THE EXAMINATION OF ARCHAEOMETALLURGICAL REMAINS; SOME RECENT EXAMPLES AND CONCLUSIONS

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Abstract

This paper starts with a description of the investigational techniques now being used and goes on to discuss some of the problems and results. Examples have been taken from such finds as mattes and slags, litharge and speiss, native copper and crucible melting, edge tools, copper and bronze ingots, and oxidation enrichment in wrought iron.

Preface

This paper is based upon an idea of Nicole Échard for an introduction to a volume intitled »Metallurgies Africains; nouvelles contributions» which she edited and which appeared in the Mémoires de la Société des Africanistes, Vol. 9, 1983, published in Paris. It seemed a very appropriate treatment for a conference on Scientific Methods in Archaeology. The original paper forms the framework which has now been covered with some more recent techniques and applications.

Introduction

The main object of this paper is to show some of the techniques used and the results obtained from the examination of archaeometallurgical material of many types.

The principal groups of finds arising from archaeological excavations are:

1 Copper base alloys: native metal, ingots and small artifacts.
2 Vitrified material; crucible slags, fuel ash slags, furnace lining from melting and smelting of copper and iron base materials.
3 Ceramic materials such as unvitrified furnace linings, tuyeres, crucibles and moulds.
4 Iron artifacts and blooms (i.e. semi- or unfinished products).
5 Slags from iron and copper smelting; hammer scale.
6 Smelting and refining products such as matte, litharge and speisses.

Techniques of examination

Removal of specimen for examination

In many artifacts such as axes and swords it is permissible to take pieces from an edge. Such pieces may be removed with two fine saw-cuts meeting at an angle of about 20°, 30 mm within the artifact. The damage may be made good with a filler. The cut should be sufficiently deep (at least 13 mm) to avoid material which has been altered by surface effects, such as corrosion and segregation (e.g. tin sweat in bronzes). In scrap metal hoards broken surfaces are available for specimens.

In thin sheet-metal artifacts such as cauldrons, specimens may usually be cut from the vicinity of badly corroded areas. If the artifact is in perfect condition it may be desirable to trepan or shell-drill a specimen, so as to leave a small hole, rather than take a specimen from the edge. The rim may have been reinforced or in some way may not be representative of the body of the artifact.

The technique of trepanning is becoming a more elegant way of removing material in all cases. This technique is still under investigation and is capable of considerable improvement. So far, we have had satisfactory results from a tool with an outer diameter of 6 mm, which is capable of producing a core 3.3 mm diameter and up to 2.5 cm long, in a solid bronze casting. In bronzes or gunmetals it is not necessary to drill through the artifact, and the core may be broken off at depths exceeding about 8 mm. The hole made can easily be filled again.

It should be possible to use a large hypodermic needle with an outer diameter of 2.0 mm, such as is used for intravenous transfusions, with a diamond or other abrasive compound to give cores with a diameter of 1.0 mm. Such a diameter is quite sufficient for metallographic examination.

Perhaps the most elegant way now available for the removal of metallographic specimens is spark machining (Electro-sparkerosion). This usually involves the immersion of a specimen in dielectric (kerosene) and the trepanning with a copper tool of the right shape and size such as a 2 mm diameter tube (Schaaber, 1974). One can now buy a molybdenum wire band-saw which works on the spark erosion principle and makes cuts only 0.15 mm wide, so that the removed specimen can be replaced after examination and the fact that it has been removed is almost invisible.

Mounting and examination

After removal of the cores or wedge-shaped pieces from the artifacts, they must be mounted in a plastic to make them suitable for polishing and etching. The processes then used are standard metallographic techniques which will be found in any metallurgical laboratory. Specimens may be polished on wet or dry abrasive paper, or on diamond-impregnated lapping wheels.

The examination of unworked iron blooms will be assisted if the pores are filled with a plastic cement before polishing: otherwise, during micro-examination, etching solutions tend to seep out, ruining the structure.

Normal etching techniques will follow and should reveal the structure of the specimen. Care must be taken to distinguish between the original structure and effects due to the cutting or trepanning of specimens. Slight cold-working on the surface of the cores or the cut edges of saw-cut specimens may originate in this way (Ancient Mining and Metallurgy Committee, 1962).

All this should be supplemented by analysis using Atomic Absorption Spectrophotometry (AAS), X-ray fluorescence spectroscopy (XRF) and X-ray diffraction (XRD) where appropriate. Electronprobe microanalysis (EPMA) is fast becoming the favourite tool of the analyst but care must be taken in the interpretation of the results, remembering that metals are not homogeneous and contain segregated regions that may have different compositions from those of the solid solution matrix. The analysis of these segregates is of course one of the great advantages of the technique.

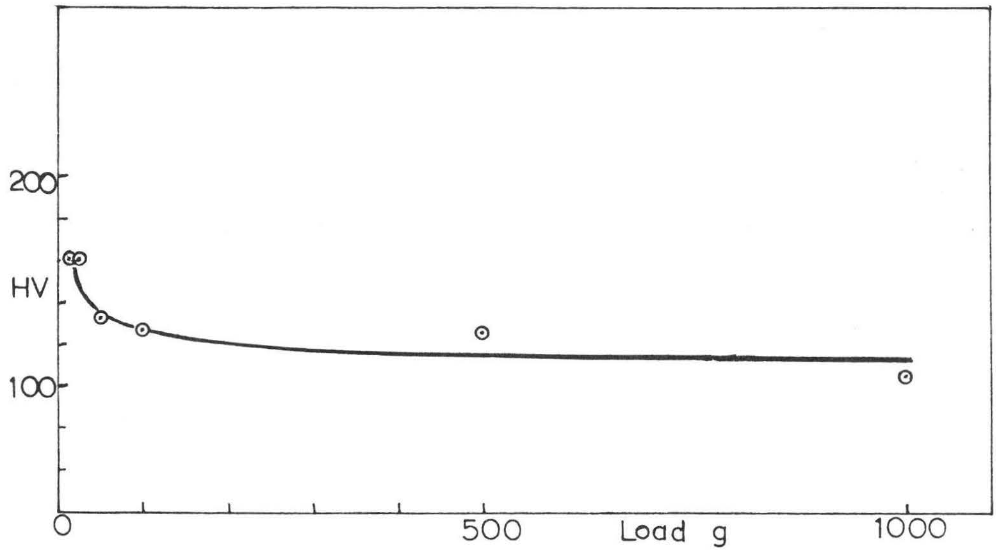

Fig. 1. Effect of load on the hardness of coarse grained ferrite with low phosphorus.

Hardness

The property of »hardness» is easily measured on these prepared specimens and can give a good idea of other mechanical properties such as strength and ductility. This is most easily done with a pyramidal diamond indenter under various loads. The load divided by the area of the impression gives the hardness in kg/mm^2. Unless one uses very low loads of the order of 50 g or so, the effect of different loads is not great (Fig. 1) and a reading obtained with a load of 500 g is comparable with that obtained with 50 kg for a single phase of adequate size. Naturally it is not possible to use a load of 50 kg on a small piece of metal one 2 mm wide, as the size of the impression may exceed the width. On very soft metals such as lead, low loads must be used, while on hard constituents large loads may have to be used to get an impression of adequate size to measure. Naturally, on polyphase metals a large load will give an average while a low load may cause the indenter to dwell on hard or soft areas only.

