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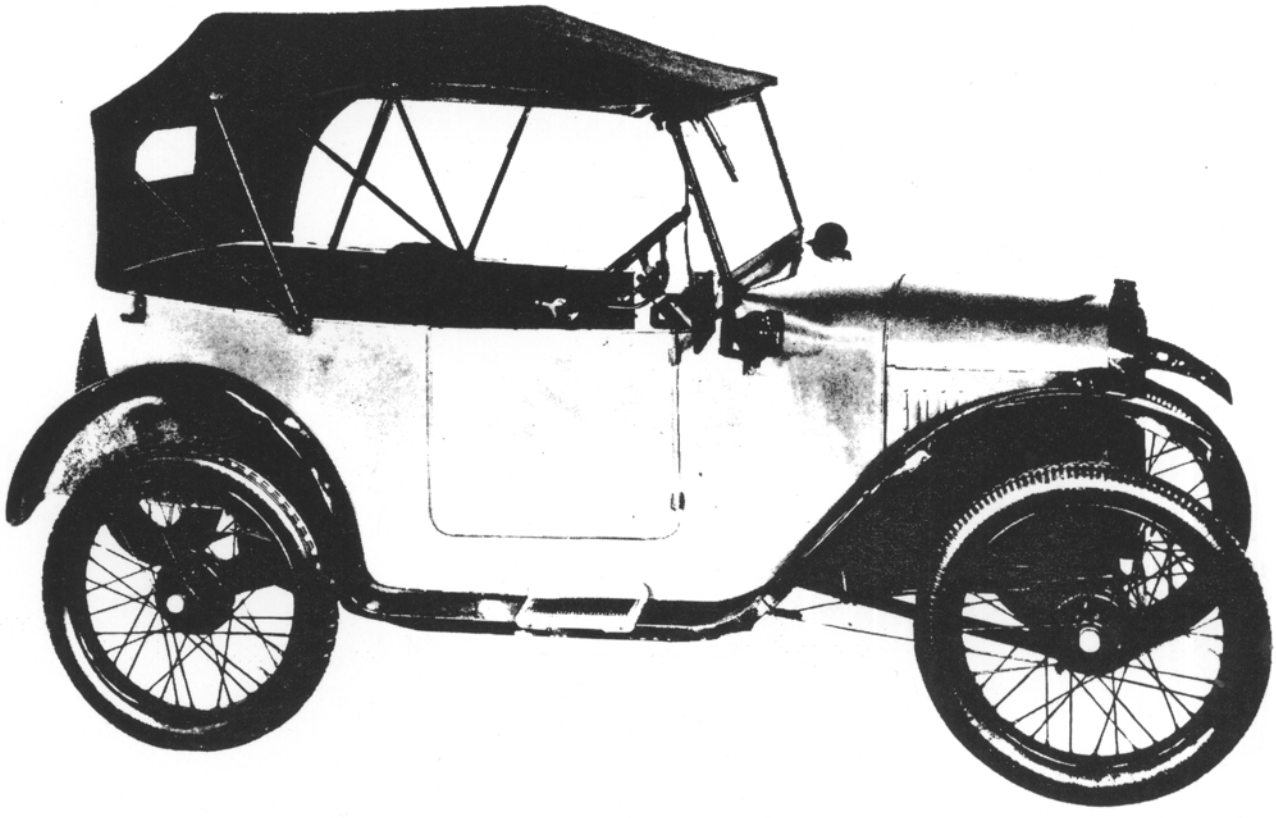

Austin Seven, 1923: The second car produced

Illustration by courtesy of the Birmingham Museum of Science and Technology

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Cover Illustration: *During the 1984 HMS Alloys conference there were several visits to Midland Museums. Notes on some of the exhibits are included in this issue. Arthur Street emphases the influence metallurgists had on the Austin Seven. The picture on our cover is of the second vehicle to be produced and is reproduced by kind permission of the Director of the Birmingham Museum of Science and Technology.*

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'Melting tin' in the West of England: A study of an old art

Bryan Earl

Editorial Note

This is the first of two papers on the experimental smelting of tin which was carried out with HMS support. This paper gives the historical background and discusses the assay techniques used in early and more recent times.

The second paper will follow in the next issue of the Journal.

Introduction

'Anyone can smelt tin' – a phrase surely uttered many times by mining historians. The clean, soft, low melting point metal with benign properties has beguiled those who have traced records of its production in the West of England. The simple reduction of its ore cassiterite (tin dioxide) by heating with charcoal was all that was needed. With no pollution to be agonised over the whole thing was really very simple. But a few attempts to accomplish the trick, soon shows there are cracks in this rash assumption. Added to this while the overall reaction appears to be the reduction of tin dioxide with carbon to release tin metal and carbon dioxide gas in fact the actual reactions involved are probably complex. Making the process efficient really did add to the problems.

With the increasing interest in the archaeology of tin in the West of England it is appropriate to make some attempts to find out more about the practical 'blowing' or 'melting' of 'white tin' the metal, from 'black tin', the cassiterite concentrate (whitetyn and blacktyn are of ancient usage). It must be said that the blacktyn of the West of England miner and the 'black coloured sand' of Pliny – a remarkable similarity – is hardly descriptive of the brown concentrate material, but black tin is virtually always used in the West of England to name the concentrate, although rather confusingly 'tin' is frequently used to denote, either the metal, the concentrate or the ore in place in the rocks. The name 'tin' seems to have come from the Chaldee language בדיל : mud or slime, which certainly is descriptive; again, it was applied promiscuously to either the ore or metal. This can be set beside the Greek word Kassiteros, which appears to have a more uncertain origin than scholars might have us accept. Kassiteros seems to have been used to denote tin metal, pewter or perhaps lead, but was probably Celtic in origin, based on 'almost separated Islands' – the mythological Islands of Tin – and not a specific reference to a metal. This indicates a fascinating possibility that the Celtic culture had considerable influence on the Greeks. Indeed Aristotle applied the epithet Kentikov to what was probably tin metal: Celtic.[1]

Originally tin metal was produced by some form of air or blast furnace: 'blowing' tin from the ore, but after the seventeenth century its smelting was increasingly by reverberatory techniques. Some sites where the blowing was done are known particularly on Dartmoor [2,3,4]. Many others undoubtedly exist. Rather general accounts of the process, often also referred to as 'melting tin' can be studied. However, the exact details of the processes used are lacking. By attempting to duplicate known techniques some of the details can be revealed and clues as to what to expect in studying old sites be established and so form basic data for archaeologists to use to help in research for fuller studies.

Historical Background

This study looks at the 'blowing' or 'melting' process for reducing the ore cassiterite to tin metal, as distinct from reverberatory 'smelting'.[5,6] Cassiterite was virtually the only ore of tin used in the West of England. In its reported form the 'blowing' process used a small shaft furnace with an air blast generated by one or two bellows. Only one good illustration of such a furnace and its layout seems to exist: in the late days of its working known as a 'castle'.[7] This was drawn in the eighteenth century and represents a rather highly developed form of furnace, agreeing quite closely with Pryce's description written a few years later. That the technique was steadily evolving is shown by Hatchett's description[8] of late eighteenth century blowing at St Austell which gives details of a different form of dust recovery flue, and Aiken's description of the early nineteenth century – an 'original contribution'.[9] This was of another St Austell blowing house furnace, briefly mentioned by Hatchett, that was made of an iron cylinder well lined with loam, a pair of cylindrical blowing cylinders rather than the bellows of the other St Austell furnace, running the tin into a float and so to an iron basin where it was kept molten and ladled out into moulds. The methods were very like those known to be in use by the seventeenth century, but the equipment was more refined. Ure's account of tin blowing, almost certainly the same furnace as that described by Aiken, gives additional details but seems to have been taken from some exhibition of about 1825.[10] This furnace probably represents the zenith of West of England blowing technique. Although such 'melting' of tin seems to have continued at one site on Dartmoor until the 1850s, this was the end of the ancient process.

In its usual eighteenth century form the tin 'castle' was a shaft furnace of stone, about six feet high with a loam lined inverted cone shaped interior tapering from about 2 ft diameter at the top to about 1 ft diameter at the hearth. A tap hole through which the molten tin and slag ran out continuously was made from the hearth. This was 1½in wide by 4in high, the metal and slag running onto the external trough-like 'float'. Another aperture was also made in the side of the furnace (apparently this was usually in the side opposite the tap hole) for a large plate of iron with holes for the nozzles (or 'nose') – the term used in the West of England – from the bellows. This was the 'hearth eye'. The nozzles were guided from about one foot above the hearth, where they came through the 'eye', with a most medieval curl, to direct the blast down onto the hearth. The furnace was fed continuously with alternate charges of black tin and charcoal, being kept full to the top – the 'hot top' of the charge – which in turn was kept cool by adding water. This avoided overheating the furnace and reduced losses of tin as fine particles, volatilised material and dust size cassiterite. No flux was used. The later descriptions note that the bellows were waterwheel powered. Thibault deduces from the figures given by Pryce (18 to 24 sixty gallon packets of charcoal to produce eight to twelve hundred weight of

tin) that the consumption was 48cwt charcoal to reduce 21.5 cwt of ore (which probably held about 65% tin metal).[11] However, such calculations are notoriously difficult because the 'hundred weight' could vary from at least 100 to 122 lbs, and the 'gallon' could be vague. Slags were either returned to the furnace, or stamped to remove tin values as prills, which again were sent back to the furnace.

In the German Erzegebirge tin furnace – early versions of which may have influenced British designs – the hearth 'eye' was the opening through which the tin and slag flowed (rather than the port for the'nose'): in the West of England this was the 'tyn hole'. Similarly, the German 'fore-hearth' was the 'flote' or 'float'.

The tin metal and slag ran from the furnace onto the shallow trough – up to six feet long – cut into a 'moorstone' (granite) block. Here burning charcoal both kept it liquid and prevented re-oxidation. Normally the tin was ladled from this float into, at first, moulds consisting of clay lined cavities cut in granite blocks; later the tin was passed from the float to a basin where it was given treatment to purify it further. When the tin was ladled from the float a certain amount of liquation effect occurred, as the higher melting point 'mount egge' or 'hardhead' – mostly tin-iron compound resulting from iron minerals in the feed – solidified on the float, the pure tin remaining liquid.

An indispensable part of the blowing operation was the concentration of the ore to a high grade feed, and stamping of the slags for the separation of tin values which were returned to the furnace. The stamps, usually waterwheel powered, were used to crush the ore or slags, concentration of the dense values being achieved by allowing the pulp coming from the stamps to settle in succession, according to density, in some form of pit or channel: this was normally a 'strake', 'tye' or 'buddle'. The pulp was often stirred with a shovel or the feet to promote the separation. The high grade material was then dug out for treatment, the section holding a suitably high grade being assessed by 'trying' on a shovel. The amount of water fed to the stamps' 'coffers' (where the crushing took place) had to be judged so that the subsequent separation could be controlled. Sieves consisting of perforated metal plates (usually copper) were put in front of the stamps to ensure the feed to the strake or buddle was not too large in size: sufficiently done so that the cassiterite had been broken free from the waste minerals. The high density 'black tin' – actually a brown mud – settled out first and formed the rich 'head', with any tin metal prills. Burning the ore concentrate in a 'tin kiln' reverberatory furnace, if impurities such as 'mundik' (pyrite) or 'silver mundik' (arsenopyrite and lölengite) had to be removed which would otherwise have spoilt the melting was well established practice by the mid seventeenth century.[6] A high grade black tin is well described by the old quip: 'feels like lead, must be tin'. The importance of the stamping in the blowing process is revealed by the large number of worn mortar stones nearly always found at blowing sites. These are usually of granite with the worn away pockets from normally three stamp heads, on several faces. Prior to the evolution of gravity stamps, crushing must have been by pounding and rubbing the ore on stone bucking blocks.

It should be noted that in the West of England 'slag' meant not only the pitch-like glassy material, originating from impurities but also sandy refuse brought out during the 'tide' – the period that the furnace worked.[5,12,18,19] An earlier term was 'cynders'.

