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SAXON SHAKUDO

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Introduction

In the summer of 1991 an excavation took place, on the brow of Andrews Hill overlooking Easington, Co Durham. It recovered traces of a number of graves, part of a largely ploughed out Anglian inhumation cemetery (Pickin 1991, Hamerow & Pickin 1995). The grave goods recovered from this excavation, along with a series of similar objects previously recovered from this site by metal detecting, were cleaned, conserved and analysed in the conservation laboratories of the Department of Archaeology, University of Durham.

Within the grave goods recovered from excavation was a copper alloy cruciform brooch which, rather than the normal green copper corrosion products, was covered in a coherent black coating with a satin like sheen. The object itself was of an unusual form and its coating was unlike anything which has previously been reported from the North East of England.

The Andrews Hill Brooch

The brooch (Fig. 1), was recovered from Grave 2 of the cemetery. There was virtually no trace of the body; only two fragments of bone were recovered indicating that it had been buried in an oxidising acidic environment. Other finds recovered from this grave included a number of glass and amber beads, a flat copper alloy annular brooch, fragments of a number of wrist clasps, a composite copper alloy mount, a small iron ring and a copper alloy bracelet. All the other copper alloy finds had normal green corrosion crusts. These finds suggested that this was probably the grave of a relatively wealthy woman, dated to the late sixth or early seventh century (Hamerow & Pickin 1995).

Fig. 1 The Andrews Hill brooch

The form of the black coated brooch most closely resembles that of the florid cruciform brooches of the Leeds and Pocock Grp V (a iv), though it lacks the side and top knobs of such brooches. A very similar brooch was recovered from Grave 30 of the Saxon cemetery at Norton (Leeds and Pocock 1971, Sherlock and Welch 1992, Fig 42), less than 15 miles away. The close proximity of two such unusual brooches raises the possibility of local production of this brooch type. The central panels of the head and foot plates of this brooch are unusually decorated with Style I zoomorphic ornament, the brooch also has lappets in the form of birds heads. The central panels each contain a flat crudely shaped garnet, which is again an unusual feature for florid cruciform brooches (Hamerow & Pickin 1995).

This brooch, like almost all brooches of this period, was almost certainly formed by casting copper alloy in a clay mould, and though the present brooch form looks as if it were originally a true florid cruciform brooch which had its terminals broken or cut off, there is no evidence to suggest such an origin. Indeed the metal in the areas where these knobs may have been attached is smooth and covered with the black coating, indicating that the brooch, as seen today, is in its original 'as manufactured' form. The small diamond shaped pieces of flat garnet are poorly shaped and crudely set. They appear to have originally been larger stones which were re-shaped and re-used for the manufacture of this piece of jewelry. This might again suggest a localised origin, well away from the centres of garnet production and shaping (Bimson 1985). The brooch would probably have originally been worn near the shoulder, as a dress or cloak fastener, the black coating on the back and edges of the brooch has become very thin through wear, suggesting that it was a well used and highly prized object.

Black Coating Analysis (EDXRF)

There could be a number of possible explanations for the black coating, but since the soil conditions on the brow of the hill are oxidising there is no possibility that the black coating could be a mineral such as copper sulphide which is formed in reducing conditions such as those seen on waterlogged sites. Indeed since the black coating which covered the front of the object and ran over onto the back in several areas was a coherent covering and was thinned through wear on the back of the brooch, it does not appear to be a corrosion product derived from its burial, but rather a deliberate coating created or applied at the time of manufacture. The black coating has been disrupted on the decorative panels on the front of the brooch, and more extensively on the back due to the action of nematode worms, whose presence on the brooch in the grave soon after burial resulted in the deposition of a conventional copper corrosion sequence in this area. Elsewhere the black coating has protected the rest of the brooch from the normal copper corrosion cycle. There was no trace of gilding, tinning or any other metallic coating associated with the brooch.

Elemental analysis of the surface composition of the metal from which the brooch was manufactured was undertaken using an Energy Dispersive X-ray Fluorescence (EDXRF) System (Link Systems XR200 X-ray Fluorescence spectrometer, using a Rhodium anode X-ray tube operating at 50 kV). The X-ray fluorescence technique only analyses the first few microns of the object surface and would consequently primarily identify the elements present on the external surface of the metal in the black coating. Analyses were performed on several areas of the black coating, (Table 1).