One method of hardness testing, using a pyramidal diamond, is the Vickers Diamond Hardness Test. The results are reported in units followed by the letters HV and then by the load used in kg. A figure of HV1 would therefore indicate that it was a Vickers hardness number with a load of 1 kg. The square indentation made with the Vickers indenter will indicate ductility or brittleness by the deformation markings occurring round it or by cracking, originating from the corners.

Metallographic examination

The first copper-base material to be considered is native copper which occurs on or below the surface in small or very large lumps (several tonnes) mixed with the host rock. It can extracted by breaking off the large lumps with stone tools or by crushing the rock and melting the particles under reducing conditions in crucibles. The natural (unmelted) metal is usually hard and the degree of cold work that can be done on it is limited. But when annealed in a camp fire at 150°C it can be further worked, and quite complex artifacts can be made without remelting. Metal submitted to such operations is usually detectable under the microscope by the presence of non-metallic inclusions of sand and iron oxide. When melted, however, it is indistinguishable from smelted copper as the inclusions will enter the slag.

The alloys most widely used are impure coppers, arsenical coppers and tin-bronzes. The latter may contain lead.

The most easily visible constituents are the »phases» that appear in the microstructure after polishing and without any development of etching. Examination before etching should be carried out as it reveals the direction of working due to the distribution of the slag phase which is one of the chief constituents of early metals. Other phases are copper sulphide and oxide particles, and lead in tin-bronzes. The latter can normally be seen when it exceeds about 1 %. But when a specimen is badly corroded, with particles and intergranular films of corrosion product, it is sometimes difficult to distinguish it from the other phases.

Another constituent visible at this stage is re-precipitated copper in cases of destannification or dezincification by corrosion. Corroded slip bands due to final cold work can also be seen near the surface at this stage.

Next, etching is normally carried out in ferric chloride or with ammonia and hydrogen peroxide. The ferric chloride is the easier of the two to use as it does not have to be made up fresh. It shows up »coring», i.e. the segregation that arises in a fast cooled structure due to failure to achieve an even dispersion of the solid solution elements. Solid solutions are phases in which the alloying elements are intimately mixed on an atomic scale.

On the whole, ferric chloride is adequate for tin bronzes; it may fail to show up grain boundaries in arsenical coppers and other solid solution alloys. The ammonia etch has a more delicate effect on the high (delta) tin phase.

Cast structures are normally recognisable by the cored »dendritic» or tree-like crystal structure that arises from segregation on fast cooling. But slow cooling will diffuse this structure and give an equiaxed crystal or »grain», one that has the same dimension in two directions at right angles. Long, »columnar» grains can sometimes occur and these show the direction of solidification.

Heating a cored dendritic structure will homogenise the alloy, i.e. it will diffuse the solid solution elements so that an even distribution will be obtained and coring will disappear, this makes working easier. If quick homogenisation is required, the metal will have to be heated to near the melting point. Raising the temperature will be more effective in homogenising the structure than increasing the time of heating. Both time and temperature will increase the grain size.

If the metal is worked by hammering after homogenising the result will depend on whether it has been done hot or cold, and what constitutes *hot* depends on the alloy. In Cu-As alloys this may be over 300°C while with tin bronzes it may be over 500°C.

If hot-worked it will leave a structure showing »twin» bands which are pieces of crystal with orientations different from the host crystal. If hot-worked at a very high temperature it will deform the slag inclusions along the direction of working. At very high temperatures these may have high aspect ratios, i.e. be more threadlike.

Cold working takes place below the temperatures mentioned above. If the starting material be a ductile solid solution, deformation markings (slip-bands) will appear and the hardness will increase. If it is done on a hot-worked alloy there will be both twins, and the deformation markings which look like closely drawn parallel lines. The latter may need quite a lot of reduction in thickness before they appear and they will disappear on annealing, i.e. heating above the cold working temperature range mentioned above.

Cold working followed by annealing gives much the same structure as hot working except for the slag inclusions. Cold work usually breaks them up into short lengths. Naturally, cold work will bend the twins where present. Annealing will eradicate most of the signs of cold work but will produce twins and leave broken slag inclusions.

Ingots

Copper ingots are always useful material to work on as they have a coarse grain structure and should indicate casting conditions, i.e. furnace cooled, or cooled in a cold mould (Figs 2 and 3). Ox-hide ingots have now been made by Merkel (Merkel and Tylecote, 1982) and we now know that the most satisfactory way to make any type of ingot is to remelt the rough pieces of copper found inside the furnace after smelting and cast them into a mould. A stone mould used for this purpose has now been found in Syria (Jaques et al., 1983). Although ingots are primary material, their trace elements give no clue to source, but this may be rectified by lead isotope analysis.

The wreck of the »Britannia» was recently found on the Goodwin Sands. This ship was wrecked in 1812 and its main cargo was Cornish copper for Madras in India. (These were found during an underwater excavation on the Goodwin Sands (English Channel) and are now in the museum at Charlestown near St Austell (Keeper R. Larn). This was in the form of plates and, curiously enough, another wreck contained small bars of the type we associate with the Early Bronze Age, like the speiss bars from Guschau (Otto and Witter, 1952) (see below). Both of these were cast into open moulds and we look forward to seeing their structure and composition.

Another interesting find is a bronze ox-hide ingot found off the Cornish coast (Tylecote, in print). This is quite a problem. Did people make *bronze* ox-hide ingots in early times or is this an odd-shaped recent production? Its corrosion crust would suggest a date at least 500 years ago, as high tin-bronze does not corrode readily in sea water.

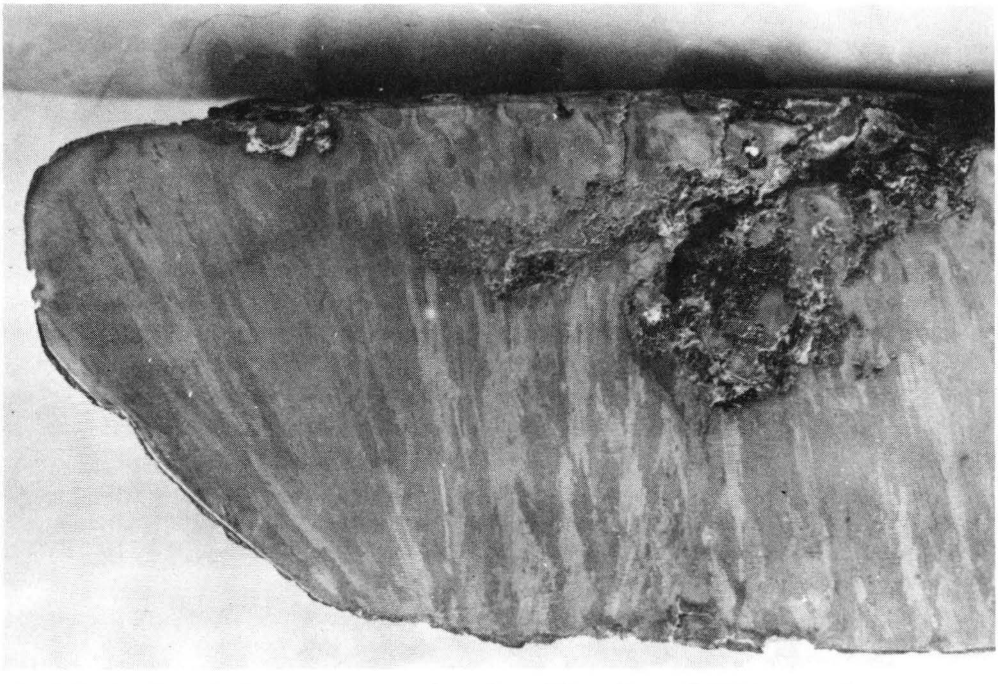

Fig. 2. Section through plano-convex copper ingot from Gillan, Cornwall. Thickness = 4 cm.