Descriptions of tin melting furnaces used in Saxony about 1895[11], and in German work during the sixteenth century as described by Agricola[1] can be set alongside the 'Alman' furnace for Cornish melting in 1671: *'Conceiving it sufficient to say, that our Furnace is no other than an Alman Furnace, I shall proceed (only taking notice, that our Lime, though the strongest I ever yet heard of, as being made of the hardest Marble, will not endure the fire in our Hearth, but we must use a particular kind of Clay) . . . Moor-Tin (ie such as is digged up in the Moors) we find runs or melts best with Moor-coal, chark't: But our Tin, which lyes in the Countrey, runs best with an equal proportion of all Char-coal, and Peate (ie Moor-coals) for the first running: but when we come to remelt our Slags, then we use Char-coal. When all is melted down and remelted there sometimes remains a different Slag in the bottome of the Float, which we term* **Mount-Egge***; And that it is mostly an iron body, though of a Tin-colour, I accidentally assured myself by applying one of the Poles of a Loadstone to it, which quickly attracted it, yet not such a quantity by far, as that of Iron.*[5] It is possible that this 'remelt our Slags' was a distinct operation not undertaken in the blowing furnace but was the melting of impure metal in a vessel, ladelling out pure tin from the slag and hardhead.

However, the earliest thorough description of the blowing process is that of Dr Cotton, written in 1664, while although being titled on the tin mines in Devonshire, does mention Godolphin mine – well into Cornwall. He went to considerable pains to describe many details of the preparation of the ore: stressing the importance of the iron stamps. Also noted were buddles for separation of the values, crazing mills for treating what had escaped the stamps (the stamps having perforated iron plates to control the size of the output) to be ground between two stones, and the stirring of the concentrate in a wooden vessel, striking this with a shaft to pack the concentrate in the bottom – later this was termed 'tossing and kieving'. Dr Cotton indicates that the tinners recognised that different degrees of crushing were required to suit the various ores, as changing of the plates in front of the stamps to smaller holes might be preferable to crazing. Small size cassiterite crystals may require more extensive grinding to liberate them from the gangue.

The black tin concentrate was carried to the blowing house 'where being cast together with Charcoals into a Furnace, as it melting by the fire of a Wall-bellows; it flows out into a stone trough and there they skim off the top of it, which is like black Pitch, and is called Cynders: This they do not cast away, but stamping it again together with the tin stone, it adds to the quantity of the tin'.

'In the melting of the tin some of the lighter parts of it are blown off, and stick in the severall parts of the Blowing house, which they cannot well take off: And for that reason they seldome repaire those houses, but rather burn them, and the tin found in them will be sufficient to build a new house . . . when the fire is to hot, it makes the tin more apt to fly, which when they perceive, they endeavour to remedy by casting water on it. When the cynders are skimmed off, they put the tin into Moulds which contain about 3, 4 or 5 hundred weight a piece, and the burners mark is affixed on it . . .'[12] Dr Cotton's blowers obviously did not make any distinction of a first and second melting.

Systems for collecting the 'tin more apt to fly' seem to have been either used or not by blowers. Carew in his 'Survey of Cornwall' of 1602 notes enlarged and improved chimneys

for catching this dust in blowing houses, but this does not appear to have been a universal practice. Pryce does not mention such systems, although Hatchett does; both were writing at about the same time.

Alas no records of any note on tin blowing appear to exist prior to the 1500s. The account that does survive from that century was written by one involved in the tin trade, but not a professional blower; he acknowledges his limitations in understanding the process, trying to report features that seemed to him to be important. This results in a tantalisingly fragmentary account. He notes that the bellows blast went in at the 'hearth eye', and the tin ran out into the 'flote' from the 'tyn hole'. It was considered important that the hearth eye and tin hole should be about twelve inches apart or 'the heat of the billows be so mighty it will quickly consume away the front of the hearth'. While this manuscript does not have the rigour of Agricola, it does have great merit in being a description of British practice made by one closely connected with the work.[13]

The manuscript is written in old English and decyphering it can prove difficult. Various interpretations are rife, often demonstrating that knowledge of the actual process would have resulted in a different appreciation of the words. Just for the record, this is my 'translation' of the critical section on blowing:

> 'I have heard the blowers of tyn report that there is great consideration to be had in the blowing house in making their hearth when they set their blowing house to work. for a blower this exprt in his occupation as sone as he cometh into a blowing house being set to work if he do but once hear the billows blowing will decerne what falt there is in the hearth and concerning the rule thereof this hath bin the opinion amongst themselves [?] if the billows be two set in the britch (in the depth of the billows I meane) then must there be [?] inches from the hearth eye to the tyn hole whereas the tyn cometh out for if the hole be ney to the hearth then will the heat of the billows be so mighty it will quicly consume away the front of the hearth, now if the billows be less breadth then ten or twelve inches will serve from the tyn hole if this be not considerd by the blower the make of the white tyn may quickly cost [?] or more in the blowing of his tyn.'

The further back in time one goes the more likely the tin furnaces were of the simple pit-in-the-ground, rather than the more elaborate shaft, type. The 'Wall-bellows' may have been hand powered rather than by waterwheel. One is struck by the 'feel' of some of the old blowing houses which very much resemble an old style blacksmith's forge. Hand worked bellows are recorded as being used for tin blowing in Mexico during the nineteenth century[11] (with a small shaft furnace), and simple pit smelting with hand blowing was still practiced in Japan at the same time.[14] Some thought must also be given to sites which could have used natural draught wind furnaces,[15] which were in use in the Far East also up to the end of the nineteenth century having a construction based on packed kaolin – readily available in the West of England.[11] The nature of the remains of ancient tin melting sites may give clues to the process that was used. The practice of remelting slags to recover their tin content, well established in England by the seventeenth century, using a different selection of fuel, could add to the value of studying the remains, as the possible introduction of a flux via the fuel ash indicates interesting problems. The emphasis on the stamping, concentration and return of the 'head' collected from the slag resulting from the first melting make it probable that at many sites any glassy slags that are found will be the reject from the final, second, treatment – the first melting slag refuse reporting as fine fragments in the tails from the concentrating operations.

'Blowing' Blast Furnace

Before the specifications for the experimental furnace could be drawn up, it was necessary to look at the dimensions of the operation. A review of the available figures for tin blowing in the West of England showed a wide range of ratios for the black tin to charcoal used for the charge. To examine this with some semblance of accuracy, determinations were made to try to rationalise these figures.

The following values were used, or found experimentally:

– Apparent specific gravity of charcoal in bulk

(a) By determination of that used in these trials: 'scooped and struck' = 0.35

(b) By Websters New International Dictionary under 'Bushel' = 0.25

(c) By Percy's 'Metallurgy – Fuel' = 0.15

– Apparent specific gravity of tin concentrate in bulk (65.1% black tin as used in these trials)

(a) 'Scooped and struck' = 2.29

(b) 'One shovelfull' = 10 to 15 lbs (best estimation)

– One gallon measure (beer measure assumed) =

$$\frac{282}{277.42} \times 10 \text{ lbs} = 10.171$$

for specific gravity = 1.0

– One hundred weight = 100 lbs (18th century value). NB The early Stannary hundred weight was 120 lbs; in the 19th century it was 115 lbs.

A tabulation of the feed ratios using these figures shows wide divergence. Using the Pryce figures, Thibault works from black tin, whereas Pryce indicates tin metal from charcoal used to produce it – this formed the basis for the calculations given here. Black tin was taken as holding 70% metal:

See Table 1

This is not very helpful in giving the actual ratio of the components of the feed used in the West of England blowing furnaces. The only one which has any confirmation from other sites is that calculated from the Aiken data (assuming a bulk specific gravity for charcoal of 0.25) which corresponds closely with the Thibault figures for several Far Eastern sites. However, Pryce was in general an accurate reporter and closely connected with mining so a bias has to be given in favour of the quantities calculated from his figures. Moreover, no corrections have been made to his figures in the annotated volume for the proposed second edition of Mineralogia Cornubiensis held in the Museum of the Royal Institution of Cornwall at Truro; amendments have been made at several places elsewhere in the book.

Source.	Furnace.	Bellows.	Charge.	Calculated Charge of charcoal to unit charge of black tin. Weight
Pryce	6 ft. high; internal size: 2 ft. square at top, 14 ins at bottom tapering conical, granite (? lute lined). Float 6½ ft. "high" (long) by 1 ft. wide (probably dimension of actual groove).	2 x 8 ft. long, 2½ ft. wide at broadest, waterwheel powered, two noses.	"Eight to twelve hundred weight of tin . . . 18 to 24 sixty gallon packets of charcoal, melted in tide of twelve hours.	3·14 (C sp.g. 0·35). 2·27 (C sp. g. 0·25). 1·39 (C sp. g. 0·15). 2·23 (Thibault).
Hatchett	Granite, 9 ft. high but aperture for charging well below top. Tin flows out into trough, ladle to basin for purification. 20 fathom long flue with circular building at end to collect dust. Small sketch in book.	Two bellows worked by waterwheel. Notes "At about a Mile from St. Austle is another Blast Furnace . . . instead of bellows has cylinders as in certain iron Founderies."	Double bulk of charcoal to tin . . . Do not smelt more than 2 cwt. at one time.	0·31 (C sp.g. 0·35). 0·22 (C sp.g. 0·25). 0·13 (C sp.g. 0·15).
Ure	6 ft. high to throat. Furnace a cylinder of cast iron, coated internally with loam. Inclined flue to chamber for dust collection. Hemispherical basin float.	Two cylinder bellows, driver by waterwheel. Two noses.	—	—
R. J. Law, (in litt.)	Illustrations agree with Pryce's description; 2 noses inclined down, 2 single acting bellows, noses opposite to tin discharge "hole". Float consisting of channel in front of eye. Has dust collecting flue and chamber.		—	—
Aiken	7 ft. high.	2 cylinders, worked by waterwheel.	Three or four shovel-fulls of ore, and two or three half bushels of charcoal.	0·98 (C sp. g. 0·35). 0·7 (C sp.g. 0·25). 0·42 (C sp.g. 0·15).
Dartmoor sites	Several furnaces examined; most about half size of those detailed above.	—	—	—
Le Grice (Trereif)*20	Inverted cone cavity, 3 ft. dia. top, 3 ft. deep. Hard clay sides, in bank of clay. Hearth c. 1 ft. dia.	Small ravine in bank ? for blast and tapping of tin.	—	—

It was hoped that an analysis of these figures would bring out some form of mean, but on looking at them it is clear that the three reports fell into three distinct groups. The first is the Pryce "rich charcoal" classification. which had to be looked into more completely. The second the Hatchett low charcoal: evidently mistaken reporting. as the amount of charcoal would be nearly all used up in reducing the cassiterite, leaving so little available for heating that the furnace would not sustain a red heat - particularly if it were a small one. The Aiken data obviously was practical; it was virtually reproduced in reports on far East tin blowing.

Table 1

To look into this more closely, it was considered that at least two degrees of 'richness' of the feed mixture would have to be tried: one with a low - say 60% weight – charcoal charge, and another high, say 200%, on black tin. It was possible that the West of England blowers had found a charcoal rich charge had advantages.

The average dimensions of the eighteenth century furnace gave a size about twice that of the remains of furnaces at several sites on Dartmoor (such as SX 663724, 552768, 553763, 555754), although some larger have been reported – these may be later, eighteenth or nineteenth century working. It seemed likely that in the heyday of the 'melting' process, before the eighteenth century, the smaller form had predominated.

Examination of Conditions for an Experimental Melting

The 'melting' or 'blowing' of tin in a bowl and blast type furnace is distinct from the 'smelting' of tin in a reverberatory furnace. The reduction conditions in a reverberatory are rather different, and the techniques quite different from 'blowing'.