The initial two edge analyses have only thin, partial black coatings, and these analyses are thus closer to the body metal composition than the others. From these analyses it would appear that the brooch metal is principally a bronze with some zinc, lead, silver and gold present. Although there are few analyses of copper alloys from the Post Roman period which contain precious metals a number of brooches from Eketorp in Denmark (Nasman 1973) and a couple of pins from Whitby (Caple 1986) have compositions with low silver contents. One Whitby pin, W202, had significant quantities of silver and gold. Small levels of silver and even gold can occur in copper alloys by three possible routes

i) Silver and/or gold may have been added to the copper alloys intentionally to produce a metal which had particular properties, e.g. that it 'magically' produced a black coating when pickled in certain liquids.
ii) Silver and gold may have been added to the copper alloys unintentionally, perhaps as silver plated or gilded metal objects included in scrap metal which was being remelted and reused.
iii) As a result of their presence in trace amount in the copper ore. One possible source of such an ore available at this period would be early copper production from the Harz Mts. The copper ores from the Harz are a complex of copper lead and silver deposits, and may have produced copper with high silver contents and even possibly some gold.

However, since traces of silver and gold rich copper alloys are uncommon in the analyses of Saxon objects (Caple 1986; Mortimer 1991; Brownsword *et al.* 1986, Mortimer, Pollard & Skull 1986; Oddy 1983) it is unlikely to be an impurity from a copper ore source and almost certainly represents a deliberate or unintentional addition.

The latter four analyses in Table 1, give an indication of the analytical composition of the black surface coating. When compared to other copper alloys of the period, it is clear the surface is rich in tin, gold and phosphorous. One may compare these results to those seen through a 'normal' corrosion crust for bronze.

The copper is depleted at the surface due to loss from corrosion, zinc and lead values are particularly depressed as their corrosion products have high solubility in the acidic aqueous environment of metal corrosion crusts. Silicon and iron values are high at the soil interface but decline towards the metal since these elements are adsorbed from the soil, whilst sulphur and chlorine values are high at the metal surface, as they are the soluble anions attracted to the anodic surface of corroding metal. Tin concentrations are relatively higher in the corrosion crust than in the metal since tin forms stable stannic oxide (cassiterite) whilst most other metal composition components have been significantly depleted.

Thus enhanced tin values may be expected through normal corrosion processes, gold as an inert uncorrodable metal may also have relatively increased due to the loss of other components such as copper, zinc and silver, but the phosphorous has been introduced. Only small amounts of phosphorous are normally seen in

Table 1: Elemental Composition of the Surface Coating of the Andrew's Hill Brooch

	Copper	Tin	Lead	Zinc	Gold	Silver	Iron	Silicon	Sulphur	Phosphorous
Edge 1	39.1	35.0	9.5	2.4	3.6	2.0	1.3	1.8	0.0	4.7
Edge 2	35.5	30.4	9.6	1.5	12.7	1.7	1.1	1.7	0.0	3.1
Front 1	38.1	30.0	8.5	1.7	14.1	0.0	1.1	2.4	0.0	4.1
Front 2	43.4	28.8	11.1	1.7	7.3	0.0	1.1	1.9	0.0	3.8
Front 3	43.9	28.8	7.6	0.7	11.0	0.0	1.0	1.8	0.0	5.1
Front 4	48.0	27.3	6.9	1.6	10.6	0.0	0.9	1.8	0.0	2.9

[All figures are normalised and have an accuracy 10% for major elements, 20% for minor elements.]

metal since it is normally lost from molten metal into the slag and gas phases, so larger quantities are due to subsequent reactions such as corrosion or patination at the metal surface.

Black Coating Analysis (SEM)

In order to further investigate the nature of the black coating a minute fragment was removed from the object, where the coating had been nicked by a trowel during the excavation process. This was mounted up on a stub and visually and chemically analysed using a Scanning Electron Microscope. The black coating material appears visually to be a mineral layer. The lack of sulphur indicated by both analytical techniques, suggests that the minerals were in the oxide, carbonate, hydroxide or phosphate form. The semi-quantitative results from these analyses were expressed as % of the mineral containing the highlighted element and are shown in Table 2.