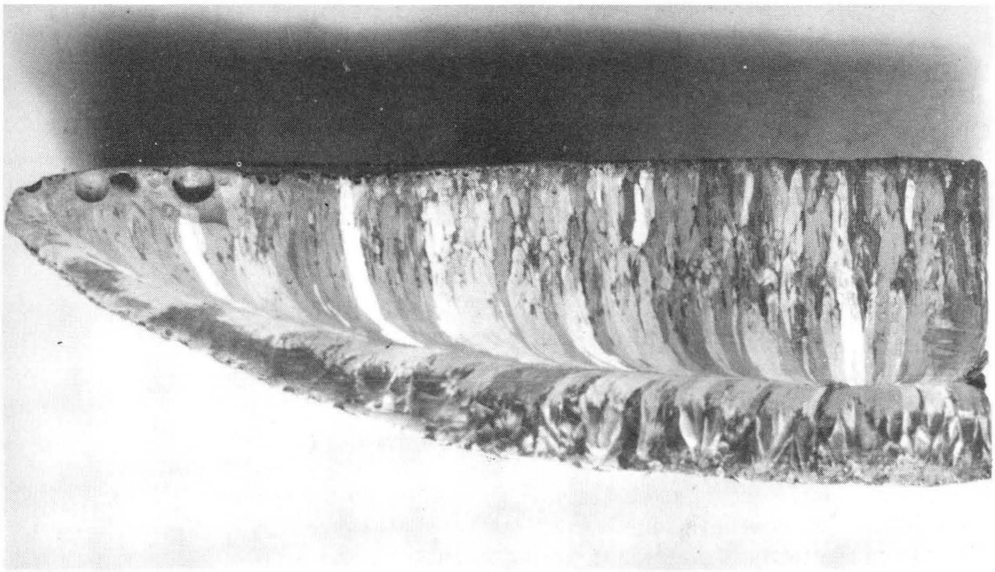

Fig. 3. Section through experimental plano-convex ingot cast into a cold mould, indicating thermal gradient. Length 75 mm.

Vitrified materials

Ash from fuel such as wood and grasses will form a vitrified product at about 1000°C or above due to the high alkali content of plant ash (Evans and Tylecote, 1967; Biék, 1970). When a certain amount of soil is fused in, then the product is difficult to differentiate from crucible slags. These are formed mainly by the reaction of the alkaline fuel ash (basic) with the crucible fabric (acid). If the metal being melted is »dirty» then the crucible slag will contain some of the dirt or slag from the melted metal which will be released and rise on melting (Table 1).

Table 1. Fuel ashes, vitrified materials and smelting slags.

	Composition wt %				
	Copper and Iron Smelting Bloomery Slag	Wood Ash (not vitrified)	Ash tree leaf ash	Coal Ash (vitrified)	Peat Ash (not vitrified)
SiO_2	10—40	1.5—6.5	5.5	24—53	3—30
FeO	$\boxed{45—70}$	0—7	0.1	8—30	10—20
CaO	0—7.0	$\boxed{14—60}$	49.6	1—12	$\boxed{24—30}$
MgO	0—2.0	1—25	10.6	0—10	1—7
Al_2O_3	0—15.0	0—2	tr	$\boxed{19—50}$	0—5
MnO	0—15.0	0—30	0.1	0—1.0	0—1
K_2O	0.3—0.7	$\boxed{10—20}$	19.0	1—2	0—1
Na_2O			1.2		0—2
P_2O_5	0—3.0	4.0—18	7.07*	0—2	0—3
S	—	0—1.5	2.0	0.1—3.0	$\boxed{5—10}$

Notes
Distinguishing figures are ringed.
* P is generally higher in leaf and bark than in wood.

Due to its alkaline nature the fuel ash will »glaze» clays such as crucibles and furnace linings. Pottery kiln ash may be indistinguishable from some metallurgical ash. But usually the metal content of the latter is very obvious. It is importent to distinguish by analysis the metals from the oxides and for this reason AAS or XRF must be backed up by metallography or EPMA.

The temperature to which a crucible or furnace lining has been taken can usually be estimated by standard tests which involve the heating and microscopical examination of unfired clays, from the same site or structure, and by comparison with the actual artifact.

Tuyeres and crucibles

The tuyeres may be prefired before being put into the furnace or fired by the heat of the furnace (Tylecote, 1981). Their ends are often contaminated and indicate the metal that has been treated by smelting or melting. Their bore is from 1—4 cm for forced draught but may be much larger if used with induced draught. The furnace end is usually a single hole, but the bellows end may be more complicated; some tuyeres are designed to take two sets of bellows. Some have a right-angled bend for special purposes such as oxidation of impurities or for a particular furnace configuration.

The crucibles have to be made of selected clays, and the local pottery clay will often not be adequate. The main problem is holding them when full of metal (Tylecote, 1982). Bronze Age tools are not adequate as they melt unless tipped with clay. It was normal practice to use green sticks which are kept from becoming too brittle by their own sap. The crucibles usually have a projection that can be gripped by crude tools, or a hole in the side so that the metal runs out when the crucible is tipped. By the Iron Age there was no problem as iron tongs could be used. Crucibles are of all shapes and sizes, but on the whole they are small. Large amounts of metal, if required, would be melted in a furnace and run from a furnace.

Iron artifacts and blooms

In most parts of the world, until the 19th century, iron was made by the direct or bloomery process in which it was reduced from ore to metal in the solid state. The impurities in the ore were rendered liquid and could run away from the bloom as a slag. The slag that remained in the bloom had to be expelled by the smith. Sometimes the solid slag and the metal were mixed so that the slaggy bloom had to be completely broken up by hammering to separate the two phases. Then the small pieces of iron had to be welded together by reheating in a blacksmith's hearth.

Most of the iron produced was single phase, i.e. ferrite, or magnetic iron in which phosphorus could be the main impurity, the rest of the impurities going into the slag. But occasionally the iron contained appreciable carbon which, like the phosphorus, made it harder. The quantity and distribution of these two elements is most important and is the main purpose of metallography. Irons with more than 0.4 % carbon can be made to benefit by heat treatment giving much harder and wear resistant tools. But this process is difficult and while carburisation was fairly widely practised, quench-hardening was not, especially in Africa.

In order to asses the quality and value of the artifacts made of iron it is necessary to analyse them for major elements such as C and P and for the trace elements, Cu, Ni, Co etc. which might give some clue as to provenance (Hedges and Salter, 1979). It is also useful to know something about the gangue elements that reside in the slag inclusions and this can be done by EPMA. The conclusions derived for copper in the section on Metallographic examination are also applicable to iron.