To gain some insight into the blowing process some preliminary work was done using the classic mouth blowpipe/charcoal block/candle flame method of the old mineralogists and miners to reduce some cassiterite. The problems associated with the formation of disseminated prills of tin metal that were all too easily produced showed that only if several conditions were satisfied would a reasonably good reduction occur. The black tin had to be of high grade, the quantity of added powdered charcoal had to be within limits, and a high temperature with a non-oxidising flame used. Even so, the deposit downstream of the blast (yellow when hot, white when cold) on the cooler charcoal, which was one of the features used to identify tin in the blowpipe method of analysis, indicated losses of metal (Fig 1). By adding a standard fusion mixture flux of potassium and sodium carbonates, a tin bead was much more readily produced. The trials showed that while molten tin is very mobile, it does not agglomerate easily. This feature has caused problems in previous work on the reproduction of tin blowing.[16] It seemed advisable to gain practical experience in the manipulation of the materials and the influence the feeds had on the outcome of the 'blowing'.

The instrumentation and cost that could do full justice to this problem were wildly beyond the constraints of this work. To try to make a virtue of necessity it was decided to use the old techniques of assay that fortunately were known and had been used by the experimenter in the past. This may help less favoured researchers to gain an insight into the limitations of the processes used by the 'old men' and highlight interesting areas for detailed study. The fire assay in particular is very similar to that described by Agricola and it is virtually certain that it was applied in the West of England by the seventeenth century.

Two controls were commonly used to guide mining and smelting operations which were well established by the eighteenth century as noted by Pryce. One was the 'vanning' technique of assay: particularly suited to assessing the values in an ore. The other was the 'fire' assay – to determine how a black tin concentrate would respond to 'melting'. According to tradition the blacksmith's hearth was often used to examine ore in the West of England.

Vanning

The vanning assay is undoubtedly very old: the trying of a sample of crushed ore on a shovel with water. Although the word 'vanning' is not used, the sixteenth century manuscript on tin working[13] gives a rather complete description: 'a quantity out of the heap' was taken on 'the point of a shovell' and washed backwards with water to displace the waste to 'show' the cassiterite. However as with his other descriptions the writer of the manuscript is a little unsure of the technique and its importance, putting more emphasis on the appearance of the particles that adhere to the wet hand when it is plunged into and withdrawn from a heap of black tin – a trial still made by old experienced tin dressers

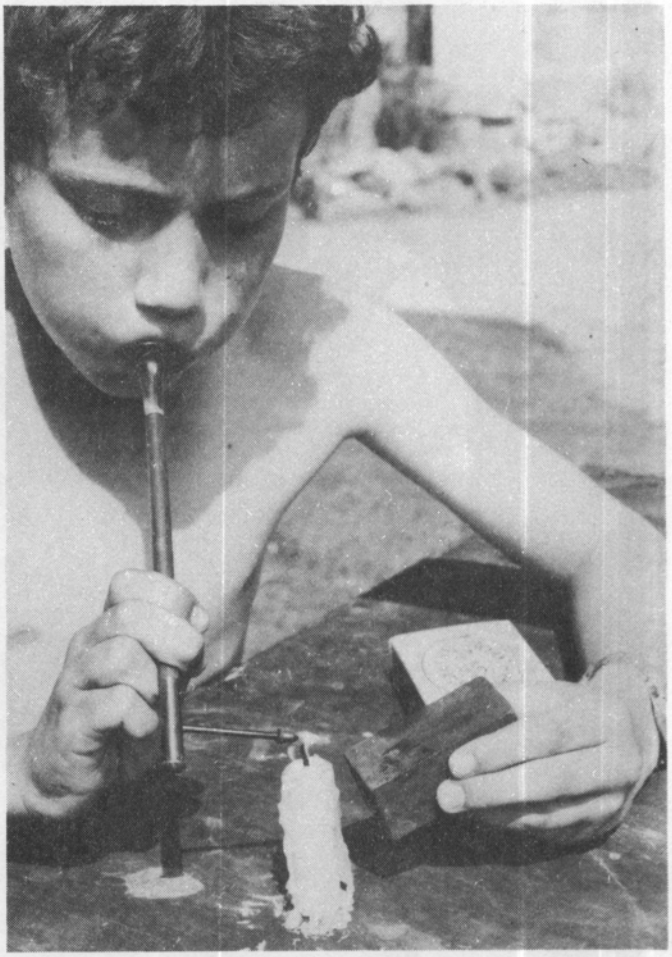

Fig 1 Blowpipe technique with charcoal block and candle.

(Fig 2). Undoubtedly the vanning method is best described by a practical demonstration. Vanning was well known to the 'Inquisitive person' of 1671 and was so named by him.[5] The special shovel that was developed for this assay was named the 'trying' or 'vanning shovell'.

The assay consists of (a) taking a sample, (b) crushing this to a suitably fine powder – 'bucking', (c) measuring off an assay – by volume originally, later (in the nineteenth century) by weighing, (d) putting the assay on a suitable shovel. By the nineteenth century this had developed to a special sheet steel blade with carefully controlled contours. The surface is maintained in the right condition by cleaning over with a pumice stone. (e) Water is then scooped on, and the material 'vanned' by a swirling

and upward fanning with a flick at the end of each stroke. The denser the material the farther it travels up the shovel to form the 'head'; ideally this should be shaped 'like a bullocks tongue'. (f) Most of the waste gangue minerals can then be removed with the thumb, and the head re-ground on the shovel with a small hammer to release any material that has gangue attached. The sample is then re-vanned. (g). The shovel with its head and remaining 'tails' now well differentiated is then dried over a fire – traditionally this should also have mugs of tea and a pasty keeping hot on the hob – and a magnet rubbed through the head after carefully sweeping the tails to one side. The magnetic material – originating either from the ore or the grinding tools – removed, the sample is then

Fig 2 Tin streamer using vanning shovel in the 1960s.

re-wetted, vanned again and the head either examined for its appearance by the old techniques: the assay might be reported as a 'shilling van' (the head area being that of a shilling coin, from a handful of sample); or the van dried again and then swept off with a hare's foot to be weighed. The result was given in a wide variety of values: 'number of barrows' perhaps being the most vague, as a 'barrow' varied from district to district. 'Pounds weight black tin per ton' is more recognisable: the black tin head being taken to hold approximately 70% tin metal, the balance being made up of small amounts of other high density minerals and gangue inadvertantly thrown up. In researching reported vanning assay results it is essential to bear in mind the wide number of reporting systems that were used, including some with an extraordinary juxtaposition of different systems of weights and measures that gave results that, remarkably, reproduced very closely those that could be expected in large scale working.

If it is suspected that the assay has sulphur or arsenic values, the measured-out sample is carefully roasted at mid-red heat on the fire, usually in a small crucible, in which it is carefully swirled about until the white arsenic fumes subside, and the assay smells 'sweet' -- clear of sulphur dioxide.

A good vanner can separate tin ore from 'mundic' (sulphides), give a good estimate of the values and gangue in the sample, and to what degree it must be ground to liberate the cassiterite economically. Remarkably good results

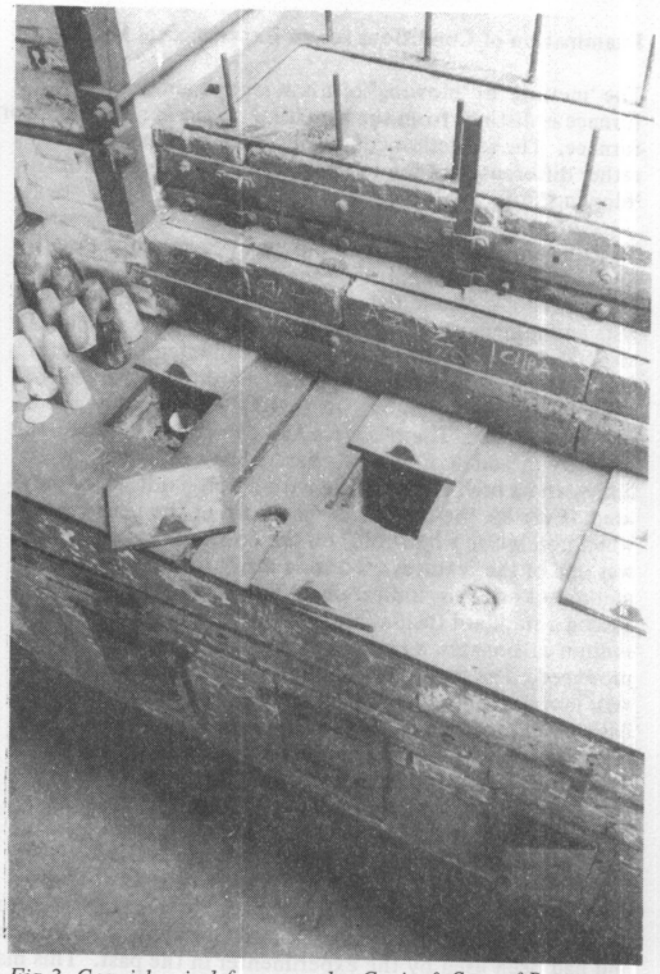

Fig 3 Cornish wind furnaces, by Corin & Son of Penzance, at the old Camborne School of Mines. The crucible is buried in the coke fire. Ashpit door at bottom, sliding door covers over fire, damper rod to flue and chimney stack at left can be seen (1972).

are possible; one major and particularly successful Cornish mine today (1984) controls its prospecting and mining operations by vanning assay. It may not appear academically nice – but it **works.** To this day the vanning assay not only gives a quantitative result it also demonstrates how an ore will react to concentrating operations very similar to those used in practice, except for flotation. Present day results are quoted as 'kilogrammes black tin per tonne'.

Fire Assay

The other assay was used for concentrates. This was the

'fire assay' where a sample was heated in a crucible with about 20% its weight of powdered charcoal or anthracite, to a 'sharp' heat (bright yellow – about 1200°C) in the charcoal or coke of a wind furnace (Fig 3). A piece of charcoal was floated on the charge to avoid re-oxidation and after about twenty minutes when the mass had melted down and the sluggish bubbling stopped a stick was used carefully to stir the mass and wipe down the sides of the crucible so as to aid the agglomeration of the remarkably un-wettable tin prills. The crucible was made of clay and filler refractory mixes at first, but by the nineteenth century black-lead crucibles were found to be more long lasting. The bright red-hot crucible was then carefully removed from the furnace, tapped on the side several times, again to reduce prilling and then the contents were poured into a smoked iron mould where the tin metal separated out as a 'lump'. The disseminated fine prills of tin virtually always produced was the 'pillion'. If the quantity of the pillion exceeded '2 in 20' (10%) it was considered the sample was of a poor grade. The pillion separated from the mass of tin metal mixed with a slag consisting of both vitreous and powdery material. This slag was crushed and vanned to recover the fine prills of the pillion and this was added to the main 'lump' to be weighed and give the assay.

The purity of the tin metal was judged by re-melting it in a ladle and pouring into a groove cut in either a marble or iron block. The cold metal was then examined; its appearance (bright: good, frosty: poor), sound on bending: a good 'cry' was expected, and the nature of the fracture when the block was chipped with a chisel: the metal should shear with a clean fracture and at the same time show a malleable start to the cut. The yield and quality from this assay was found to resemble quite closely that which could be expected from full scale melting.

Ore Material

These two methods were now used to examine the materials to be used in experimental blowing: how they could be manipulated and what the nature of the metal and slag produced might be. The vanning technique was also readily applied to assess the nature of the 'tin slimes' found at a typical blowing house site, where they had been cut into and exposed at a river bank. With the way in which ores respond to the blowing process, some form of assay is vital as a control to ensure the melting will 'work' with any degree of success.