The initial image Figure 2, shows a cross section through the whole black coating fragment. The analysis of the overall composition of the coating is given by analysis 1 in Table 2. The right hand edge of the cross section, (Fig. 2), equates to the outer surface of the coating and has a composition indicated by the second analysis. The third analysis represents the composition in the centre of the section, whilst the fourth analysis represents the composition on the left hand edge of the section. This latter area was the inside edge of the coating, next to the metal. It appears from these and the other spot analyses taken through the section that there are two forms of mineral present in the black coating:

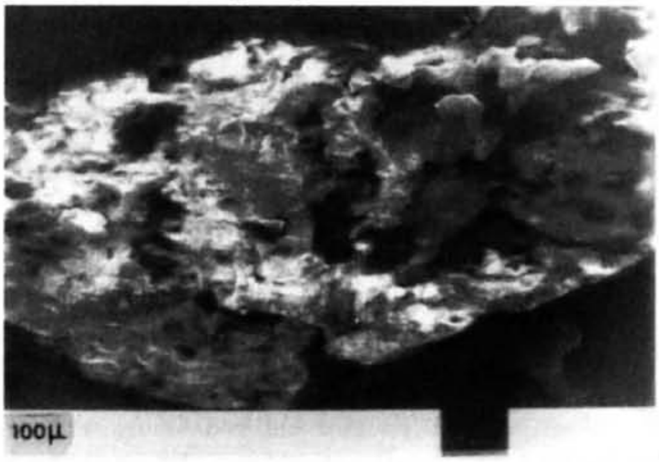

Fig. 2 Cross Section through the black patina of the Andrews Hill brooch

i) A dense phase, prevalent on the inner and outer surfaces, which is rich in tin, probably stannic oxide, with significant quantities of copper and smaller amounts of phosphorous and lead minerals invariably present.
ii) A less dense vesicular phase, prevalent in the centre of the coating layer, which is rich in copper minerals, with significant amounts of tin minerals.

Traces of silver, zinc and it is suspected gold are distributed throughout these phases. The lack of chlorine or sulphur as well as the uneven distribution all indicate that this is probably not the product of a normal corrosion process, but some form of coating or surface treatment. In some instances copper alloys have been shown to corrode in an uneven manner producing a banded structure, with tin rich bands produced within the corrosion crust due to Leisegang phenomena (Scott 1985, Wouterers et al 1991). Although this phenomena may generate the analytical variations noted above in the tin content, it does not account for the density and coherence of the coating, the lack of chlorine or sulphur or the correlation of gold and silver in the alloy with the occurrence of the black coating found on the Andrew's Hill brooch.

Table 2: Elemental Composition of the Black Surface Coating of the Andrew's Hill Brooch – Semi Quantitative SEM Analysis

	Major (<50%)	Lesser (10-50%)	Minor (10-0.5%)	Trace (>0.5%)
Whole X-Section		Cu, Sn		Ag, Pb
Outer Edge of X-Section	Sn	Cu	Ag	Pb, Sb, Zn, Si, Fe, Cl, P
Centre of X-Section	Cu	Sn		Pb, Ag
Inner Edge of X-Section	Sn	Cu	Pb	Ag, P
Outer Surface (Dense)	Sn	Cu	P, Pb	Ag, Zn
Outer Surface (Dense)	Sn	Cu	P, Pb	Ag, Zn
Outer Surface (Vesicular)	Cu	Sn	Ag, Zn	Sb
Outer Surface (Vesicular)	Cu	Sn	Fe, Sb	
Outer Surface (Vesicular)	Cu	Sn		Pb

[The percentage figures quoted are estimates based on the analytical spectra and refer to the percentage of mineral containing the element mentioned which is apparently present. Gold was not detected and may have been eliminated from the analytical programme due to the use of gold coating for SEM samples]

Black Coatings Considered

The creation of deliberate black patination on copper and its alloys, has been known in Japan since the 14th century AD (Harris 1993) and this decorative metal-working technique has been termed *shakudo* (Savage & Smith 1979). Work in the early 1990s by La Niece (1990) and Craddock (1994) (La Niece & Craddock 1993) showed that this technique had been far more widely used in antiquity than previously realised. Historical texts describing a black bronze as well as actual objects exhibiting a black patina have now been identified from 18th Dynasty (1550–1295 BC) Egyptian (*hsmn-km*) as well as examples from ancient Mycenae (Craddock & Giumlia-Mair 1993). The Romans knew of black bronze ("Corinthian bronze") and we have both Roman texts which describe it as well as objects which exhibit the phenomena. Examples have also been recovered from 15th century AD China (*wu tong*) (Wayman & Craddock 1993) and historical references indicate the use of a black copper alloy (*zi khyim*) in Tibet in the 10th century AD. The historic references to these black copper alloys usually indicate the presence of precious metals in the alloy. In many of the objects which have this black metal patination, analysis has shown that either the copper or bronze base metal of which the object is composed has a small percentage of gold and silver or just gold present (La Niece & Craddock 1993). Where records exist of the process, such as Gowland's records of the *shakudo* process practiced in Japan in the 1870s, the metal surface is described as being polished and then after cleaning (de-greasing) being treated with a variety of aqueous acidic solutions such as mixtures of copper acetate (verdigris), copper sulphate (blue vitriol) and either aluminium potassium sulphate (alum) (Murakami 1993) or potassium nitrate (nitre) (Craddock & Giumlia-Mair 1993) in very dilute solution. This created the dense deep black patina over the metal surface.