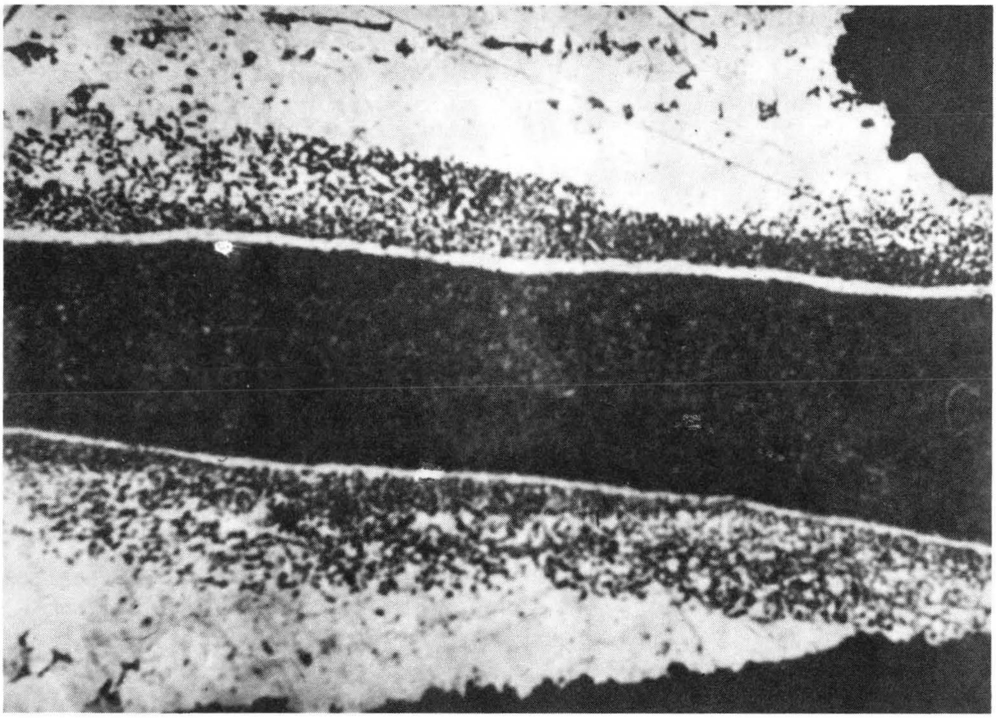

Fig. 4. Arsenic enrichment bands in a knife from Skåne. (after Thomsen) ×50.

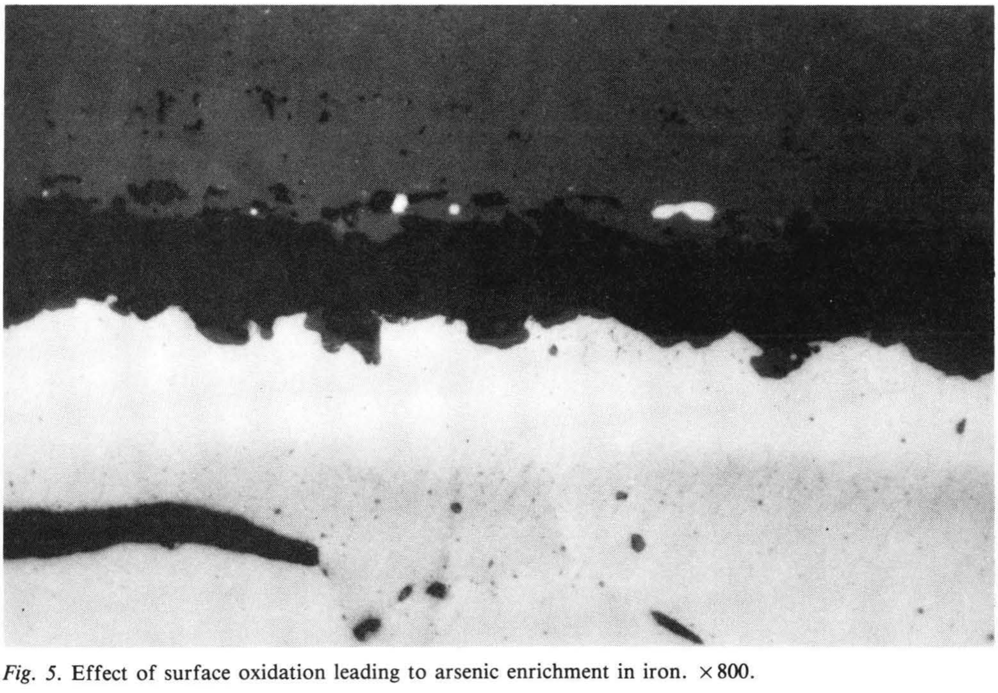

Fig. 5. Effect of surface oxidation leading to arsenic enrichment in iron. ×800.

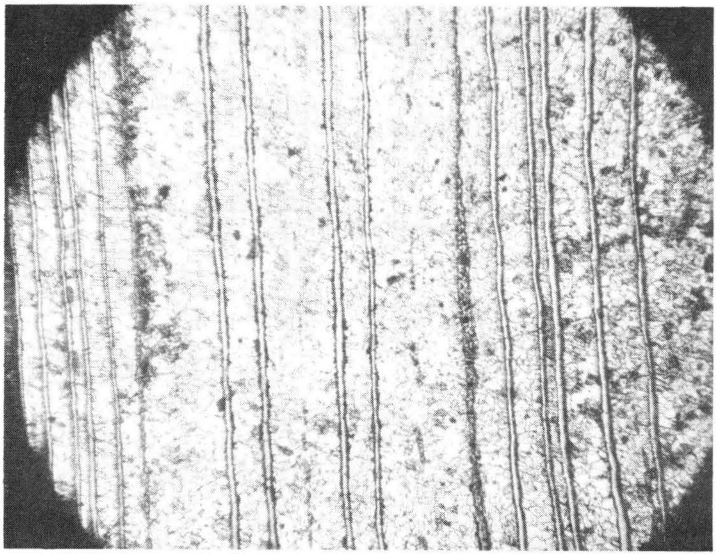

Fig. 6. Nickel-iron laminate formed by folding over nickel and iron strips. (after Tholander) ×50.

Fig. 7. Laminations of iron on the back of a steel-cored knife from medieval Goltho, UK. ×7.

Iron and segregation effects

The classic paper by Evans and Chilton (1955) showed that wrought iron can be highly segregated material due to two causes. (1) The reduced solubility of some of the impurity elements such as copper and sulphur, which, upon being reduced with the iron, segregate and (2) the oxidation enrichment of certain elements on an oxidising surface (Fig. 4). Thomsen (Tylecote and Thomsen, 1973) and others have already drawn attention to the second and its effect on structure (Fig. 5). The first may have an effect on corrosion rate.

There are other ways in which »enriched» layers of »impurity» elements may be obtained in iron, and Tholander (1979) has shown how high nickel streaks can be obtained by laminating a high nickel layer by folding over the low nickel and high nickel irons many times (Fig. 6). The diffusion of nickel is slow due to its having the same atomic-radius (Å) as iron (Fe = 1.27; Ni = 1.25).

