Investigating methods of minting Ancient Greek silver plated copper coins: studies in Neutron Tomography, Texture and Phase Analysis

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Since 2014 the ACNS has worked with the ACANS at Macquarie University to study a particular type of silver coin minted in southern Italy around 550-450bce. Analysis of over 80 of these incuse coins has taken place, one of them turned out to be a 'fake', a thin silver foil 0.4mm thick over a Copper base. Two other coins of similar age, known to be 'fakes' of silver over copper were then studied to look for details on the manufacturing method of these coins, were they officially minted due to a silver shortage or illegal?.

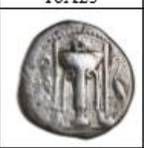
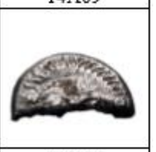
Inv.	07GS527	16A25	14A09
			
City	Metapontum	Kroton	Athens
Year	510-470 BC	510-480 BC	525-515 BC
Diameter	24 mm	~20 mm	~17 mm
Weight	8.1 g	7.4 g	6.7 g

Table 1 – Properties of the silver plated coins under study

Neutron Tomography

The plating technique of the set of coins via neutron tomography provides critical information on macrostructure and morphology. In all cases the silver plating was applied by diffusion bounding to a copper core, but noticeable differences in the coating structure, and in the silver-copper ratio suggest different procedures, variations in effort required to complete the work, and finally variation in the expertise available to undertake plating. There is no evidence of a soft solder material (Tin, Lead), hence temperatures of around 770C were needed (the silver-copper eutectic) to form a good bond. Coin 16A25 shows clear evidence of repeated silver plating of the copper core – this hadn't been noted in the literature to our knowledge. Elemental composition & porosityhas been calculated (Table 3).

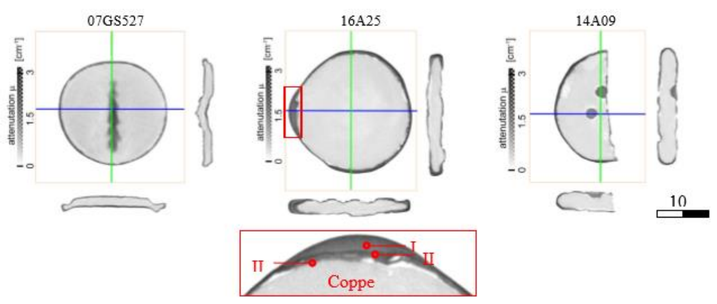


Figure 1: Maps of the planes cropping the reconstructed volume of each coin are shown together with the corresponding cross sections. The scale bar at the left of each figure indicates the colour code for the attenuation coefficient. A detailed view of the multi-layered plating is reported for coin 16A25 at the bottom.

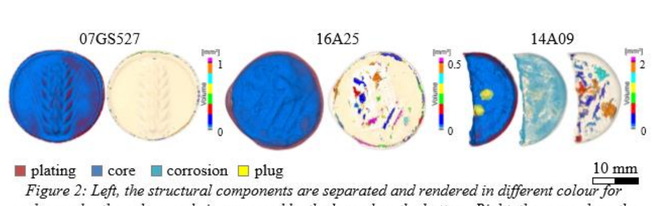


Figure 2: Left, the structural components are separated and rendered in different colour for each sample; the colour code is expressed by the legend on the bottom. Right, the maps show the distribution of porosities. A scale bar on the right side of each figure indicates the coding colour-volume.

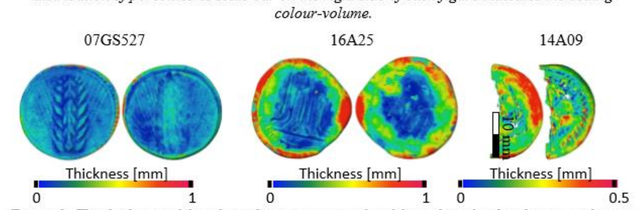
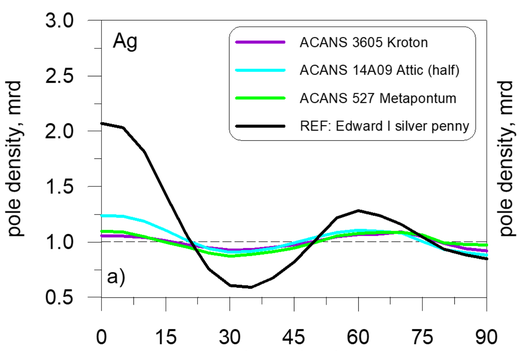


Figure 3: The thickness of the silver plating is reported in false colour for the obverse and revere of each coin. A scale bar indicates the coding colour-thickness.

