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Keywords

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Tin
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Keywords:

Early Anglo-Saxon period; X-Ray Fluorescence Analysis; Non-ferrous metals; Copper alloy; Tinning; Silvering; Mercury gilding.

Archaeological excavation was carried out at Blacknall Field, Pewsey in Wiltshire, between 1969 and 1975 by the Wiltshire Archaeology and Natural History Society, with Department of the Environment funding. The excavation uncovered the largest early Saxon cemetery excavated in Wiltshire and one of the largest recovered from Wessex. 109 graves were discovered containing a variety of grave goods including a number of high status burials containing weapons, fine jewellery and dress fittings.

Assessment of the composition of 57 individual items of the non-ferrous metalwork from Blacknall Field has been carried out to determine the metallic composition of objects and nature of decorative finishes which have previously been described as 'silvered', 'tinned' or 'gilded'. It is often difficult to distinguish from superficial appearances between surface coatings, in particular between silvering and tinning and many objects labelled as silvered in museums are in fact tinned (La Niece, 1993:201). Therefore this analysis has been carried out in order to avoid further confusion to insure that the correct identification of surface coatings and metallic composition can be included in the site publication.

Methodology

Analysis was undertaken by the authors, Conservation student Interns from University College London, using the EDAX- EAGLE II, X-Ray Fluorescence Machine at the Centre for Archaeology, English Heritage.

Energy dispersive X-ray Fluorescence (XRF) has the advantage over other analytical techniques for its purpose in this assessment because it enables non-destructive analysis of whole artefacts. However, XRF can not be used as a quantitative technique on the Blacknall Field objects because corrosion will have caused a change in the ratio of elements present and added additional elements such as oxygen, carbon, sulphur and chlorine which were not present when the object was manufactured. It can therefore give a list of the elements present but only a rough indication of their relative quantities. Additionally, XRF can only provide analysis of the surface of an object. This is more than adequate for determining the composition of surface coatings such as gilding or tinning but the corroded surface layer of a copper alloy artefact does not accurately represent the composition of the un-corroded original metal. This means that where in this report the copper alloys from Blacknall Field are divided into copper, bronze, gunmetal and brass, results are meant as a suggestion but can not be relied upon.

Objects were analysed on both sides at 40kV and between 200 and 400 mA. Wherever possible smooth surfaces were targeted and repeat analyses were run for consistency. Each component of the object was analysed including rivets, pins and different surface finishes.

Results

In table 1 the term bronze is used to mean copper alloyed with tin; brass is copper alloyed with zinc; gunmetal is copper alloy containing zinc and tin in approximately equal amounts; and leaded bronze, leaded

gunmetal or leaded brass contain the element lead in a proportion equal or more than the other components in the alloy.

Grave No.	Object description	Metallic composition	Composition of surface coating and any other components
SK19	Square headed brooch	Leaded bronze	Gold, mercury gilded.
SK21	Great square headed brooch	Bronze with iron pin	Gold, mercury gilded
SK21	Pair of saucer brooches	Leaded bronze	Gold, mercury gilded
SK22	Scabbard bindings	Leaded bronze with bronze rivets	Gilded (mercury not detected) with strips of silver inlay
SK22	Buckle	Impure copper with bronze buckle pin	Silver coating
SK22	Pomel	Leaded bronze	Tinned surface
SK22	Buckle plate	Bronze with copper rivets	Gold, mercury gilded and a silver plate on the back and a central garnet.
SK27	2 small long brooches	Bronze with iron pin	Tinned surface
SK30	Pair of disc brooches	Gunmetal	Tinned surface
SK31	Small square headed brooch pair	Leaded bronze	Gold, mercury gilded
SK38	Button brooch	Bronze with buckle pin lower in lead	Gold, mercury gilded
SK38	Buckle	Bronze with pin of lower tin concentration	
SK44	Pair of button brooches	Leaded gunmetal	Gold, mercury gilded
SK47	Belt fitting	Iron	Brass rivet
SK48	Disc brooch	Leaded Gunmetal with iron pin	Tinned surface
SK48	Annular brooch	Bronze	Tinned surface
SK50	Small saucer brooch pair	Leaded Bronze	Gold, mercury gilded
SK53	Lead object	Lead	
SK54	Bronze' Plate with rivet holes	Leaded Bronze	Tinned surface
SK55	Composite brooch pair	Impure Copper	Gold, mercury gilded with glass central bead
SK56	Pair of saucer brooches	Leaded Gunmetal	Gold, mercury gilded
SK56	Ring	Silver	
SK56	Large ring	Impure copper	
SK57	2 'Silvered' copper alloy strips	Leaded Gunmetal	Tinned surface
SK57	Belt slides	Bronze	Tinned surface
SK60	Pair of applied saucer brooches	Leaded Bronze	Gold, mercury gilded and glass central bead
SK63	Belt slide	Leaded Gunmetal	
SK67	Gilt button brooch pair	Leaded Bronze and iron pin	Gold, mercury gilded
SK78	Disc brooch pair	Bronze with iron pins	Tinned surface
SK85	Two small-long brooches	Leaded Gunmetal and iron pin	Tinned surface
SK90	Rim clip	Bronze	Brass rivets
SK93	Small long brooch pair	1st brooch - Leaded Bronze 2nd brooch - leaded gunmetal	Tinned surface
SK94	Silvered' stud	Leaded Gunmetal	Tinned surface
SK94	Shield boss	Iron	Silver foil apex
SK95	Purse mount	Iron	Silver inlay
SK102	Perannular brooch	Leaded Gunmetal	
SK104	Pair of saucer brooches	Leaded Gunmetal	Gold, mercury gilded
Sk104	Finger ring	Silver	
Sk104	Buckle	Gunmetal buckle plate, leaded bronze buckle pin, bronze buckle ring and impure copper rivets	

Table 1. Summary of analytical results.

