Cremated: Analysis of the metalwork from an Iron Age grave

V. Fell [a]

[a] English Heritage, Centre for Archaeology, Fort Cumberland, Eastney, Portsmouth PO4 9LD, UK

Abstract

The grave finds from an Iron Age cremation in southern England include a group of iron implements and a copper pin. The condition of the metalwork is quite exceptional. Surface deposits on the iron implements reveal traces of haematite, whereas the copper pin is covered in a thick layer of tenorite. These deposits are high temperature oxidation products deriving from the cremation pyre rather than from corrosion processes.

Résumé

Les trouvailles d'une tombe à incinération de l'age de fer dans le sud de l'Angleterre inclurent un groupe des instruments en fer et une épingle en cuivre. La condition de préservation de ces objets de métal est bien exceptionnelle. Des couches sur la surface des instruments de fer contiennent de hématite tandis que l'épingle en cuivre est couvrit d'une forte couche de ténorite. Ces couches sont les résultats d'oxydation à hautes températures provenant plutôt du bûcher de crémation que des procès de corrosion.

Keywords: haematite, tenorite, XRD, XRF, SEM

1. Introduction

A group of implements, probably part of a craftsman's tool kit, was recovered with a cremation burial at the prehistoric site at White Horse Stone, Kent, in southern England (Figureure 1). The cremation is radiocarbon dated to 490 – 160 cal BC. The shallow cremation pit was excavated in 1998 by Oxford Archaeology in advance of extensive development for the channel tunnel rail link, for CTRL (UK) Limited.

The group of implements comprises two iron knives, four iron awls and a whetstone, plus a small loop-headed copper pin. The awls may well have been used for working skin products, conceivably untanned hide rather than leather owing to their large size, or coarse textile. The small knife would be very suitable for cutting skin, leather or fibres. On balance however, it seems possible that the implements once formed part of a tool kit of a skin or leather worker.

The condition of the metalwork is quite exceptional. The iron implements are only superficially corroded, with fine surface detail preserved and clearly visible under the chalky soil deposits. For example, the larger knife has a clear bevel on both sides of the cutting edge. The tips of the awls remain sharp and their tangs are pristine. However, there is no evidence of any associated mineralised organic materials such as handles. Instead, there are small areas of bright red deposits near to or on the tangs of four of the six iron implements. Another distinctive feature of the awls and larger knife is the dense and lustrous, dark grey to black appearance of the metal surface under the soil (or under the red deposits).

The non-ferrous metal pin is covered with a thick layer of porous black powder with occasional green areas visible. As a consequence of its appearance, the pin was initially thought to be made of a silver alloy.

It is generally assumed that bright red deposits on archaeological ironwork are often haematite resulting from burning in oxidising atmospheres. This red colour is invariably present on freshly forged iron together with a very smooth and compact black oxide layer. One of the first people to comment on the presence of haematite on

Corresponding author: TEL: +44 2392 856787: FAX: +44 2392 856701: email: vanessa.fell@english-heritage.org.uk

Figure 1. Metal artifacts from the cremation pit

burnt archaeological iron was Leo Biek, who noted in particular that haematite was a component of fire-scale on freshly forged iron, and it could also be formed as a consequence of conflagrations of buildings and other structures (Biek 1963, 133-4; Blackwell and Biek 1985). Other citations for cremated ironwork include King Harry Lane cemetery, Hertfordshire, where three iron nails were found to be in ‘pristine condition having been burnt with the ‘calcined bones’ (Stead and Rigby 1989, 111). At Westhampnett Bypass, West Sussex, the fired metalwork was noted for its fragmentary condition, discolouration and distortion or ‘molten’ appearance (Northover and Montague 1997). On the continent, the well preserved iron surgical implements from a Middle Iron Age cremation in Bavaria are described as having a ‘fine fire-patina’ (de Navarro 1955, 232).

Despite this general acceptance, analysis of the deposits on archaeological artifacts does not seem to have been attempted. This group of iron implements provided the opportunity to characterise the surface layers and to determine how they relate to the cremation.

2. Methods of analysis

The implements were initially x-rayed and also examined under a binocular microscope at low magnification for features of relevance to their technical descriptions. This included close examination for evidence of mineral preserved organic materials such as handles and containers.

The pin was analysed by energy-dispersive x-ray fluorescence (XRF) in an Eagle II x-ray fluorescence spectrometer with lithium-drifted silicon detector. A sample of the black deposit from the head of this pin was removed for x-ray diffraction (XRD) analysis, and the pin was again analysed by XRF to verify that the composition did not alter substantially below these layers. Surface samples from three awls and the larger knife were also analysed by XRD.