At the start of this investigation a difficulty appeared as no large scale source of high grade black tin was available in Cornwall and Devon. The mines now find it unprofitable to dress their ores to better than about 40% tin metal for the smelter. Another difficulty was to obtain a reasonable quantity of material that would be the same or similar in character to that used by the blowers of several hundred years ago. The first problem was overcome with the help of South Crofty mine – working tin lodes 2000+ ft deep – which supplied a quantity of its 40% concentrate, from which sulphides and arsenides had been removed by flotation. Mr J Turner of Camborne School of Mines generously offered to concentrate this material to a grade more representative of that used by the blowers, this work being entrusted to Mr Tony Clarke, who worked it up to 65.1% tin metal grade by tabling and passing through a 'Record' rotary magnetic separator. Skilful manipulation was required. Even so, after three passes through the magnetic separator it was found the iron values could not be eliminated. With the setup available, 'burning' the concentrate would have been difficult.

To compare this material with the ancient black tin, a traverse was made of lode exposures in the West Penwith coastal area and by bucking and vanning a sample large enough for two small 'meltings' was obtained. It was felt that this black tin should represent quite closely that won from old workings on lode exposures and shoad stones. This black tin was taken to hold approximately 70% tin metal. Even with this material some magnetics could be extracted with an Alnico magnet; several passes of the magnet removed the iron residues ground off the crushing tools, but magnetic material that seemed to originate from the lodestuff remained. Treatment of the lodestuff 'fines' also gave some magnetics. However, the iron content was obviously lower than that in the CSM concentrated South Crofty material some of the magnetics of which probably were the residues from heavy media material used in its dressing at the mine. The coastal traverse lodestuff concentrate was given a preliminary 'burn' at dull red heat in an earthenware crucible, using a gas blowlamp.

As it has often been asserted that the early workers won a large proportion of their tin from stream deposits and this yielded a particularly pure metal, it was very desirable that a sample of this nature of material should be examined. Through the kindness of Mr Justin Brooke a quantity of such stream tin was obtained. This was as worked by a Mr Wilson of Bickington in Devon, one of the last true stream tin workers, who considered it rather 'irony'. It consisted of rounded brown granules up to c 5mm grain size. It appeared to be the sieved product of a typical Devon stream deposit – a first step concentrate. On crushing, the granules broke to show material that was largely hematite and limonite, but some were made up of quartz holding lodestuff: mainly tourmaline and chlorite. The powdered sample was vanned and yielded a black tin, taken as 70% metal, giving a produce of approximately 1¼% tin metal which showed the sample was quite representative of such Devon streaming. It was noticed under the microscope that along with the cassiterite some pyritic minerals were present. This strongly indicates that stream ores need not necessarily be as pure as has often been suggested; the hard lodestuff had not been significantly broken down by water and weathering. Although much iron oxide was present in the 'grain tin' sample, this was soon washed away after crushing and it would not have been difficult to stamp and buddle the sample up to a good grade.

Unfortunately not nearly enough sample was available to attempt any form of fire assay or blowing, but it did indicate the similarity between some stream deposit 'tin' and exposed lode ore. No doubt some iron minerals would report in the black tin concentrate made from such a deposit. The writer hopes soon to be able to provide evidence that much of the early tin was produced from shallow mined lode material of a similar nature to this 'grain tin'.

Comparing Samples by Fire Assay

Because of the limited quantities of the samples available the work had to be on a smaller scale than usual. To heat the crucible a bowl shaped furnace was formed with a clay/sand/charcoal mix (equal volumes) in a marmalade concentrate can. The charcoal fuel used in this was blown using a 5mm dia bore brass pipe nozzle connected via a variable aperture bleed valve made of cardboard tubes, by polythene pipe to the blast output of an 'Electrostar' tube vacuum cleaner found abandoned on a waste tip. The aperture was varied to give the blast required at the furnace. The crucible was located in the burning

charcoal after being charged, and a clay cover put on to prevent blocking by pieces of charcoal fuel as it was fed onto the furnace. A perforated can cover was inverted on the furnace to enable sufficiently high temperatures to be achieved (Fig 4). With this arrangement the crucible could be heated to a bright yellow heat – estimated by thermo-couple to be c 1200°C. It was found that this degree was necessary to ensure adequate reaction and settling of the assay. The impression was gained that the melting point of tin dioxide (1127°C) had to be passed: none of the reactions directly involved in its reduction appeared to be solid state in nature.[17]

The crucible was made by pasting a porridge-like wetted

Fig 4 Fire assay. The crucible holding the sample-charcoal mix in the furnace at the start of the heating. More fuel is about to be piled over the crucible and the furnace cover put on. The temperature will be raised to 'bright yellow' by blowing. Dia of containers = 10 cm. Dimensions of crucible for the small fire assay used in the work: 3 cm od x 4.5 cm high; wall thickness 3 to 5 mm, hemispherical base.

mix of equal volumes of potters clay, ground charcoal and ground firebrick onto a damp paper tissue laid over a 'Sparklet' bulb, and drying carefully. This gave a crucible that worked well and stood the temperature; the mixture formed the basis for that used later to line the tin blowing furnace. As 'home made' apparatus was a notable feature of West of England mining pilosophy, such equipment was held to be no drawback. Care was needed when drawing the part dried crucible from the bulb mandrel.

The charge for each assay was a thorough sieved mix of 100 grains of the sample (the old system of weights as used by the early assayers proved very convenient) and 20 grains of powdered charcoal (1 gramme approx =15.4 grains). This was poured into the crucible which was then buried in the charcoal of the furnace, which had been adjusted to a dull red temperature. The blast was then increased and the crucible heated over a span of fifteen minutes to the full fire and held at that temperature for half an hour. Towards the end of the heating period the cover was removed and the assay stirred with a wood stick – the contents being watched to ensure the sluggish bubbling of the charge had subsided and the whole melted down. At this point the crucible was removed and its contents carefully tipped into the smoked cavity of a cast iron button mould. The button of tin was removed after cooling, the slags that separated on top of it then being crushed and vanned to recover fine tin prills which were then added to the button for weighing. The behaviour of the different samples could be watched during the assay and an assessment made of the likelihood of excessive prilling or not. The resultant metal was examined for appearance, presence of magnetics (iron 'hardhead' tin-iron compound) and malleability. The following comparisons were sought:

(a) The behaviour of the 40% South Crofty concentrate as taken from the stockpile.

(b) The result from the upgraded 65.1% Sn South Crofty/ CSM material.

(c) The response from the 70% coastal black tin.

After a number of trials to develop a suitable crucible and gain some ability in manipulating the process the following assays were made:

Sample	South Crofty 40% Sn concentrate	65.1% CSM upgrade of South Crofty material	'70% Sn' concs of coastal traverse
Yield of metal	33 grains (33%)	56 grains metal (55 gr. in button. 1 gr. in prills – 56% total)	56 grains metal (53 gr. in button, 3 gr. in prills – 56% total)
Nature of metal	Brittle, magnetic prills, disseminated in glassy brown slag, along with a few small prills in powdery, mainly charcoal, slag.	Button malleable, rod gave 'cry' Prills hard, magnetic.	Button malleable and non magnetic, prills slightly attracted to magnet.
Nature of slag	Glassy brown. Had to be crushed to release prills. Cassiterite traces in powdery slag seen on vanning.	Relatively small quantity, treacle-like consistency floating on pool of metal in crucible. Cooled to dark brown glass with vesicles, only traces of metal. Powdery slag held traces of unreacted cassiterite, along with charcoal.	Small amount of dark brown glassy with vesicles. Very few tin prills Powdery slag held trace of cassiterite

By this assay the CSM/SC conc. held the same tin content as the 'Coastal Traverse' concentrate, but was less pure.

In every case the slag consisted of both a glassy and powder phase.

Because very limited amounts were available of some specimens, only one assay was made on each sample. While it is not claimed that these assays show any particular accuracy, it is claimed that they do show what may occur with a given sample. Old, and indeed present day (1984) Cornish assay is reported from usually only one van of a sample. This has been found to be quite adequate and sufficient to control normal work.

By the thermocouple probe the temperature in the crucible was 1150°C or above. This temperature was needed to ensure the assay reacted to give a melt that was not too pasty or viscous. A lower temperature yielded very dispersed tin prills which only showed signs of coalescing if the feed was rich – over c 60% Sn – in a very sticky, dirty, matrix. While the loss of tin in the assays appear to be approximately the same, in fact they are higher with the low grades of feed, as the content of the tin-iron compound 'hardhead' is greater as demonstrated by the response of the metal to the magnet. There is a notable interrelationship between the iron and silica containing minerals in the feed when slagged, the iron having a great influence on the proportion of tin that can combine with silica and so be lost in the slags. An early discussion on this is given by Mitchell. [18] The results found are born out in the detailed description of early tin assay methods quoted by Beringer. [19] Assays of ores of c 40% metal were expected to show considerable losses: '. . . It should be brought nearer 70% . . .' to give reasonable work. This may be taken to reproduce in miniature what will occur in the blowing furnace.

The complementary value and limitations of the two methods of assay showed up when samples of the South Crofty/CSM concentrate were examined. The vanning technique, which was normally only used for ore and intermediate concentrates, showed that the sample held something approaching 70% metal, but an insufficiently close cut could be made to put great confidence on this figure. On the other hand the fire assay (the one which was normally used for concentrates) gave a result only 9% different from the value determined at Camborne School of mines using XRF assay; which is not noted for accuracy on concentrates. Bearing in mind the discrepancies that can occur even with the latest assay methods, it is evident that the old assays were indeed practical.

The results indicated that while the CSM upgraded South Crofty material was not entirely the same as the coastal traverse black tin, it should respond in a similar manner in a blowing furnace. Encouraged by this, the design and construction of two types of melting furnace went ahead.

References

1 Georgius Agricola: 'De Re Metallica', Hoover translation, Dover, 1950.
– Encyclopedia Britannica, 14th edn, 'Cassiterides'.
– Rees, Cyclopedia, London 1819, Vol VI: 'Cassiterides'. Vol XXXV,' Tin'.

2 R H Worth: 'Worth's Dartmoor', David and Charles, 1967.

3 D B Barton: 'A History of Tin Mining & Smelting in Cornwall', Barton, 1967.

4 William Pryce: 'Mineralogia Cornubiensis', Pryce, 1778,

5 An Inquisitive Person: 'An Account Touching the Mines of Cornwall and Devon . . .', Phil Trans, vi, 1671.

6 B Earl: Journal Trevithick Society, 1983 (10), 10. 11.

7 R J Law: in Litt, Trevithick Society.

8 'The Hatchett Diary', edited by Arthur Raistrick, Barton, 1967.

9 A & C R Aiken: 'A Dictionary of Chemistry and Mineralogy, . . .' Arch and Phillips, 1807.

10 Ure: 'Dictionary', Longman, 1875 edn, pp 1005, 1006.

11 P J Thibault: 'Metallurgy of Tin', Australian Mining Standard, 1908.

12 Dr Cotton: 'An Account Concerning the Tin-Mines in Devonshire', mss in the library of the Royal Society, 1664.n.

13 Harlean mss No 6380, British Museum.

14 W Gowland: Archaeologia, 1899, **56**, 269-322.

15 Justin Brooke: Communication.

16 H M Friede and R H Steel: 'Tin Mining and Smelting in the Transvaal during the Iron Age', Journal S African Mining and Metallurgy, July 1976, p 541 et seq.

17 J H McLain: 'Pyrotechnics', Franklin Institute Press, 1980.

18 J Mitchell: 'Manual of Practical Assaying', Hippolyte Bailliere, 2nd edn, 1854 p 302, 303.

19 C & J J Beringer: 'A Text Book of Assaying', Griffin, 2nd edn, 1889: section on Tin.

Biography

Bryan Earl. Educated privately. Worked for six years coalmining at Cresswell, Whitwick and Chislet collieries. Camborne School of Mines to train as a mining engineer. Ten years with Imperial Chemical Industries working on the development and application of explosives. Cranfield Institute of Technology (MSc). Consultant mining engineer, particularly interested in industrial archaeology.