Discussion

The qualitative results of the X-Ray Fluorescence from Blacknall Field show that the majority are bronze, or gunmetal, many containing a significant amount of lead. Only one of the objects can be classified as brass. This is typical of the Early Anglo-Saxon period where bronze and gunmetal were favoured and few objects were constructed from brass (Mortimer *et al* 1986 & Mortimer *et al* 1996).

The XRF results indicate that the same alloy was not always used to construct different components of objects. For instance, the buckle from SK104 has a 'gunmetal' buckle plate, a bronze buckle ring, a leaded bronze buckle pin and rivets composed of impure copper. This could be unintentional on the part of the metal-smith but slightly different alloy compositions may have been purposefully selected because they were favoured for different constructional demands. It seems that relatively pure copper was selected for constructing the rivets in the corners of the buckles from SK104 and SK22. It is possibly that this was intentional selection because copper is a softer metal than its alloys making the rivets easier to hammer flat and 'close' over the rivet hole in the object (Coghlan, 1975: 116). SK 93, a pair of long small brooches, both have a matching tinned surface but one of the brooches was found to be made from leaded bronze and the other from leaded gunmetal. Of all the brooch pairs this is the only one found to have a difference in composition between any two matching brooches. This indicates that all brooch pairs except this one were probably made at the same time from one melt. It was not unusual during the Anglo-Saxon period for brooch pairs to be made from different melts.

Analysis of the surface coatings on the 57 Blacknall Field objects reveal that 24 are gilded. XFR detected that the gold contains small amounts of silver and all but one contained mercury indicating that the gilding was applied by the method commonly used during the Anglo-Saxon period, known as mercury gilding.

Mercury or 'fire' gilding is carried out by first of all preparing the metal surface to be gilded by abrasion and chemical cleaning. The gilding is then applied by dissolving gold in hot mercury and rubbing this mixture onto the object's surface. Once coated, the object is heated to between 250 and 350°C to boil off the mercury until its surface colour changes from grey to gold and leaves behind a firmly bonded layer of gold (Oddy 1996). Depending on the length of time and temperature to which the object is heated, a small amount of mercury will not evaporate and remain incorporated in the gilding and can still be detected using XRF. Mercury gilding gives the best result on surfaces which do not contain significant amounts of lead or zinc. Pure copper and to a lesser extent bronze can be mercury gilded most effectively. The benefits of using copper alloys with quite pure composition was evidently either not well known or not considered of importance for the metal-smiths of the Blacknall Field objects because many of the gilded objects are leaded and contain significant amounts of zinc.

Two objects (SK56 and SK104 finger rings) are constructed from solid silver. Three objects have a silver coating or inlay. The silver contains a small amount of copper but is relatively pure. Buckle and buckle plate (SK 22) have silver coatings which appear to have been attached mechanically by hammering and then were securely pinned into place. The shield boss (SK 94) has a silvered apex and rivets. The silver layer on the boss is thin silver foil which was probably attached to the iron boss by mechanically keying it and possibly adhering into place (La Niece, 1993: 202).

Eighteen objects have a tinned surface. On at least two of these (e.g. SK94, 'silvered stud') the tinning has been previously confused with silvering. Tinning was a common method of applying a white metal coating to copper alloys to give the illusion of silver during the Anglo-Saxon period. The tin would have been applied to the objects by first preparing the object surface by cleaning and possibly roughening it slightly. This can be seen on the surface of the disc brooch SK78 in figure 1. The object was then heated to just above the melting point 230°C and tin metal wiped over the surface (Mortimer, 1996).

Conclusion

Non-destructive XRF analysis has revealed that the non-ferrous metal objects from Blacknall Field are quite typical in composition for the Early Anglo-Saxon period, with many bronze, gunmetal and leaded copper alloys and few brass. However, without sampling and carrying out quantitative analysis on the objects these conclusions are questionable. It is thought that some alloy selection for different functions took place with softer metals selected for constructing the rivets. Also characteristic for the Anglo-Saxon period, gilded surfaces were applied using a 'fire' or 'mercury' gilding technique and tinning was more common than silvering for applying a white metal surface to non-ferrous objects. Certain objects have previously been described as 'silvered' but it is now possible to correct this identification to 'tinned'.

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Figure 1. SK78. Two disc brooches showing cast bronze brooches with iron pins. Surface is roughened in order to prepare it for 'tinning'.