Samples in the order of 1 mg were ground in an agate mortar and mounted on a flat single-crystal silicon sample holder, designed to reduce background scatter. X-ray diffraction data were collected on a Philips PW1840 diffractometer using cobalt K_α radiation (wavelength 0.179026 nm) incorporating a solid-state silicon detector. A search-match computer programme (Philips, based on JCPDS files) was used to identify unknown components in the diffraction patterns by comparison with standards in the powder diffraction file. Jeweller’s rouge powder (haematite) was also employed as a standard.

The larger knife was also sampled for metallographic examination (see Figure 1), which will be reported on elsewhere, although the opportunity was taken to examine the oxidation layers by scanning electron microscopy with energy-dispersive x-ray analysis (SEM-EDS) in a Leo 4401 Stereoscan electron microscope.

3. Results

XRF analysis of the pin showed that it was made of relatively pure copper with a trace of tin (Figure 2). The crystalline components determined by XRD are shown in Table 1. The black deposit from the surface of the pin was tenorite (CuO). Samples of the red deposits from the iron implements comprised haematite (Fe_2O_3), sometimes with calcite ($CaCO_3$) plus trace amounts of soil components, such as quartz. Samples of the grey-black layers on the iron comprised mainly magnetite (Fe_3O_4), with goethite (FeOOH) and lesser amounts of haematite and calcite.

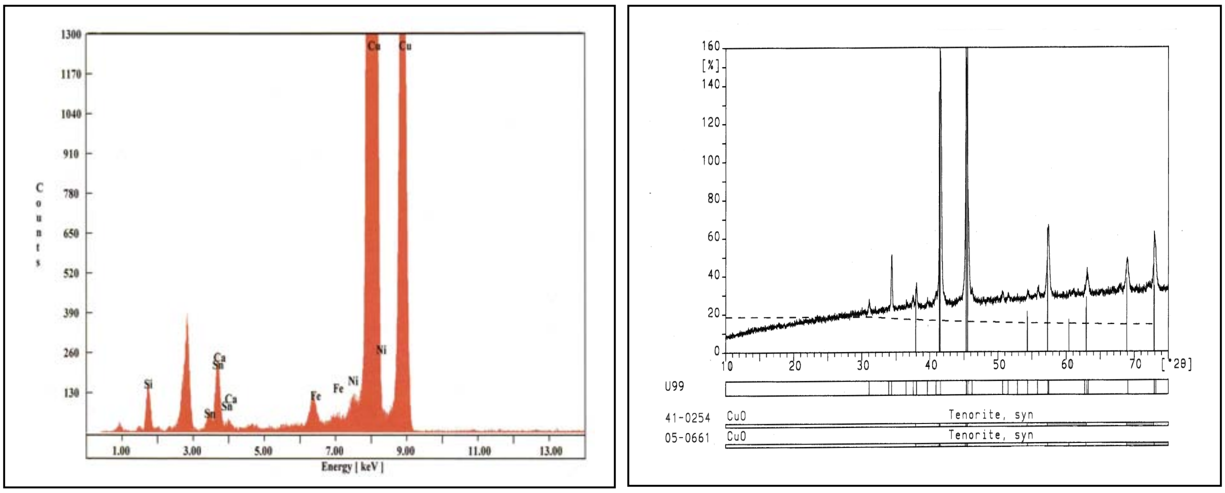

Figure 2. Non-ferrous metal pin 112. Left: XRF spectrum shows copper to be dominant. Right: XRD spectrum of the surface black layer shows mainly tenorite

Table 1. Results of XRD analysis

Artifact	Sample	Crystalline components
Knife 106	Red deposit from the tang	**calcite** haematite
Awl 107	Corrosion blister from stem	**magnetite** goethite (haematite)
Awl 107	Grey-black product from stem	**magnetite** goethite (calcite haematite)
Awl 108	Red deposit from the tang	**calcite** haematite
Awl 108	Grey-black product from stem	**magnetite** **goethite** (haematite calcite)
Awl 110	Red deposit from the tang tip	(haematite)
Pin 112	Black powder from the head	**tenorite**

Major constituents shown bold, minor shown normal and trace levels are bracketed

Analysis of the oxidation layers by SEM-EDS did not show any significant difference in oxygen concentrations between the metal and the outer surface. However, the thin oxidation layer of c. 100 µm thickness did reveal a distinct compact and well-formed outer layer of c. 15 µm thickness (Figure 3). There was also a compact middle layer, which in places had a columnar appearance; whereas the innermost oxidation layer appeared more ragged, presumably where corrosion has occurred.