A series of 3 plated coins: Ag texture



A series of artificial coin-like samples made at the controlled condition (temperature)

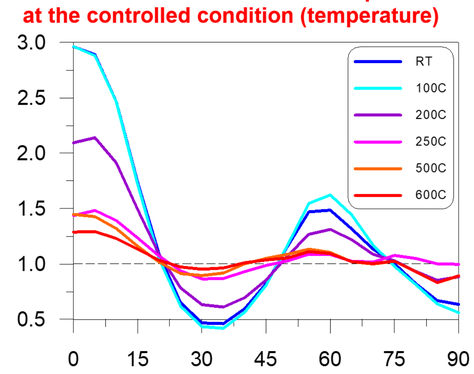


Figure 4 (Left) Pole figures for the 3 plated coins and a reference hammered silver penny of similar size, produced by a known room temperature technique
Figure 5 (Right) A set of artificial silver blanks produced under temperature controlled conditions.

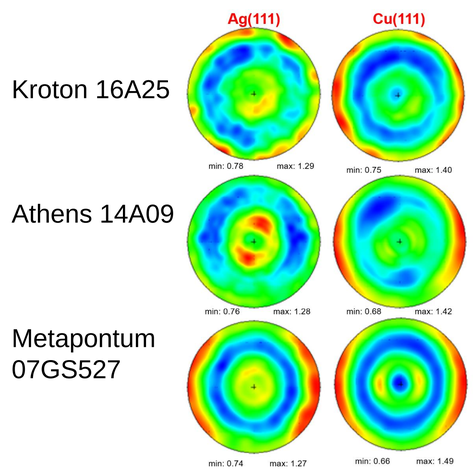


Figure 6 Pole figures for Silver (111) and Copper (111) for the 3 plated coins.

Neutron Texture Analysis

The neutron texture analysis on the silver plated coins was compared to various blank artificial silver coins manufactured at the ACNS to allow comparison of the texture measurements. The results show that the process temperature was relatively high, around 700C. This also confirms what the tomographic analysis indicated, no low temperature solder type material was used.

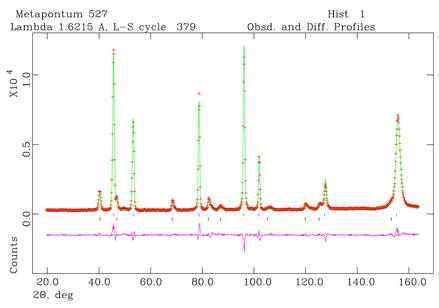


Figure 7 – Neutron Diffraction data of the plated Metapontum Stater (07GS527)

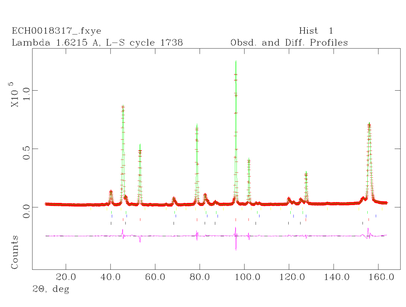


Figure 8– Neutron Diffraction data of the Kroton Stater (16A025)

Neutron Diffraction

Neutron Diffraction was undertaken on Echidna on all 80 incuse coins, only the coin Metapontum 527 was shown to be plated. Rietveld analysis was performed on all 3 plated coins. Analysis of Kroton 16A25 confirmed the presence of 5 phases, Cu, CuO, and 3 the different Silver phases. Each with slight variations in Copper content (0.5%,2.5% and 10%).