Analysis of Japanese *shakudo* has shown that it is primarily composed of cuprite (Cu_2O) (Murakami 1993), which though normally a dense red mineral is clearly formed in these circumstances as a black mineral, probably due to the presence of gold impurities in the alloy (Murakami 1993). Initially formed from impure 'mountain metal' (*yamagone*), the later purified metal most favoured for shakudo was pure copper with 3–5% gold. Analysis of Corinthian bronze and *hsmn-km* by Craddock and La Niece has also confirmed that the black patina is due to the copper oxide cuprite, and not as had previously been suggested sulphides. It is clear that the presence of gold, and possibly silver, in the copper or copper alloy and the treatment of the surface with an appropriate solution was seen to give such consistently good patination results, that this alloy was deliberately created and utilised by many different cultures. Craddock and Giumlia-Mair (1993) suggest that the use of this technique initially developed in Ancient Egypt and gradually spread out to the Mediterranean civilisations and thence across Asia through Tibet to China and Japan, where it is refined and reaches its artistic zenith as *shakudo*. The cuprite coating is usually a thin, coherent coating, in some cases only 2nm thick, which protects the metal beneath from further corrosion.

The patination of copper alloys to achieve a wide range of colours including black can be achieved using many different treatment solutions and alloys (Hughes & Rowe 1982). It is possible to achieve a black finish merely though heating bronze to 600°C in an oxidising atmosphere. Analysis has shown that not all black patinated copper objects of the Ancient Egyptian or Mediterranean civilisations contained gold. It appears that true *hsmn-km* or *Corinthian bronze* was often associated with gold or silver inlay and the high quality thin tough coat of black patina created on copper alloyed with gold was a subtle cultural appreciation of quality. Inferior black patinated poor quality copper alloy objects were also created (Craddock & Giumlia-Mair 1993). The popularity of *shakudo* particularly amongst the samurai (warrior) classes in Medieval Japan is related to the appreciation of black finishes and minimal decoration which expressed the concepts of wabi (inner richness in outer poverty) and sabi (the beauty of desolation) (Harris 1993). The social meaning of colour will invariably have been the dominant effect in determining the production and use of patinated jewelry.

There are, however, another series of dense black patinas, those formed on high tin bronze objects such as Dark Age belt buckles and belt fittings and the mirrors of both the Roman and Chinese civilisations. Historic references indicate that the mirrors were originally the silver colour of polished high tin bronze; consequently the black patina has formed slowly during burial often covering broken or damaged surfaces. The high tin metal alloy which typically contains 15–27% Sn has a eutectic + crystalline structure. When it corrodes the copper rich phase is preferentially lost, as well as any lead globules, to leave a copper-tin inter-metallic phase present. This slowly corrodes to form a stannic oxide SnO2 the black mineral coating which, under Scanning Electron Microscope examination, shows a pattern of inter-linked irregular cracks across its surface (Meeks 1993). Shoukang and Tangkun (1993) identify the black layer as typically 100–250 microns thick with a three layer structure, with denser outer and inner layers and a less dense central layer. There is no gold present in these high tin bronze alloys and the patinas typically have 60–70% tin and 5–15% copper (Meeks 1993, Shoukang & Tangkun 1993). As a result of a high correlation of occurrences of dense black patinated objects in the acidic soils of Southern China

(Shoukang & Tangkun 1993), it appears necessary to have acidic burial conditions in order to create the dense black patina.

It would appear that the Andrew's Hill brooch contains elements of both black patina traditions. The metal composition indicates a continuation of the decorative black patination of gold rich copper alloys, the Roman Corinthian bronze tradition into the Anglo Saxon period. The wear on the back clearly suggests a deliberately created patina formed as a decorative layer and worn away during use. The high tin concentration,