Some early tin ingots, ores and slags from Western Europe

Neil Beagrie

Abstract

The article concentrates on tin ingots from South-West England and their context and dating evidence. Attention is drawn to two tin ingots with handles from Cornwall and possible Roman parallels from the Mediterranean. Other tin ingots from England of Roman or Early Medieval date are also discussed. Finally discussion is focussed on Sardinia, where small cassiterite deposits are known and some Prehistoric tin finds noted, and on the Castro de Carvalhelhos in Northern Portugal, where large quantities of Roman slag and ore have been retrieved. The author emphasises the problem of recognising the frequently corroded and fragmentary remains of metallic tin and the necessity of improving the retrieval of such remains and tin ores and waste products.

Introduction

Tin ingots of any period from the Prehistoric to the Medieval are relatively rare, virtually all known or alleged examples being from maritime wrecks or from the mainland of South-West England. The concentration of finds in the South-West of England is particularly notable with some 68 ingots or pieces of 'Jew's House Tin' being recorded. The majority of these have not survived and only the barest of details are known.

Handled Tin Ingots

Of particular interest amongst these, are two ingots weighing about 10.5 kg each, found at a depth of 2.5 m in a streamwork in the Pentewan Valley (SX 0147 to 0151), near St Austell in Cornwall. The ingots were found in the early eighteenth century and are now lost and only known from a brief description and a drawing of one of the ingots by William Borlase.[1] This drawing shows a highly distinctive ingot consisting of a semi-circular handle and a main body with a flat upper face but with its underside divided by a deep median groove into a 'double ingot' shape (Figure 1,E). Borlase noted that the ingots were much corroded when found with a kind of rust or scurf-like incrustation enclosing the tin, so the rather clean appearance of his drawing may be an attempt to restore the ingots to something like their original appearance.

These ingots are of great interest in that they closely resemble and may belong to a rare and well-dated group of Roman handled tin ingots. The best known examples of this group are the 18 tin ingots found on the Port Vendres II wreck on the south coast of France close to the Spanish border, but others are known from a wreck off Cape Bellavista, Sardinia and a possible example may have been found on a wreck at Lavezzi in Corsica.

The Port Vendres ingots have been published in two groups: the first 14 in Gallia in 1975[2], followed by another four in Archaeonautica in 1977[3]. The ingots ranged from c.3 to 10.49 kg in weight and were classified into three types (Figure 1, A, B, C). Type One consists of a handle with an ingot body in one piece, often with decoration moulded in relief on its underside; Type Two of a handle and an ingot body normally without decoration but whose underside is divided by a central depression into two halves; Type Three of a handle and an ingot body of two separate, parallel rectangular blocks linked by 'runs' of metal.

The Port Vendres ingots are particularly important for their numerous inscriptions and the close dating possible for the wreck. One of the inscriptions cannot pre-date 41/2 AD and the rest of the cargo belongs at most to the ensuing decade.

There is an interesting reference to a Roman relief from Pompeii, which shows a metalworker's shop with what may be tin ingots of this handled type hanging on the wall.[4] When the Port Vendres ingots were published this was the only possible parallel known for this distinctive ingot type.

Since then attention has been drawn to another group of handled tin ingots found on a wreck off Cape Bellavista, Sardinia. Other material found with these ingots included a number of iron blooms of the 'stumpfbarren' type and seven lead ingots, two of which had the inscriptions E D CERDO and DAGUTIUS G F on their convex surfaces and these are suggested to date to between 30 BC and 10 AD. The tin ingots weighed up to approx 10 kg and their identification as tin has been confirmed by Tylecote.[5] From drawings there would appear to be 6 tin ingots: four belonging to Port Vendres Type One, another of Port Vendres Type Three and finally a small, oval, plano-convex ingot[6]. One of the Type One ingots has impressions and partial impressions of MARO, a common Italian name of both the Republic and Empire, and a cross moulded in relief on its underside (Figure 1, F).

It is possible that a further example of this handled ingot type may be recorded from the Lavezzi II wreck off Corsica. The cargo allows this wreck to be dated to the second half of the first century AD. Amongst the finds illustrated is an item described as a 'weight or sound ? of lead' (Figure 1,D)[7]. This bears such a striking resemblance to a handled tin ingot that it seems possible that a misidentification may have occurred and the metal is in fact tin, especially as tin and lead are frequently confused by archaeologists relying on the external appearance of the metal for identification.[8]

All surviving handled tin ingots, apart from the Pentewan examples, are likely to date to within the first century AD. No examples are known from any other period. It seems possible therefore, that the Pentewan ingots could date to the late first century AD, given the parallels for their shape amongst the Type Two ingots from Port Vendres. In addition there is some evidence for tin production in the late first century AD at St Mawgan in Pydar (SW8735 6562) in Mid-Cornwall[9], and some limited form of exploitation at this time in this area has also been assumed from Roman finds in streamworks around the fort at Nanstallon (SX 034670). The finding of two Early Roman ingots in a streamwork in Mid-Cornwall is therefore at least feasible, and possibly the Pentewan ingots could represent Cornish

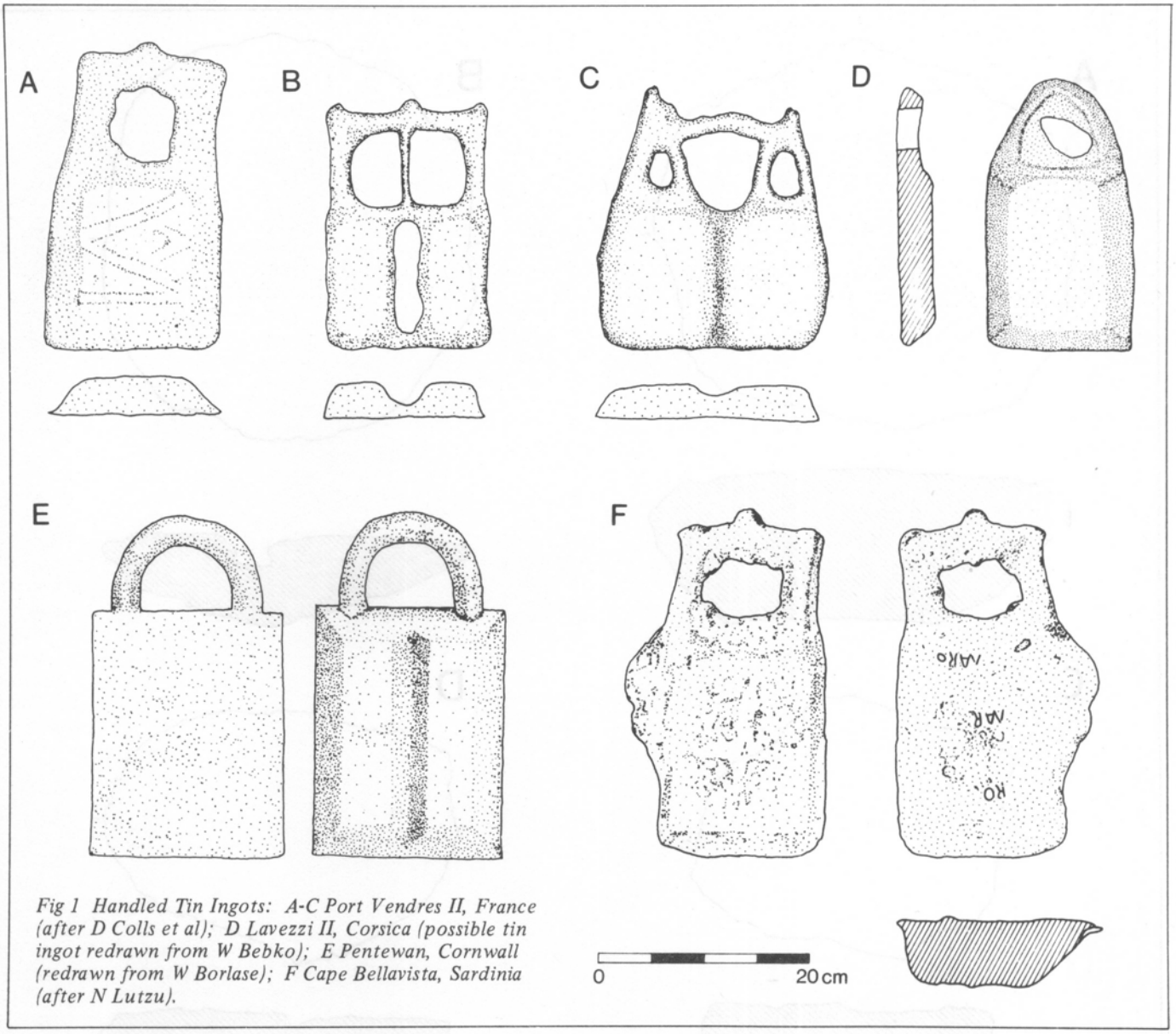

Fig 1 Handled Tin Ingots: A-C Port Vendres II, France (after D Colls et al); D Lavezzi II, Corsica (possible tin ingot redrawn from W Bebko); E Pentewan, Cornwall (redrawn from W Borlase); F Cape Bellavista, Sardinia (after N Lutzu).

products imitating a Roman form first produced in Iberia.

Other Roman Ingots

There is no evidence as yet from South-West England for tin production in the centuries immediately after the first until the late third or fourth centuries AD. For the Late Roman period we have three ingots or possible ingots, which are datable either on the basis of stamps or archaeological context.

The best known of these is the ingot from Carnanton (SW 886640), in North Cornwall. This was found in about 1819, 0.76 m under the surface and close to the remains of a 'Jew's House'[10] The ingot is boat shaped in plan and has a semi-circular cross-section at one end tapering to a point at the other and weighs 17.5 kg.

In about 1890, Haverfield discovered that the ingot bore the impression of several stamps and he published several descriptions fully discussing their significance.[11] These stamps are now very difficult to read, partly because of the blistering of the ingot surface but also because the tin had been stamped when it was quite cold. As a result of this the dies tilted and only part of any stamp was clearly rendered and many unsuccessful attempts at impressing them can be seen. Two or possibly three different impressions are present.

The first of these consists of a rectangular border with a helmeted head facing right. In front of this head is an area of corrosion suggested by Haverfield to obscure another emblem, perhaps a small shield. The helmeted head bears a resemblance to th e heads of Emperors on some Late Roman coins, but unfortunately is not easily derived directly from a coin proto-type[12]. In fact the only evidence for the dating of this stamp or the ingot as a whole, is the general resemblance of the helmet to types of the late third or fourth centuries AD, for example the Guisborough or the Chalon helmets[13].

