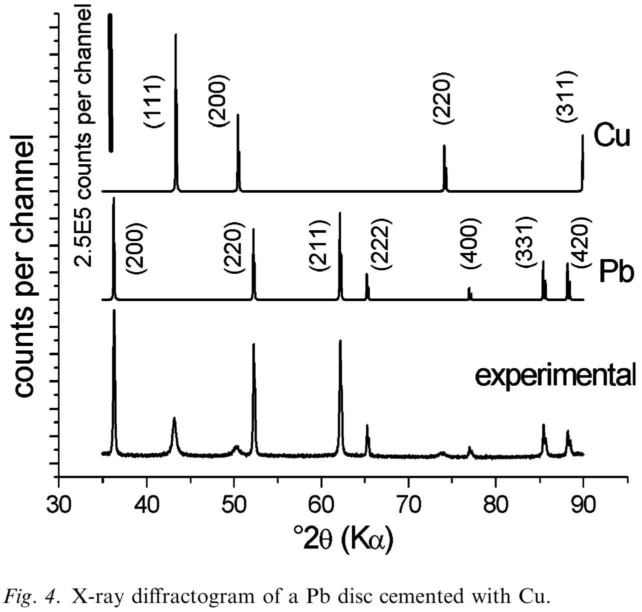

Fig. 4. X-ray diffractogram of a Pb disc cemented with Cu.

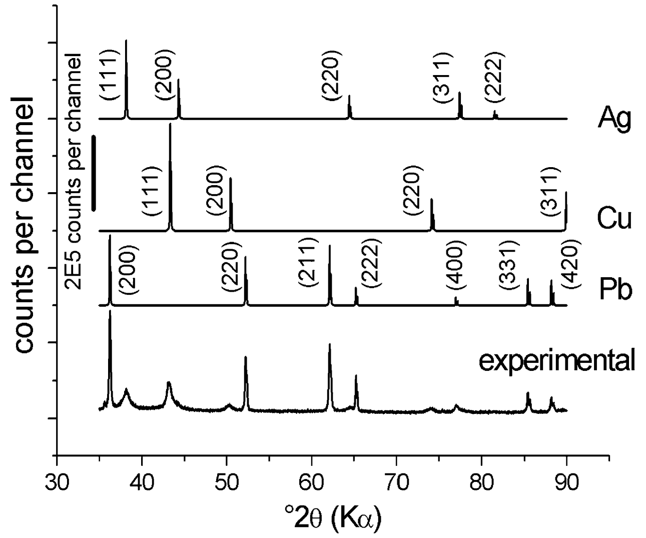

Fig. 5. X-ray diffractogram of a Pb disc who underwent two subsequent cementation treatments (Cu onto Pb, followed by Ag onto Cu), without achieving the complete dissolution of the intermediate Cu layer.

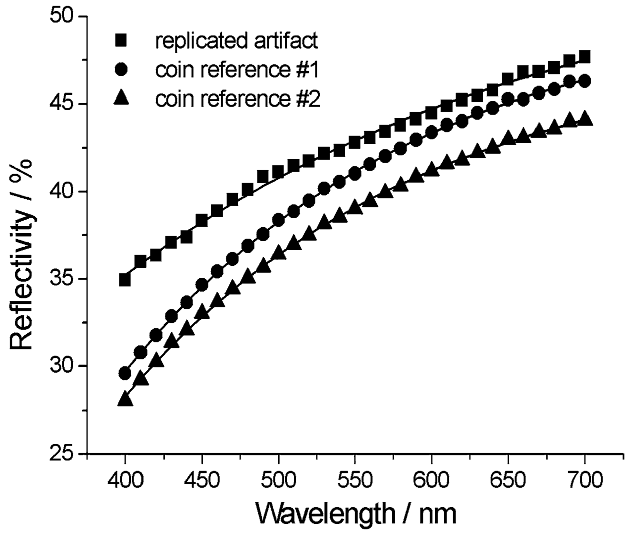

Fig. 7. Spectral reflectivities of the replicated duplex coating and of two genuine Ag coins from the same hoard (the lines are fits with a harmonic oscillator model of the electronic structure of Ag).

onto a Pb substrate from simple salt solutions by simple dipping resulted in the formation of a blackish powdery deposit on the Pb surface. Different approaches to the achievement of a deceptive thick and adherent Ag layer – not documented in the scientific literature – could of course be attempted, based on an electrolyte able to complex Ag(I) without passivating the Pb substrate, such as tartrate ammoniacal, acetate ammoniacal. Nevertheless, from the point of view of the present metal electrochemical science, the duplex approach seems more viable, to the best of our understanding, in order to provide a sound explanation of the strategy adopted by the ancient forgers.

While the results of these experiments may not change opinion on the electrochemical skills of the ancient Western Greeks, they demonstrate the feasibility and effectiveness of this reconstructed technology as a viable silvering technique for a calculated coin counterfeiting strategy.

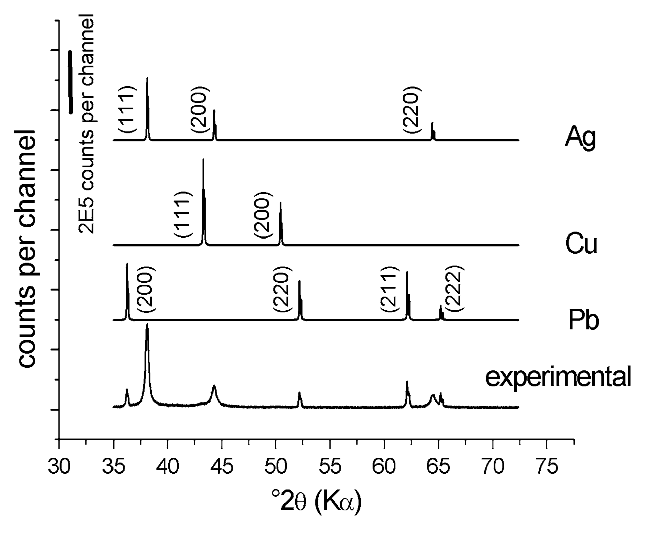

Fig. 6. Diffractogram pertaining to a duplex cementation process (Cu onto Pb, followed by Ag onto Cu), in which the Ag deposition reaction was given completion.

In this regard, it is worth noting that patina layers on archaeological findings may have been lost for two reasons: (i) environmental attack (ii) inappropriate restorative treatment [7]. As noted in the Introduction of the present paper, the coins from the Parabita hoard were contained in a sealed vessel and, moreover, these objects were not given any cleaning treatment; this may be the reason why the coating of item # 13 still survives, though missing over most of the surface area.

This investigation opens up several problems that are relevant to both the technologies of heritage conservation and restoration and electrochemical surface science. Among these the following can be pinpointed for future cognate studies: (i) the importance of handling procedures of historical artefacts based on the knowledge of the electrochemical and mechanical (in particular tribological) performance of metallic and ceramic coatings (ii) the archive search for similar examples of metal plated archaeological items, which might have escaped identification owing to the fact that very often the scholars in charge of the study of these objects have limited surface-science skills.

Table 1. CieLab parameters of the replicated duplex coating and of two genuine Ag coins from the same hoard.

	L	*a*	*b*	*c*	*h*	Δ*E* (Replica vs. Reference)
Replica	71.40	0.69	5.34	5.38	82.65	0
Ref. #1	70.11	0.94	7.95	8.01	83.29	2.92
Ref. #2	68.65	0.94	7.72	7.78	83.08	3.65

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