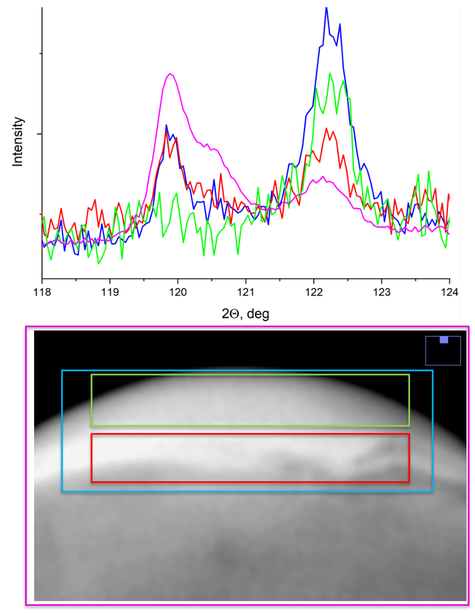


Figure 10 Neutron Tomograph of the Triplet structure of the Ag(311) reflection of 16A025 with 3 distinct silver layers of different alloying. Colours correspond to the fig 9 above, showing 3 separate slices measured on Echidna.

Figure 9 (left) The multiple phases of 16A25 can be most easily separated around 2θ = 122 . The green layer is (mainly) the outer most (final) silver layer. The red and purple lines are other phases, the blue is the sum of all phases present.

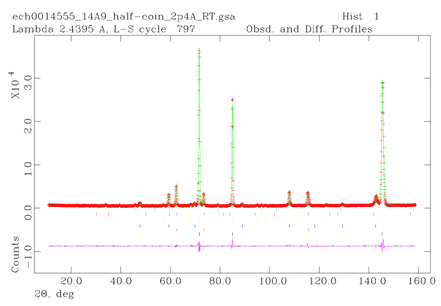


Figure 11 – Neutron Diffraction data of the half-coin 14A09 showing the silver outer layer and copper core.

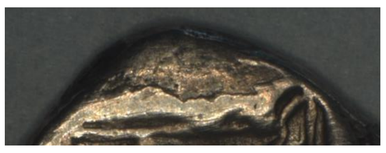


Figure 12 – Optical image of the replated area of 16A25 that was subject to analysis on Echidna.

Alloy composition (assuming Ag-Cu system) determined by Neutron Diffraction				
Coin	Phase	wt%	vol%	Purity of Phase
Metapontum				
07GS527	Cu	64.8	68.3	At least 99.5% pure Cu (e.g. 0.2% of Sn or 0.5% of Ag)
	Ag	35.2	31.7	99.2 pure Ag (0.8at% of Cu)
Kroton				
16A25	Cu	61.3	65.1	Pure Copper
	Ag1	19.9	18.1	0.% Cu in Ag
	Ag2	8.6	7.8	2.5% Cu in Ag
	Ag3	8.7	7.9	10% Cu in Ag
	Cu2O	0.7	1.1	
Athens				
14A07	Cu	59.2	59.2	At least 99.8% pure Cu (e.g. 0.04% of Sn or 0.2% of Ag)
	Ag	31.9	27.2	99.8 pure Ag (0.2 at% of CU)
	Cu2O	8.3	12.3	
	CuCl	0.6	1.3	

Table 2. Composition of each phase based on Rietveld analysis and calculations of the d spacing in comparison to Vegard's law).

Summary

Using a combination of 3 neutron technique a wealth of information on the manufacturing process of plated silver coins can be ascertained non-invasively. Diffraction indicated the presence of the Copper core, Tomographic analysis allowed calculations of the porosity, silver to copper ratio, and the presence of re-plating. Texture analysis, comparing with prepared silver blanks, allowed for information on the processing temperatures used. Tomoography and Diffraction gave very similar results for the Ag-Cu ratio.

There is clearly no intermediate layer between the silver and copper, meaning diffusion bonding had to take place, the texture analysis strongly suggests this and indicates a process temperature of around 700C. The skills required to make the plated coins exceed those need to simply make a pure silver or copper coin. Hence making the 8.1g of silver into 3-5 plated coins instead of 1 pure one must have been worth the time and effort involved. Re- plating of 16A25 indicates the process was not always perfect.

Table 3: Results of the plating and porosity analysis of the 3 silver plated coins.

			07GS527	16A25	14A09
Plating feature	Min/max thickness	mm	0.13 – 1.49	0.06-3.75	0.06 – 0.80
	Mean		0.28	0.46	0.34
	Standard Deviation		0.11	0.36	0.19
Volume	Total	cm^{-3}	0.42	0.83	0.73
	Porosity	%	0.1	0.8	1.7
	Silver		32.9	36.8	19
	Copper		67	62.4	70.5
	Plugs & Mineralisation		-	-	8.8
Mass	Silver	g	1.5	3.2	1.5
	Copper		6.6	4.2	5.2

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