The second stamp consists of an inscription of four letters. It is important to recognise that Haverfield's reading of this inscription was always uncertain and that his first publication suggested that the inscription was IENN or IFNN and it

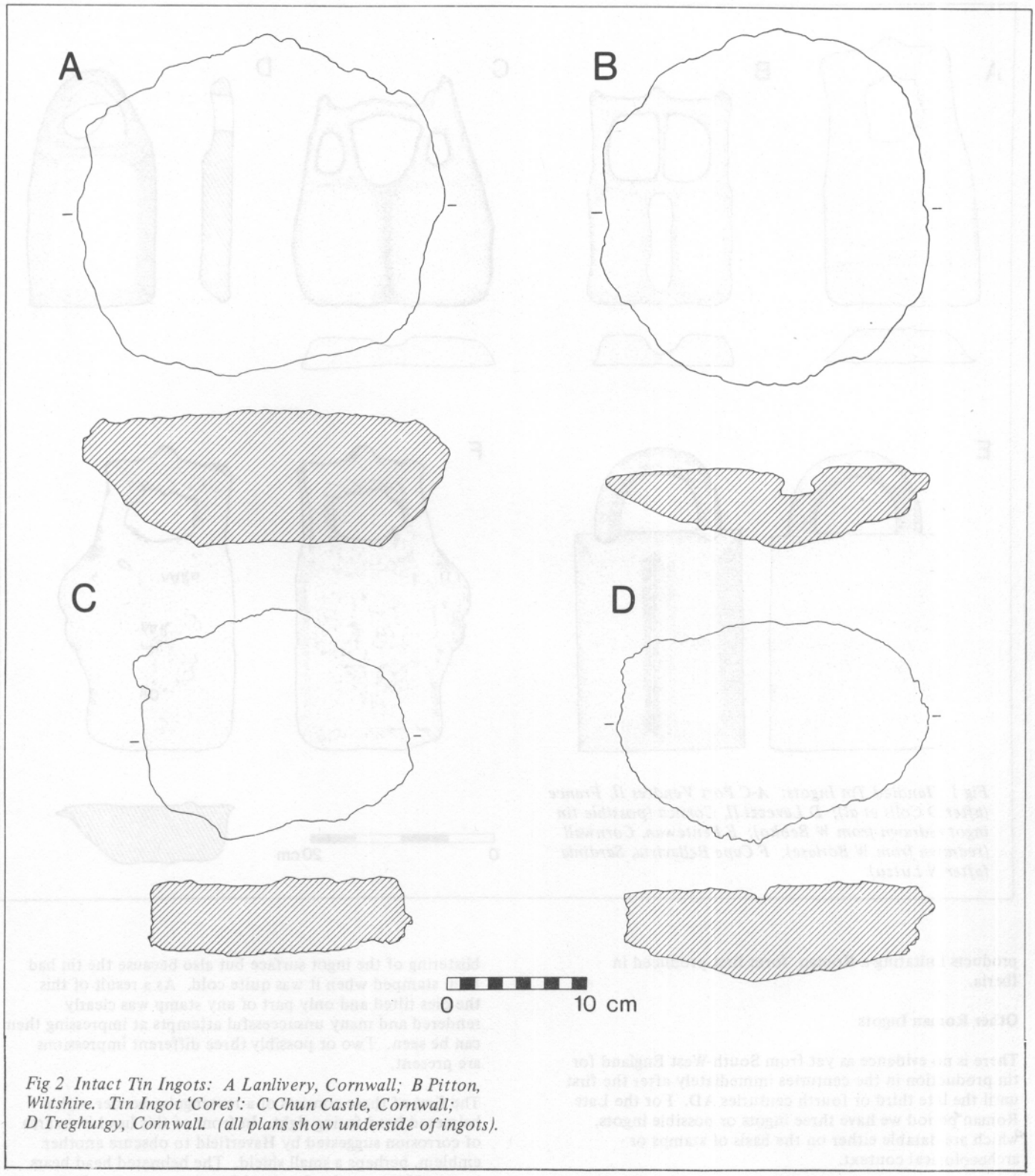

Fig 2 Intact Tin Ingots: A Lanlivery, Cornwall; B Pitton, Wiltshire. Tin Ingot 'Cores': C Chun Castle, Cornwall; D Treghurgy, Cornwall. (all plans show underside of ingots).

was only in later publications that the reading DDNN arose as it corresponded to a known formula for Dominorum Nostrorum on other metal ingots. Everyone who has examined the ingot since Haverfield has suggested that the reading DDNN cannot be present and I fully agree with this.[14] The reading IENN seems almost certain and it is therefore unfortunate that the reading DDNN has been perpetuated rather uncritically. Regrettably it does not appear possible at present to put forward an acceptable explanation for the abbreviation, but there are also many obscure formulae on metal ingots elsewhere, which cannot easily be explained.

The possibility that a third stamp exists on this ingot has been raised by Roger Penhallurick of Truro Museum. This stamp is heavily affected by corrosion but the profile of a head can be discerned. This in the past has always been assumed to be another incompletely rendered stamp of the helmeted head mentioned previously, but when examined very closely the profile seems distinct from

this. The heavy blistering prevents any certainty but it seems likely that two different heads are portrayed on this ingot.

The second Late Roman ingot from the South-West was found on Par Beach, St Martin's Isles of Scilly (SV 932153). It was examined by Tylecote in 1969 and he described it as a thin and much corroded plano-convex ingot. The corrosion product was dense but the metal core was highly ductile and therefore pure.[15] The ingot was found by O'Neil in an early excavation on a hut on the shoreline and it was dated by him to c 200-400 AD. Unfortunately no drawings or details of its weight are known (Refs 15a and b). Some tin corrosion product now in Truro Museum from the excavation at Par Beach may well be part of a corroded ingot rim, possibly from the same ingot.

A more recent find is the tin ingot from a small univallate enclosure or 'Round' at Trethurgy (SX 035556), near St Austell in Cornwall. The site was occupied from the third century into the Post-Roman period and was completely excavated in the early 1970s in advance of china clay waste dumping. The tin ingot was found inside structure U on the site and was associated with Late Romano-Cornish pottery.[16]

The ingot would originally have been roughly oval in plan, about 30 by 21 cm across and plano-convex in cross-section with a maximum depth of 7.5cm. It is now highly corroded: the thin outer rim of the ingot has broken up to leave a main fragmen t or core weighing about 7 kg (Figure 2,D). The weight of all the surviving fragments is 12.5 kg which might suggest that the original ingot weighed 10 kg or more. A fragment was analysed by XRF at the Ancient Monuments Laboratory but the only elements detected apart from tin were iron and manganese, both suggested to be almost certainly present in the adhering soil and the results were consistent with the original tin metal having been very pure[17].

Unfortunately despite a secure context, it is still very difficilt to date the Trethurgy ingot closely. The association is with Late Romano-Cornish wares, which are not well dated and it is only possible to suggest in advance of further work, a date between the late third and early fifth centuries AD[18].

Possible Roman Ingots

Another well stratified tin ingot was recovered in early excavations at Chun Castle (SW 40503395), Penwith, Cornwall[19]. Although close dating is not possible, the ingot was sealed beneath a floor level and other evidence suggests an Iron Age to Post-Roman date for occupation of this site[20]. Again the ingot appears to be completely oxidised, the outer rim having broken up to leave a core weighing approx 5 kg (Figure 2, C).

It is possible that some other large, plano-convex ingots, which are otherwise undated may, and it is only may, date to the Roman period. Of these I think the recent find of a tin ingot in a copse near pitton in Wiltshire (SU215302) is particularly notable as this is the sole example of a tin ingot found in England outside Devon or Cornwall. It was found by a metal detector user, who discarded it as a rusty milk churn lid. Although this seems comic, it is perhaps worth stressing that hardly any corroded tin has been correctly identified as such at first sight, so this is not an isolated example of a tin ingot being overlooked or misidentified.

The ingot is unusual in being almost circular in plan, measuring about 23 by 25 cm across with a plano-convex cross-section not more than 6 cm deep (Figure 2, B). It weighs 10.1 kg and has a heavily mineralised crust but the metal core is substantial and has been shown by analysis to be pure tin[21].

Another interesting and very large plano-convex ingot was found in Lanlivery (SX 0859) in Cornwall[22]. This is now in the Geological Museum in London[23]. It is slightly oval in shape, 26 by 23.5 cm across, a maximum of 10 cm thick and weighs c 21 kg. It has a pronounced bun or flan shaped cross-section very similar to many Roman copper ingots (Figure 2,A).

The ingots from Carnanton, Par Beach and Trethurgy are the only reliable evidence for a revival in Cornish tin production in the Late Roman period. The reasons for and the scale of any such revival have been linked to developments in the Romano-British pewter industry or Iberian tin production. The inter-relationships of either of these, particularly Iberian production with Cornish tin is rather speculative at present and there is a serious need for detailed archaeological fieldwork and research in these areas.

Early Medieval Ingots

Developments in the Sub-Roman and Early Medieval periods are equally obscure. Wooden shovels from tin-works at Boscarne (SX 0367) near Bodmin in Cornwall and Abbaretz in Brittany have carbon 14 dates which may suggest exploitation at this period[24]. Apart from these the only possible archaeological evidence of this period are four ingots from Praa Sands (SW 580279) in Cornwall. These have an associated carbon 14 date, which suggests they may be Early Medieval in date.

The Praa Sands ingots form a varied and interesting group. They range from 0.758 to 3.856 kg in weight. The largest example is circular with a diameter of 18 cm and a plano-convex cross section. It has markings in relief like a St Andrew's cross on its underside (Figure 3,A). The other ingots are also unusual in having a lop-sided, plano-convex cross-section, which gives them a distinct appearance (Figure 3, B, C, D).

A detailed metallurgical examination of one of these ingots showed that the metal was c 99.5% pure and that most of the remainder was iron present in discrete, duplex crystalline inclusions of inter-metallic tin-iron compounds. The thin, brownish crust covering most of the ingot surface was found to be mainly SnO_2 with a little SnO and this is very similar to results on other tin corrosion products.[25]

The ingots were found after exceptional storms along the South-West coasts had scoured away sands at Praa to reveal an underlying level of highly organic silt associated with a submerged forest floor containing many substantial timber fragments. Possibly this was the remains of a watercourse overcome by moving sands. One ingot was noticed protruding from this deposit by children and a search by them revealed the other three ingots.

The precise site of the find was subsequently excavated in the hope of finding further ingots but without success. Material from the silt in which the ingots were embedded produced a carbon 14 date of 684 + 70 AD[26]

Sardinian Cassiterite Deposits

Moving on from South-West England I would like to mention some of the work on Sardinia recently published in this

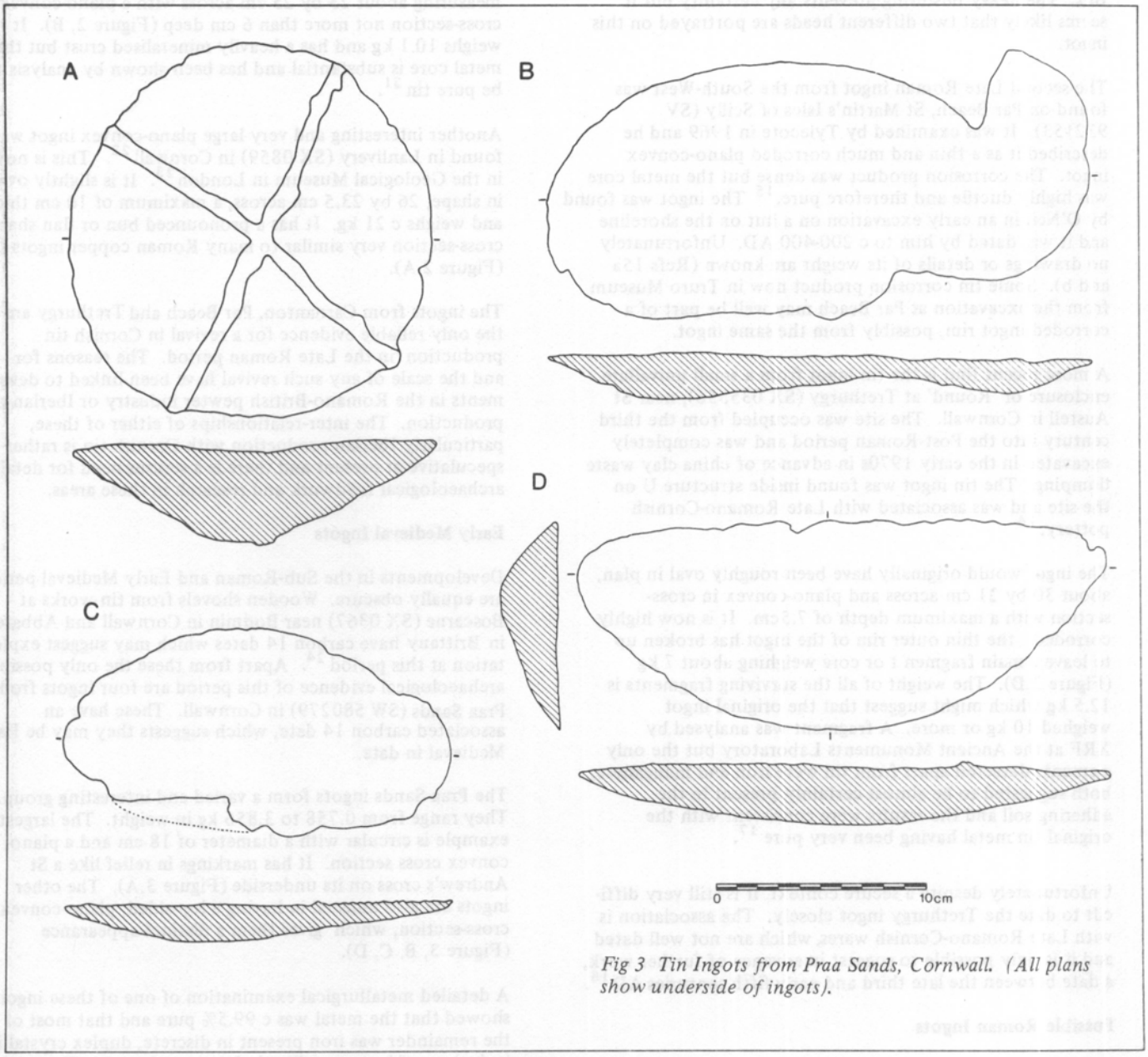

Fig 3 Tin Ingots from Praa Sands, Cornwall. (All plans show underside of ingots).