EPMA has revealed many examples of linear segregation (see back of medieval knife in Fig. 7). The main segregation element here is nickel (Fig. 8). Li Chung (1979) (an archaeometallurgical group in China) has done a very elegant piece of work on some meteoric iron inserted into a Shang Dynasty bronze axe. As the iron was totally rusted, the problem was to determine whether it was man-made iron or meteoric. EPMA showed the alternation of high Ni and low Ni expected of an octahedrite iron meteorite

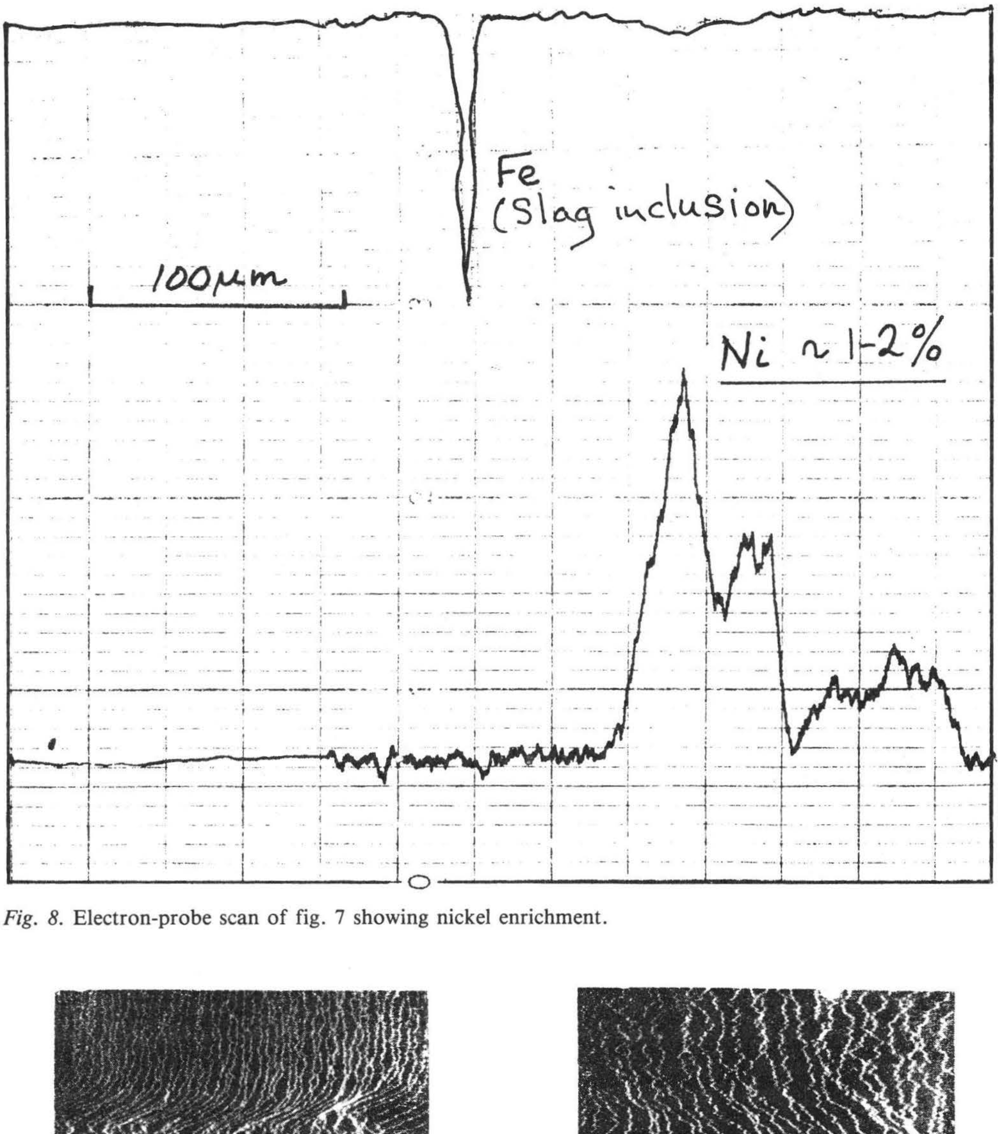

Fig. 8. Electron-probe scan of fig. 7 showing nickel enrichment.

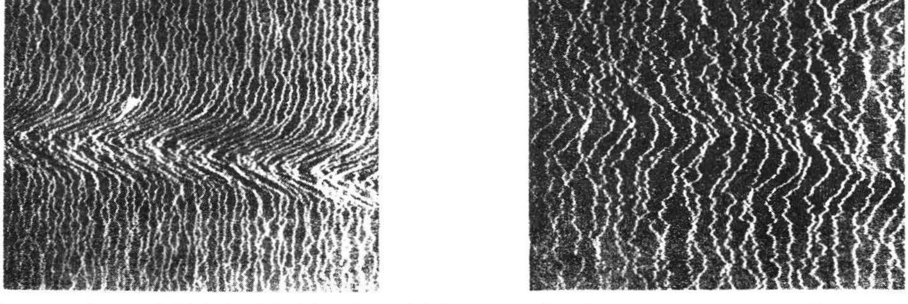

Fig. 9. **Austenite bands high in nickel in a low nickel-iron matrix of a rusted meteoric iron blade inserted** into a Shang Dynasty bronze axe. (after Li Chung).

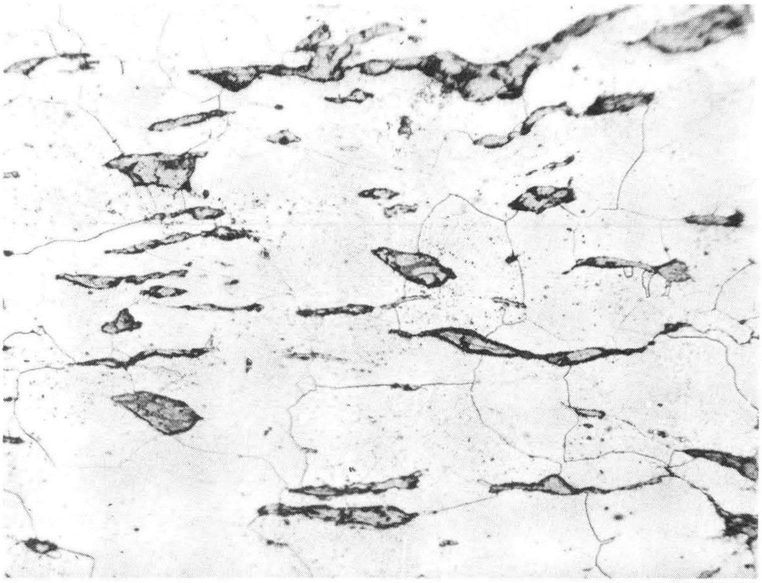

Fig. 10. Slag inclusions in wrought iron.

where the alpha and gamma phases contain high and low Ni respectively. This work was possible because the nickel does not diffuse in the rust (Fig. 9).

The examination of rust which is often all that remains of an iron artifact can sometimes show the original structure as a »relict» in the rust. Recent work by Nosek and Mazur (1984) has shed light on the relative rusting characteristics of pearlite and cementite.

Slags

Slags are long-lasting and normally tied to their point of origin. They are therefore one of the most important artifacts and show what was produced and from what type of mineral.