4. Discussion

When iron is heated in air it forms multi-layered oxide scales comprising wüstite (FeO), magnetite and haematite, the precise composition of which is temperature dependent (Birks and Meier 1983). Wüstite is the most iron-rich oxide, forming adjacent to the metal, whereas haematite is the most oxygen-rich, forming next to the atmosphere. Heating below 570°C, a two-layered scale develops consisting of magnetite next to the metal and haematite on the surface. Above 570°C, wüstite forms below the other two iron oxides, next to the metal, giving the sequence: metal, FeO, Fe_3O_4, Fe_2O_3 — the ratio of which are roughly 95:4:1 at 1000°C (Birks and Meier 1983, 75). Through the migration of electrons outwards, the scales increase in thickness particularly at elevated temperatures when the wüstite will form the thickest layer. Nevertheless, this wüstite layer is unstable and will break down to iron and magnetite below 570°C under certain conditions (Kofstad 1988, 9). However, if wüstite is quenched or rapidly cooled, it can be retained without transformation (Scully 1990, 39; Massalski et al. 1990, 1742). Factors such as temperature and partial pressure of oxygen will affect the growth rate and composition of the various oxides, as well as the precise phases to be formed. The latter will affect the defect structure of the crystals and their electrical conductivity and, presumably, stability over time and stability in the ground.

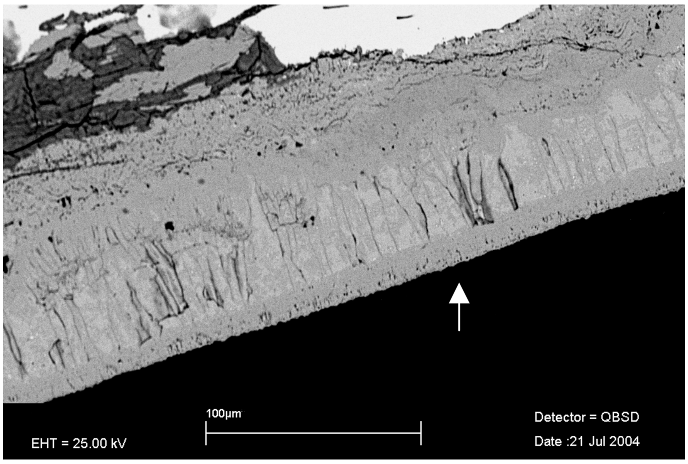

Figure 3. Backscattered electron image of section through the iron knife 106, showing metal at the top (light) with slag (dark grey), oxidised layers running diagonally across the centre (pale grey, c. 100 µm thick), and mountant at the base (black). Note the well-formed outer oxidation layers, in particular at the surface (arrowed).

The nature of the oxide phases – dependent on the factors described above – may explain why burnt iron artifacts often retain the distinctive grey/black surfaces which are usually resistant to corrosion. These layers are very similar to those on flake hammerscale, the by-product from the forging of iron and often found on archaeological excavations at the sites of smithing hearths (McDonnell 1986, 48). Sometimes archaeological burnt iron artifacts are found in hollow condition – a phenomenon reminiscent of spherical hammerscale with its dark and lustrous skin of variable compositions comprising wüstite, magnetite, and fayalite ($2FeO.SiO_2$) and other glassy components due to the presence of slag from the smelting process (Unglik 1991). However, the explanation for the hollowness of the examples may be different. In the artifacts it seems likely that if the protective layer of well-formed magnetite becomes damaged, perhaps as a result of contraction during cooling, a corrosion cell might develop, leading potentially to voiding due to corrosion. A contraction effect may be visible at the centre of the oxidation layer in Figure 3.

The presence of haematite on the archaeological ironwork from White Horse Stone suggests that the implements were fired in the cremation. The lack of a handle on any of the implements supports this, and the handles themselves may have provided additional fuel for the cremation given that the haematite is present on or near to the tangs of the implements. The other iron oxides present, magnetite and goethite, are probably a mixture of high temperature oxidation products and corrosion products. Certainly the appearance of the ironwork, with its dark and lustrous surface that has protected the surface detail, suggests that the firing process has been critical to its exceptional condition.

The thick black surface layer of the copper pin from the grave group comprises tenorite suggesting that this artifact was also likely to have been placed in the cremation. When copper is heated in oxidising atmospheres it will invariably yield the black cupric oxide, tenorite ($Cu0$), familiar to everyone who has annealed or soldered any modern copper alloy. Beneath this, closer to the metal, there will form the red cuprous oxide, cuprite (Cu_20) sometimes visible as a thin pink layer on initial heating (Untracht 1982, 416) and forming at lower partial pressure of oxygen.

In summary, the metalwork from this cremation was shown to have oxide layers which are characteristic of heating to high temperatures in normal or oxidizing atmospheres. These finds were presumably placed on the cremation pyre. The iron in particular has been preserved in an exceptional condition due to the protective nature of the oxide layers.

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