Journal [27]. This makes interesting comments on the presence of cassiterite on the island. The geological maps show it as occurring in small amounts on the contact between pegmatites and granite in conjunction with lead and zinc in the Leni valley in the Iglesiente.

Another deposit is a vein at Punta di Santa Vittoria on Mount Linas, which is being tested for its economic viability. A sample of this vein consisting of a mass of black cassiterite crystals in quartz showed the cassiterite to be extremely pure containing between 77.5 and 83.8% tin[28]. This analysis of vein ore compares very closely to the purity of the pebble of stream tin from the Iron Age and Romano-British settlement at St Mawgan in Pydar (SW 87356562) in Cornwall, which was found to be between 78.7 and 79.7% tin and which is the only specimen of cassiterite from an archaeological context in Western Europe for which quantitative analysis has been published. [29]

There is no evidence from Sardinia for the working of these very small cassiterite deposits in Prehistory, so perhaps we should regard them as of no more than of geological interest. Potentially however they could be of interest to archaeologists as minor sources of tin within the Mediterranean.

Sardinian Tin Finds

A number of tin finds are also known from archaeological contexts in Sardinia. Apart from the tin ingots from Cap Bellavista on the east coast mentioned earlier, some finds came from early excavations at Forraxi Nioi, a Nuraghic settlement. An account of the excavations by Fiorelli describes a crucible filled with tin [30] and Cambi also refers to a crucible containing grains of incompletely reduced cassiterite and 10 kg of cassiterite in the form of pieces 1 to 3 cm in size from this site.[31]

Recent re-examination of these finds by Tylecote concluded that the 10 kg of cassiterite was undoubtedly the remains of an oxidised and broken tin ingot and is corroded man-made material and not natural cassiterite. Similarly the crucible would appear to be a small furnace 50 cm in

diameter at the top and some 70 cm deep, possibly intended for bronze production by the melting of metallic tin and copper. [32]

Other early tin finds from Sardinia may include 'cassiterite' and 'fused tin' in the votive hoard at Abini (Teti)and an ingot of 'pure tin' from Lei (Sa Maddalena) weighing 0.7 kg [33]. Although the identifications may require confirmation, these finds along with the tin ingot from Forraxi Nioi would appear to form a very small but interesting concentration of early tin finds on Sardinia.

Castro de Carvalhelhos

Some early tin ingots have been alleged from elsewhere in Western Europe but in the absence of reliable identification or adequate publication these are difficult to discuss. Therefore I should like to finish by discussing the finds of cassiterite and tin slag from the Castro de Carvalhelhos in Northern Portugal, which has been under excavation since the 1950s. The site is perhaps already known from the report published on the tin slag [34]. This and the analysis of the Middle Bronze Age slag from Carloggas [35], near St Austell in Cornwall, are the only reports on ancient tin slags from Western Europe. What is perhaps less well known is the sheer quantity of evidence recovered from the site or the nature of the dating evidence.

The first important find occurred some 12 or 13 years before the opening of excavations, when four youths discovered a large pit containing cassiterite cut into the granite on the eastern slope of the site. In four days of washing and panning over 200 kg of cassiterite were recovered from this pit deposit. Later enquiries suggested that the cassiterite may have been deliberately hidden and was associated with remains of fibulae, coins, coarse pottery and much charcoal and quartz [36].

The excavations up to 1966 found very little stratigraphy in the hillfort and there were relatively few finds apart from large quantities of charcoal and tin slag. The majority of the slag was present as extremely finely crushed fragments and by 1966 over 1570 kg of this finely crushed slag had been recovered. In addition to this 'pieces' of slag weighing 0.3 to 0.4 kg each, some believed to be complete, were found but unfortunately no further details are given.

The dating of the site is based on coins and fibulae. The coins apart from some modern strays were all Roman and first or second century AD in date. The fibulae were also Roman dating to the first or second century or more generally between the first and fourth centuries AD. The excavator was in little doubt that the evidence of tin production was also Roman in date [37].

One interesting point to arise from this site is that the 200 kg of cassiterite was retrieved from the pit deposit by systematic washing rather than hand picking. I doubt whether the majority of cassiterite on archaeological sites can ever be found if one relies on chance hand picking for retrieval or that such hand picked specimens are particularly representative. Hopefully more reliable sampling will be adopted on tin production sites in the future.

Conclusions

In conclusion to what has necessarily been a selective discussion, I would like to stress that very little analysis or archaeological research has been carried out on early tin. This seems regrettable given the clear potential for obtaining more information from the archaeological record rather than the sparse details in the literary evidence. A major problem in achieving this has been a failure in the past to retrieve or recognise the often fragmentary or highly corroded remains of early tin ingots and artefacts, or its ores and waste products on production sites. Hopefully this is another problem, which will be corrected in years to come.

Acknowledgements

The author is grateful to many people for information and discussion of early tin finds. Particular thanks are due to Prof R F Tylecote and also to Roger Penhallurick, Leo Biek, Justine Bayley, John Casey, Richard Scrivener, Henrietta Quinnell, Les Douch, Malcolm Todd and Charles Thomas. I am also grateful to the County Museum, Truro and the Geological Museum, London for access to their collections and to Mike Rouillard and Sean Goddard for their assistance.

Notes and References

1 W Borlase, Natural History of Cornwall (Oxford 1758), 163 and plate XX figure XIX. My Figure 1,E is redrawn from Borlase but employs a different drawing style.

2 D Colls et al, 'Les Lingots d'etain de l'epave Port Vendres II', Gallia 1975, **33,** 61-94.

3 D Colls et al, 'L'Epave Port Vendres II et la commerce de la bétique a l'époque de Claude', Archaeonautica 1977, **1,** 11-18.

4 D Colls et al, loc cit (in note 3), 17-18 with photograph and drawing.

5 R F Tylecote et al, 'Copper and Bronze Metallurgy in Sardinia', Hist Metall 1983, **17** (2), 73-4.

6 Unpublished drawings by Natalina Lutzu, Ministero Per i Beni Culturali ed Ambientali Soprintendenza Archeologica, Sassari, Sardinia.

7 W Bebko, 'Les Epaves Antiques du Sud de la Corse', Cahiers Corsica 1971, 1-3, 4-5 and 29-34. The possible tin ingot is shown in plate 24 figure 157. My Figure 1,D is redrawn from this.

8 This possibility was first suggested by A J Parker in 'Spanish Exports of the Claudian Period: the significance of the Port Vendres II wreck reconsidered', Int J Naut Archaeol Underwater Explor 1981, **10** (3), 221-8. The Cape Bellavista ingots were also thought to be possibly of lead when first found (see R F Tylecote et al loc cit (in note 5), 74).

9 L M Threipland, 'An excavation at St Mawgan in Pydar, N Cornwall', Archaeol J, 1956, **113,** 33-81. This refers to 'tin slag' from several of the excavated features. Analyses of 2 samples were published: one a cassiterite pebble, the other a 'slag', The'slag' consisted of 79.71% tin and was suggested to be partially reduced ore. From the analysis it seems equally likely that it represented corroded tin metal. R F Tylecote in 'Early tin ingots and tinstone from Western Europe and the Mediterranean', in A D Franklin et al (Eds), The Search for Ancient Tin (Washington 1978), 49-52, refers to a specimen of a crusted plano-convex ingot from this site and gives an analysis. In 1983 the author was only able to locate a few small pieces of tin corrosion product labelled 'Lead ?/Tin ? slag St M '49 house W' amongst some 'slags' of unknown composition (Box

189 St Mawgan in Pydar Excavations, Truro Museum). Since then the remains of the ingot have been located and conserved at the Institute of Archaeology, London and returned to the Truro Museum.

10 An entry in a local newspaper 'The West Briton' for 27th July 1821 refers to the find. See also Thomas Hogg, Manual of Mineralogy (Truro 1825), 75. The newspaper account states that the ingot was found within a few yards of the head of the spring, which would suggest the grid reference given .

11 F Haverfield, 'Roman Inscriptions in Britain, 1890-91' Archaeol J 1894, 49, 177; Proc Soc Antiq London 1901, 2nd series 18, 117-8; Mélanges de Gaston Boissier (Paris 1903), 251.

12 I am grateful to John Casey for discussing possible parallels between this stamp and Late Roman coinage.

13 H R Robinson, The Armour of Imperial Rome (London 1975). For Guisborough see plates 391-3; for Chalon plates 394-6.

14 R B Warner, 'The Carnanton Tin Ingot', Cornish Archaeol 1967, 6, 29-31; G Boon, 'Apercu sur la Production des Métaux non Ferreux dans la Bretagne Romaine', Apulum 1971, 9, 473-4.

15 R F Tylecote, loc cit ref 9, p 50.

15a B H St J O'Neil, Ancient Monuments of the Isles of Scilly. London, HMSO, 1961, p 10.

15b The Scillonian Mag, 1949, Vol 24, 163-4.

16 H and T Miles, 'Excavations at Trethurgy, St Austell, Interim Report', Cornish Archaeol, 1973, **12**, 25-9.

17 Information from Justine Bayley, Ancient Monuments Laboratory.

18 I am grateful to Henrietta Quinnell for discussing the dating with me.

19 E T Leeds,'Excavations at Chun Castle in Penwith, Cornwall', Archaeologica 1926, 76, 205-240.

20 C Thomas, 'Evidence for post-Roman Occupation of Chun Castle', Antiq J, 1956, **36**, 75-8. The 'tin smelting furnace' would appear to be post-Roman but the date of the ingot (a separate find) is still uncertain.

21 Information on the analysis kindly provided by Prof Tylecote.

22 Information at the Geological Museum, London. See also W J Henwood, 'On the Detrital Tin Ore of Cornwall', J Roy Inst Cornwall 1871-3, **4**, 252.

23 Geological Museum Inventory, No MI 12608.

24 For Abbaretz see J R Jannot, 'La Production D'Etain de la Peninsule Armoricaine a L'Epoque Antique', Actes du 97e Congres National des Societies Savantes 1972, 107. The carbon 14 date is 650 + 100 AD. Boscarne is unpublished: information at Truro Museum. The date is 710-910 AD, presumably 810 + 100 AD. In assessing both dates allowance must be made for possible use of heartwood for the tools as well as for the standard deviation, etc.

25 Information from Leo Biek.

26 Ha 962 November 1974, 1290 + 70 b.p.

27 R F Tylecote et al, loc cit (in note 5), 63-8.

28 R F Tylecote et al, loc cit (in note 5), 67, 69 table 7.

29 L M Threipland, loc cit (in note 9). It is a pity that no early ore concentrates have been recovered, as the analysis of these would be of greater interest. Most individual crystals or stream pebbles of tin are likely to be very pure.