Slag inclusions in metal may give useful information of this sort but may be modified by fluxes and fuel ash introduced during working and by reactions with their surrounding material (Fig. 10). Phosphorus, for example, can diffuse in iron, from slag into iron or vice-versa, depending on the conditions. EPMA is making this type of work possible, but it has still to show useful results.

The problem of whether a copper slag is a crucible slag or a smelting slag is to a certain extent resolved by composition. The former tends to be low in iron and high in fuel ash components like Na, K and Ca, i.e. basic. The latter are high in iron and lower in silica (less basic). This type of argument was used to resolve the question of whether a certain slag from Niger was the product of crucible melting of oxidised native copper or the smelting of ores (Fig. 11) (Tylecote, 1982). From the composition shown in Table 2 and its physical characteristics is was decided that it was a crucible slag. Naturally, such a basic slag will react with the more acid crucible and incorporate alumina.

Normally it is possible to divide the slags physically into »tap», i.e. slags run out of the furnace, and »furnace» slags remaining in the furnace at the end of the operation. But there is usually no difference in the composition.

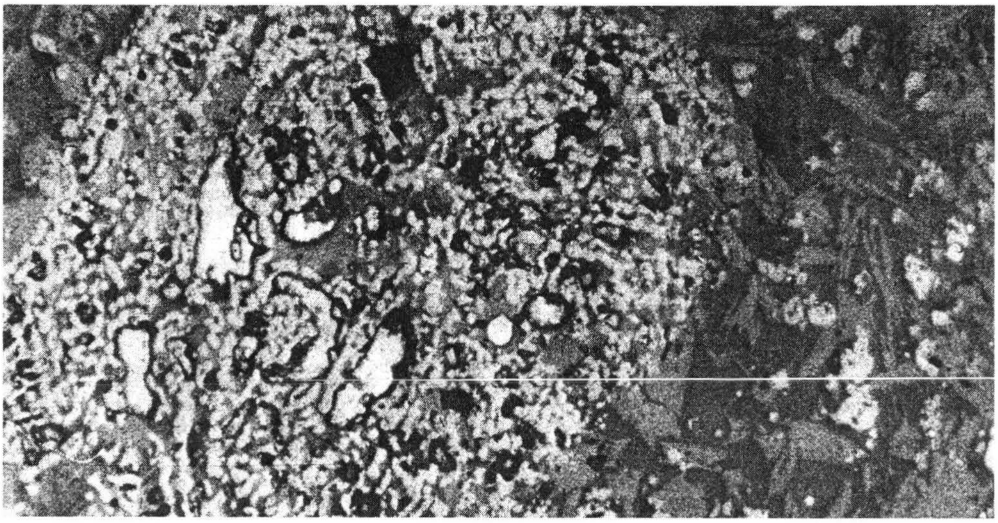

Fig. 11. Photomicrograph of slag from Furnace 24, Site 162 at Afounfoun. × 500. The area shown is reddish and shows on the left large light areas of copper in an oxidised matrix. On the right are silicate crystals in a vitrified matrix.

Modern methods of examination such as EPMA allow the scanning of slag sections so as to analyse the metal inclusions and the matrix. But sufficient scans must be made if a reliable estimate of the overall composition is required. On the whole it is best to analyse the phases present and not attempt to give a somewhat meaningless »average». Slags from lead, antimony and zinc smelting will all contain their respective metals so these can be easily recognised for what they are.

Other methods of examination are the normal metallographic sections, and thin section petrography. But compared with EPMA metallography, the latter is time consuming.

Table 2. Crucible melting slags from the Agadez region of Niger.

	A	B	C	D	E	F	G
%	Site 162, (c. 800 BC)					Site 175 (2nd mill BC)	
	F 10 (1)	F 10 (2) (inclus.)	F 14	F 24 Red	F 24 (inclus.)	F 1 (matrix)	F 1 (inclus.)
SiO_2	44.4	42.4	43.0	49.0	1.6	59.0	4.12
CaO	29.6	28.5	27.0	22.7	1.0	1.4	0.15
MgO	10.8	10.2	10.0	8.9	3.2	1.0	4.10
Al_2O_3	7.1	7.0	7.9	7.7	nd	22.5	7.24
FeO	1.5	1.5	2.1	1.2	0.4	6.7	19.44
Na_2O	2.99	1.2	2.6	1.1	nd	1.3	nd
K_2O	1.1	1.0	0.9	1.2	nd	3.1	0.32
Cu*	0.34	5.9	1.2	5.7	93.9	nd	nd
MnO	0.38	0.4	nd	0.3	nd	0.2	nd
TiO_2	0.53	0.6	nd	0.6	nd	1.4	62.53

* Metallic copper, not oxide.

nd = not detected (less than 0.1 %, if any).

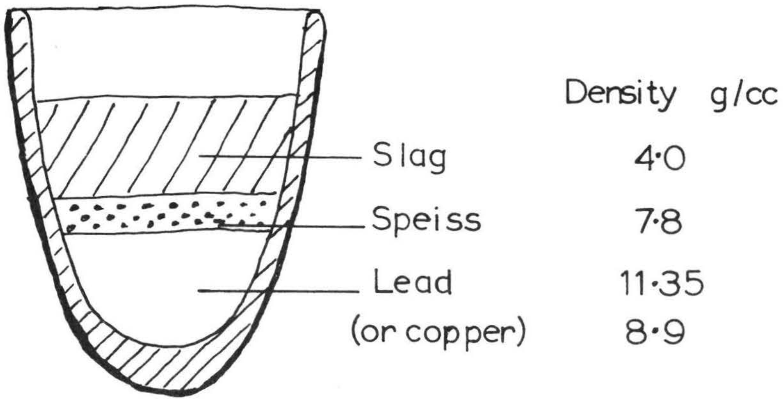

Fig. 12. Settling of copper, speiss and slag in a crucible, with densities.

Smelting and refining products

Another group of material is often overlooked and misunderstood. When copper ore containing substantial quantities of iron and arsenic is reduction smelted, a cake of copper metal may be formed at the bottom with slag on top because of the difference of density. But between these two phases there may often exist a thin layer of what is basically iron-arsenide, Fe-As, with varying amounts of Ni, S, and other non-ferrous elements present. This is known as a *speiss* (Fig. 12). The densities are as follows: —

	g/cc
Cu	8.9
Speiss	5—8
Slag	3.5—4.0

The composition of some speisses are given in Table 3, and the structure is shown in Fig. 13. Such materials have been found at Rio Tinto by Rothenberg and Blanco

Table 3. Composition of Speiss %.

	Guschau (E. Germany) 1	Romania (Maramures) 2	Rio Tinto (Spain) 3	4	Japanese* (Gowland) 5	Modern (Bray) 6
Cu	44.54	36.3	1.32	21.0	72.7	3
Sb	12.97	0.2	6.57	1.9	4.27	1
As	16.49	16.5	18.75	8.2	11.37	23
Pb	—	31.2	2.43	7.1	8.53	—
Ag	0.50	—	(111)	(3798)	1.33	0.24
Ni	15.92	—	—	—		12
Co	4.50	—	—	—	—	20
Sn	0.34	—	—	—	0.93	—
S	—	1.9	2.78	4.7	0.33	—
Fe			66.27	13.9	0.13	18
Bi			tr.	—	—	—
Au			(8.5)	(34)	—	—
CaO			0.50	—	—	—
SiO_2			0.35	—	—	—
Zn					—	—
Al					—	—

( ) ppm; * This is not a true speiss; it could perhaps be a pseudo-speiss.