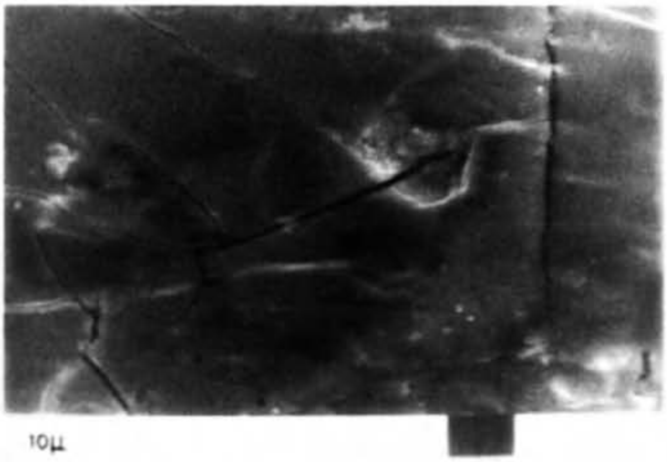

Fig. 3 Surface cracking on the dense surface layer of the black patina on the Andrews Hill brooch

crazed outer surface, Figure 3, and three layer patina structure with less dense central layer would suggest the natural corrosion of a high tin bronze in an acidic soil, though it should be noted that the tin levels are much lower than those seen in the Chinese or Roman mirror patina. The presence of gold in the alloy would probably have induced any copper phase to form black cuprite as it corroded or patinated. Thus the black patina on the Andrew's Hill brooch is probably composed of a combination of stannic oxide and cuprite, with different ratios of these minerals in the three layers of the patina. If this is indeed a deliberate patination, then on the basis of the metal analysis it must be seen as a continuation of the Corinthian bronze tradition. Given its tin content it differs from the later pure copper Japanese *shakudo* tradition. It may be that the Corinthian bronze tradition became confused or degenerated and used on high tin bronzes with deliberate gold addition creating a mixed stannic oxide cuprite black mineral patina.

Craddock and La Niece suggest that they have identified the presence of a black patina on a number of Celtic Irish and Anglo-Saxon pieces of metalwork (Craddock 1994), and this metalwork can have a high tin content. There is also another example of a Saxon brooch with a smooth black coating, which originally came from Maltby, Yorkshire, and is now housed in the Ashmolean Museum 1909.263 (Hamerow pers comm). There is also at least one other example of this black coating on an object from the Post-Roman period which has been analytically investigated: a bangle from Cannington, Somerset which was recovered from the grave of a child. The grave was probably of 7th century AD date, and the excavator felt that the bangle was of British rather than Saxon manufacture. This find was the subject of an analytical investigation by Bayley, Hirst and McDonnell (undated). The analyses of small fragments of the sheet metal of which the bangle was composed indicated that the metal was a tin bronze (8–9% tin) with 2–3% gold present and a trace of silver. The analyses of the exterior of the bangle's surface gave much higher levels of tin. Approximately 38% of the bangle's exterior patina was tin mineral, with less than 2% gold and significant quantities of phosphorous 2–3% also detected. In this instance the corrosion/patination process appeared, from the element distribution maps, to have enhanced the tin and lead contents and reduced the copper content. The gold level had not been enhanced significantly by the corrosion/patination of the metals surface. Bayley and co-workers suggest that in the absence of any evidence to the contrary that the black layer was probably a form of cuprite, which Murakami (Murakami et al 1987, 1988) had proposed as the black coating formed in *shakudo*. With the additional information from the Andrew's Hill brooch, it would now appear likely that the Cannington bangle may also have a patina composed of two phases; a cuprite rich and a stannic oxide (cassiterite) rich mineral phase.

Conclusion

The *shakudo* technique of blackening copper alloys which contained small quantities of gold was a well understood decorative metalworking technique throughout much of the ancient world. The presence of gold appears necessary as a catalyst or impurity to form a black form of cuprite (La Niece 1990; Murakami 1993). However, the patina on the Andrew's Hill brooch appears to have a second tin rich phase, probably related to the presence of stannic oxide (cassiterite), in addition to any gold catalysed copper rich cuprite. The presence of a bangle from Cannington with an almost identical alloy composition and coating adds credence to the suggestion that this is a deliberate decorative metalworking tradition. The occurrence of phosphorous and lead is noted as being associated with the tin-rich phase in both the Andrews Hill and Cannington objects and it appears likely that the phosphorous in particular may thus have a role in forming the black patina observed on these British post-Roman high-tin objects. It is possible that this two phase tin and copper patina may represent the evolution and continuation of the Roman Corinthian bronze tradition.

Further examples of smooth black coated copper alloy objects need to be identified and analysed in order to build up an analytical and typological base for understanding the extent and nature of this decorative metalworking tradition. It is particularly important to establish if we are now identifying:

i) the products of a widespread simple and well understood deliberate patination technology which develops from the Corinthian bronze tradition;
ii) a specialised alloy the output of one or more workshops which for a limited period of time produced black coated copper alloy objects in Post-Roman Britain;

or

iii) rare examples of objects made from an unusual alloy whose natural corrosion forms a deceptive black patina.

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