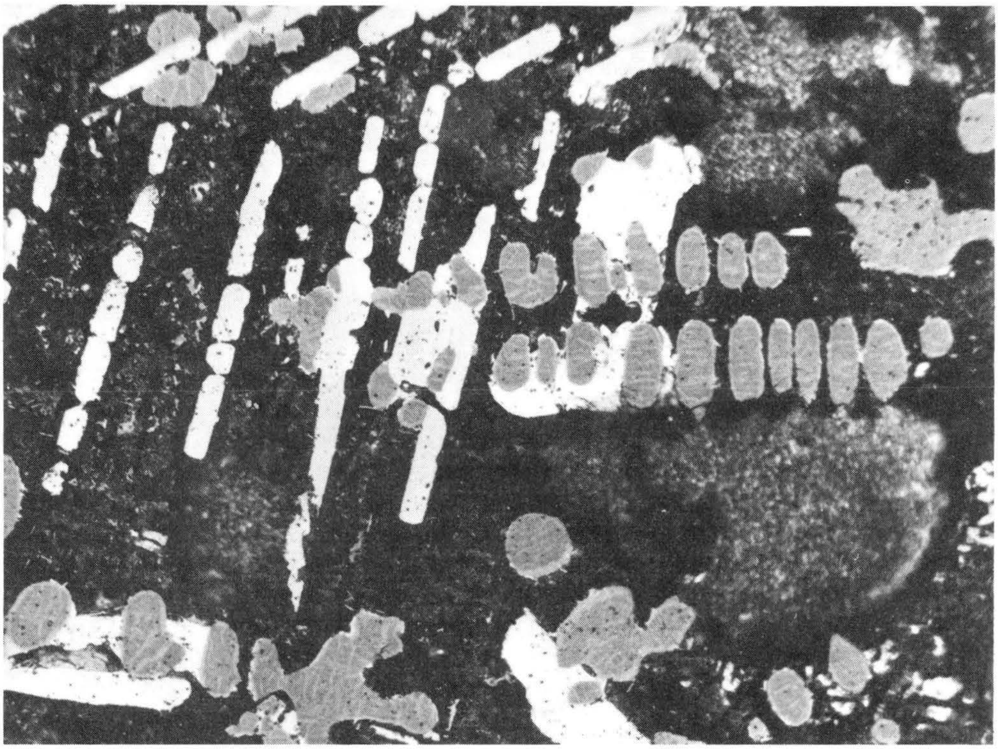

Fig. 13. Structure of speiss. (dendrites, CuS; broken acicular phase, FeS; Matrix Cu, Pb, Sb and Fe). × 500.

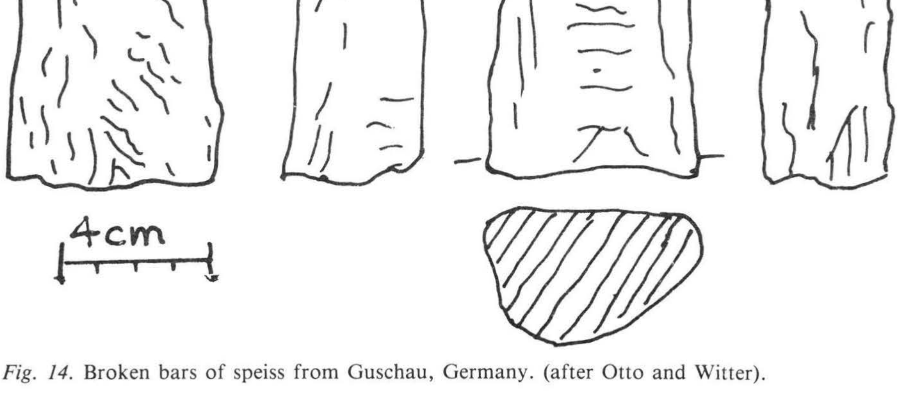

Fig. 14. Broken bars of speiss from Guschau, Germany. (after Otto and Witter).

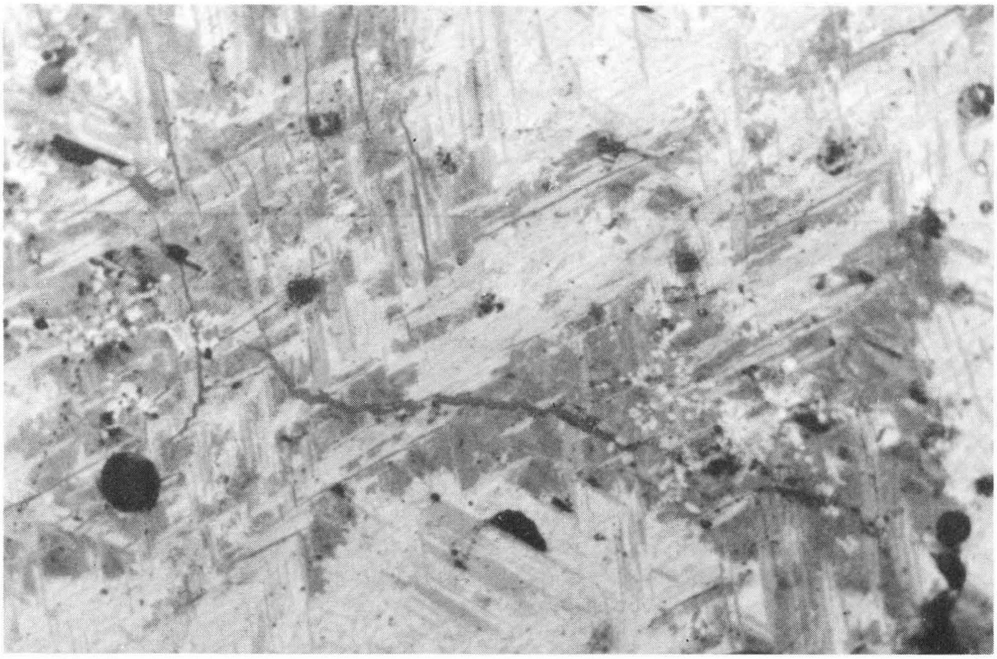

Fig. 15. Widmanstätten structure of copper matte. ×200.

(1982) and Salkield (in print), but the first published example is that from Guschau in Germany by Otto and Witter (1952). The material has been cast into an open bar mould and is roughly of trapezoidal section (Fig. 14) (See Table 3 for composition).

This poses an exciting question. Assuming that the Guschau people cast it into bars intentionally, then what were they going to do with it?

The probable answer to this question is that they intended to use it as a »hardener», i.e. an addition agent to increase the strength of copper by making it arsenical. If the iron and sulphur content were roughly balanced atomically, the As and Ni would stay with the copper and the FeS would form a layer on top. This is one way by which the Copper Age people could have produced their arsenical copper.

Speisses are also produced in lead smelting and the compositions do indicate the primary metal that was being melted. For example, copper smelting gives rise to the speisses shown in cols. 1 and 6 of Table 3, and lead to that in cols. 2 and 3.

Another product, well known to those investigating the Austrian Mitterberg, is *matte* (CuS or mixed CuS and FeS). This is easily produced when not all the sulphur has been removed by prior roasting and the process is reduction smelting. The structure tends to be Widmanstätten with one phase precipitated on the octahedral planes of the other (Fig. 15). The density is about 5.0, depending on the iron content.

These two products are difficult to recognise at a glance. Both are brittle but their density and colour gives some indication as to what they are. Matte tends to be black, like slag, but of higher density. Speiss tends to be silvery and also of higher density than slag but lower than that of metal. Many attempts have been made in more recent times to find a use for it. Salkield states that it was sent from Rio Tinto to the foundry at Seville in the 17th century (Salkield). Roasting it will expel the arsenic and leave Ni and Fe which would harden copper.

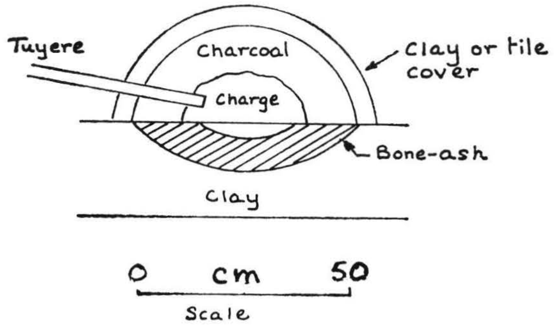

Fig. 16. Roman period cupellation furnace from the UK.

The third product is litharge, and a considerable amount of this may be found on medieval sites. It is PbO and can occur in two crystalline forms, the alpha (tetragonal) form and the beta (rhombic) form both of which are reddish-yellow in colour. They are either the product of silver refining or silver production. In Attic Greece, at Laurion, it was being made in the 5th century BC in large amounts and little attempt was made to convert it back to lead (Conophagos, 1980).

In the first-refining-case the lead is added to the silver to absorb the impurities, leaving pure Ag behind. This is all done on a »cupel», a shallow, saucer-shaped refractory container usually made of bone ash (Fig. 16).

Naturally, the composition of the litharge will reflect the original composition of the silver and show whether it results from Cu-Ag coins for example, when it will contain much copper, or from Cu-Sb-Pb-Ag materials, when it will contain antimony as well as copper.

Litharge produced by the cupellation of lead to produce silver metal will normally be very pure (see Table 4) although in Attica it may contain some zinc.

Table 4. Composition of Litharge %.

	Rio Tinto (Spain)	San Pedro (Huelva)	English, 1925	Winchester (Saxon)		Laurion Attica (5th cent.)
				Matrix	Inclusion	
PbO	68.05	73.5	85.8	95.6	55.9	Rem
CuO	0.36	2.42	3.42	0.5	48.6	(360)
S	2.72	0.21	0.30	0.4	0.8	—
Sb	1.02	0.20	2.24	—	—	—
As_2O_5	0.89	0.06	—	—	—	—
Fe	4.89	1.9	0.17	0	0	(500)
Al_2O_3	1.33	—	—	1.0	0	—
CaO	2.30	—	—	0	0	—
MgO	0.45	—	—	—	—	—
SiO_2	6.8	6.4	—	0.8	0	—
Au	(3.4)	(18.3)	—	—	—	—
Ag	(205)	(568	—	0	0	(75)
H_2O	4.1	—	—	—	—	—
CO_2	0.52	Tr.	—	—	—	—
Sn	—	—	0.50	0	0	—
Bi	—	—	—	—	—	(30)

( ) ppm.; —, not determined; 0, sought but not detected.

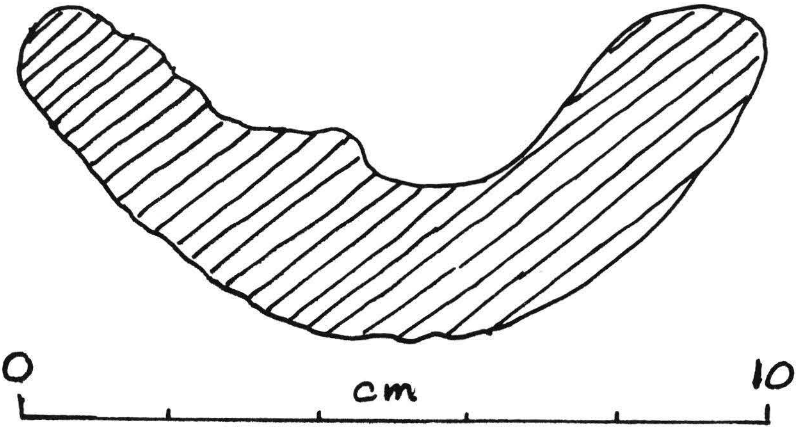

Fig. 17. Section through litharge cake from medieval Winchester.

Fig. 17 shows one of about 6 cakes found on a medieval site in Winchester U.K. Its analysis is given in Table 4 and shows that it probably came from a debased coinage metal of the Ag-Cu type, like that from Hengistbury Head.

Conclusions

It will be clear that an immense amount of information can be obtained from the examination of the artifacts, particularly the slags which withstand weathering more than the rest. Materials represented and techniques used are the main results. Provenance and origin are not so reliable, as so many people have found. But indications are possible. In this respect most bronzes contain a little lead, and therefore lead isotope examination should be used when available as a method of identifying possible ore sources.

As far as copper base alloys are concerned we can tell the difference between cast and wrought metals and whether they contain lead or not. Unless tin is present in large amounts it is not always possible to distinguish between brass and bronze without analysis for Sn and Zn. But we can learn a great deal about the standard of the casting and the degree of working and therefore the general level of technique. The trace elements determined by AAS may give us a clue to the mineral source. But on the whole this aspect has been disappointing, partly because so many mineral deposits have much the same composition and partly because from the earliest times scrap metal circulated and was continually remelted. Even so, general trends are often present when sufficient analyses are done of the artifacts from a single region or period.

The analysis of crucible slags will usually tell us what sort of metal was melted as the slag will entrap particles of the metal. Analysis of the crucible fabric may tell us where the clay came from. Moulding materials are often contaminated with the metal being cast.

All early iron in Europe and Africa was wrought iron made by the direct process of reduction from the ore. This was relatively pure, apart from the slag, but certain elements such as Cu, Ni, P and Co can point to a specific ore body. It must be remembered that a smith can use metals from various sources with very different compositions. Pieces of scrap metal will be welded together and when the artifact is analysed it is importent to know exactly which part it relates to.

For this reason blooms and billets (virgin material) are more important than the artifacts. But, of course, they may have been carried a long way. When cast iron is found it is likely to date after AD 1300 or be a Chinese import.

Furnace linings will sometimes indicate the metal treated. Smelting furnaces will be contaminated with slag and this slag should normally show the metal smelted. But smithing furnaces can remain remarkably clean as also can crucible melting furnaces, as the walls of both are only in contact with charcoal. Usually, crucible furnaces will contain driblets or prills of the metal being melted, but one cannot rely on this as they may have been cleaned out for re-use or the prills collected for re-melting.

The temperature to which the lining has been subjected does not specify the maximum temperature used in the furnace, as this may have only existed around the crucible in the centre, the charcoal near the sides being less affected by the heat.

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