30 S Fiorelli, NSc, 1882 (July 15), 308-311.

31 L Cambi, 'Problemi della metallurgia', Studi Etruschi 1959, 415-432.

32 R F Tylecote et al, loc cit (in note 5).

33 M Guido, Sardinia (London 1963), 165-7.

34 H Maia e Costa, 'Nota sobre as escorias encontradas no Castro de CArvalhelhos', Trab de Antropol e Etnol, 1965-6, **20** (1-2), 173-180.

35 H Miles, 'Barrows on the St Austell Granite, Cornwall' Cornish Archaeol, 1975, 14, 35-8.

36 J R dos Santos Junior, 'O Castro de Carvalhelhos', Trab de Antropol e Etnol, 1957, **16**, 25-62.

37 J R dos Santos Junior, 'Duas campanhas de escavacoes no Castro de Carvalhelhos (1965-6)', Trab de Antropol e Etnol, 1965-6, **20** (1-2), 181-190.

Biography

Neil Beagrie read archaeology as an undergraduate at Durham University. Since 1982 he has been researching a M Phil on Iron Age/Roman tin production and exchange from South-West England at Exeter University. He organised the conference on 'Approaches to Ancient and Medieval Tin' held at Exeter in March 1984 and the article in this volume is based on a paper given at that conference.

The apparent tinning of bronze axes and other artifacts

RF Tylecote

In my first book[1] I mentioned the problem of 'tinned' bronzes, ie that there are three possible methods that could give rise to tin plating or tin enrichment on the surface of bronzes. These are: (1) corrosion leading to preferential dissolution of the copper and surface enrichment by the residual tin; (2) inverse segregation or 'tin-sweat'; and (3) dip tinning or stick tinning of the bronze object.

Judging by the correspondence in the columns of 'Antiquity' this problem is still causing a lot of interest.

In this paper I wish to outline the problem and report the results of some experimental work on the subject and point the way to other experiments that need doing.

1. **The Corrosion Possibility**

I take this first because it is a post-burial problem and not a feature of the original artifact. The finding of a piece of severely corroded tin bronze dagger dated to about 1500BC at Caerloggas, Cornwall, has shown us how a tin bronze can corrode to completion[2]. Here, an arsenical tin bronze has corroded in such a way that the density has been changed from 8.8 to 2.36 and the composition (oxides) to include Sn 50-80%, Cu~5% and As 10-20%. There was of course some porosity. Clearly the expected dissolution of the copper has taken place but the stability of the tin and arsenic oxides has preserved them. No metallic tin was detected.

We know that the corrosion resistance of pure tin in soils is poor. This can be seen by the examination of the Cornish plano-convex ingots which in most cases are covered by a thick crust of SnO and SnO_2. Whether or not the poor corrosion resistance of tin is due to the beta - alpha transition below 13°C or some more normal electrochemical corrosion process is not important here. But pure tin is theoretically anodic to copper and low tin-copper alloys, so that once the tin coating is perforated one would expect rapid undermining of the tin in contact with the copper by the normal electrolytic process. On the other hand, if the surface consisted of the high tin-copper alloy layers, they would resist this process better and might even be cathodic to the parent metal. They would also be a bright tin colour and in this respect would not be inferior to pure tin itself. We would therefore expect an alloy layer to more adherently survive while a pure tin coating would be detached and converted to oxide.

Perhaps the first case of high tin surface compositions on bronzes was that reported by Smith and Macadam for axes in the Edenkillie hoard in 1872[3], where the following analyses were given:-

	1	2
Tin	24.36	32.78
Copper	15.49	18.14
Carbonate and hydrate of copper	60.15	49.08

If one assumes that the original core metal contained 10-15% Sn, this is not a very considerable degree of enrichment and it is possible that what has been analysed is no more than a typical patina in which the more insoluble tin has remained and the more soluble copper has been oxidised and leached out. One wonders whether any of the tin was in the oxidised state. But the fact that this degree of tin enrichment attracted attention suggests that some at least is, or was, present as a metallic tin-copper surface layer.

There are some very odd cases where, for example, tin-rich eutectoid is left in the surface corrosion product almost unattacked (Fig 1). This shows the surface corrosion layer of a bronze billet from Croft Ambrey[4].

The bottom shows a heavily corroded homogenised bronze which has been corroded along the equiaxed grain boundaries of the solid solution. The islands of eutectoid remain in the patina almost unattacked and would give a high tin value if analysed, not unlike Smith and Macadam's results. What seems to have happened is that there was surface enrichment in the tin during casting and the surface had a hyper-eutectoid composition, ie over 13.9% Sn, so that when homogenised to get rid of the cast cored structure, the excess tin in the surface was left in the eutectoid condition while all the eutectoid in the matrix was dissolved, as its composition was less than the limit of solid solubility for tin in copper. (The tin content of the matrix was in the range 5.7 - 6.2%).

Fig 1 shows that under the particular corrosion conditions, the eutectoid was cathodic to the solid solution. This is not unusual in corroding bronzes.

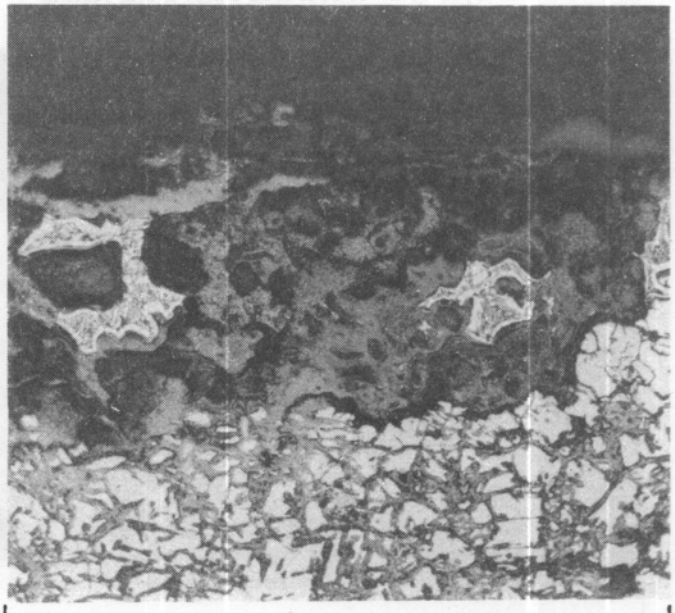

Fig 1 Section through the surface of a billet from Croft Ambrey showing the residual delta phase in the corrosion layer. X170.

2. Inverse Segregation

Inverse segregation occurs during the solidification of an alloy when, in the case of a copper base alloy, the primary dendrites are richer in copper and the residual liquid is richer in solute. At some stage this enriched liquid is forced to the surface, presumably through still-open channels and fills the space between the mould and the solidified metal surface. This space has been created either by shrinkage of the solid-liquid metal or by the thermal expansion of the mould. Enrichment of the segregating metal can be considerable, for example in the case of a modern leaded beta brass with 60% Cu, the exudation composition was 91% Zn, 4%Pb and 5% Cu. But a lot depends on the rate of cooling – fast cooling tends to favour segregation as do high thermal contraction coefficients. Bronze behaves in a similar manner. The very few alloys known to expand on solidification do not show inverse segregation.

This subject is still being discussed in the metallurgical press. An early review was published by N B Vaughan[5] in 1937.

A case of inverse segregation of a bronze is shown in Fig 2. This is a 10% tin-bronze which was cast into a warm cast iron hemispherical mould and 'tin-sweat' was fairly common on the surfaces in contact with the cast iron. The hardness of the bronze was about 80 HV. It had the usual alpha - (alpha + delta) eutectoid structure. The tin sweat had a hardness of 140 HV and is clearly not pure tin which has a hardness of 5.0 HV. As expected the tin-rich material did not etch in ferric chloride, confirming the cathodic nature of the phase. The hardness suggests a mixture of the delta and epsilon phases with a composition of 35-40% Sn. But it might well be the alpha + delta eutectoid with a lower tin content and an electron probe analysis is needed.

Many of the Scottish EBA axes (Fig 3) appear to be tinned, and McKerrell[6] has attempted to find the reason for this (Table 1). A section through DA 38 from Balnoon (Fig 4) showed a thin layer of silver-coloured outer metal resting upon a thin corrosion layer (Fig 5) like that of the Barton Stacey axe (see below). In some places the silvery layer was found to be in contact with the underlying bronze. This is in fact very like a gilded layer on a corroded bronze. Similar results on other specimens are also given in Table 1.

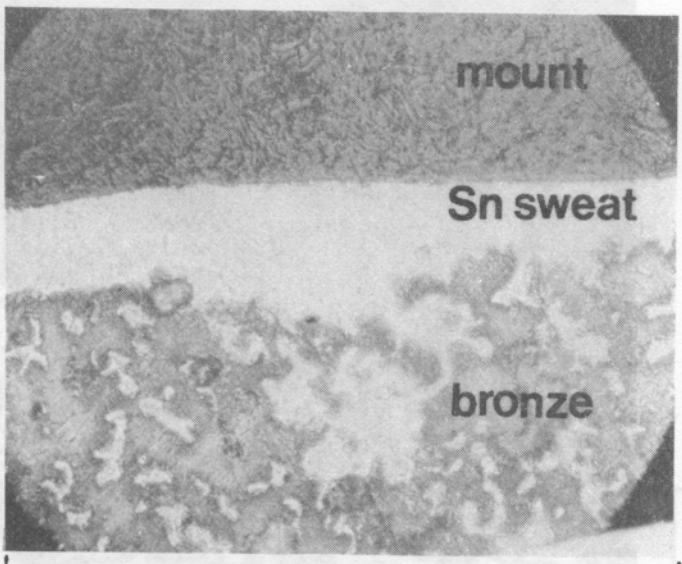

Fig 2 High tin layer produced by inverse segregation on a 10% tin bronze. X400.

After experiments which resulted in the successful surface enrichment of arsenic by inverse segregation[7], McKerrell tended to favour inverse segregation as the prevailing mechanism in the surface enrichment of tin in bronzes. But of course, as C S Smith[8] has shown, in the case of the Horoztepe bull it is possible to surface enrich copper with arsenic by a cementation process in which the volatile arsenic is absorbed by the copper surface when it is heated under reducing conditions in an arsenic compound. Therefore, although inverse segregation gives some silvery surfaces to arsenical coppers, it is not even in this case the only mechanism for doing so.

Another contribution on this subject drew attention to an unfinished dagger blank or ingot which had an arsenic-rich as well as a tin-rich surface (Table 2). This is an example of either corrosion enrichment or inverse segregation[9].

Out of 14 Scottish tinned EBA axes, 12 were found in association with other material and it is suggested that this indicates a deliberate selection of coated axes for deposition in hoards. This archaeological point was taken up in a further contribution on the subject emphasizing the need for metallographic examination. It is suggested that tinning represents an early stage of decoration which was later supplanted by the use of punched motifs[11].

3. Dip Tinning

The finding of tin smelting slag in the 1500 BC site at Caerloggas shows that metallic tin was used at this time and bronzes did not need to be made by the cementation process. The tinning of axes could therefore be carried out either by dip tinning where the artifact is inserted into a crucible full of molten tin (mp 232°C) or by 'wiping' of the hot bronze axe with a stick of tin, or with tin pellets.

Today tinning is usually done by dipping or by melting with the aid of a soldering iron. This has to be done with the aid of a flux or in a reducing atmosphere. Due to the solubility of tin in copper and **vice versa**, tinning of copper is a good deal easier than most other metals. Bronze is equally easy. In the bazaars of the Near East tinning is a common operation and is carried out on bronze or brass vessels by fluxing and heating the vessel to the melting point of tin and wiping tin around the inside of the vessel[12].

Tinning Experiments

In our experiments, a high tin bronze with a hardness of 185 HV was dip-tinned using a ZnCl paste flux. The tin-pot was held at a constant temperature and the specimen (at 20°C) was inserted into the molten tin for a controlled time. The conditions were as follows:

No.	Temperature °C	Time, sec
1	320	10
8	271	10
10	234	2
12	259	15

The thicknesses of the tinned layer varied from 4 to 50μm.

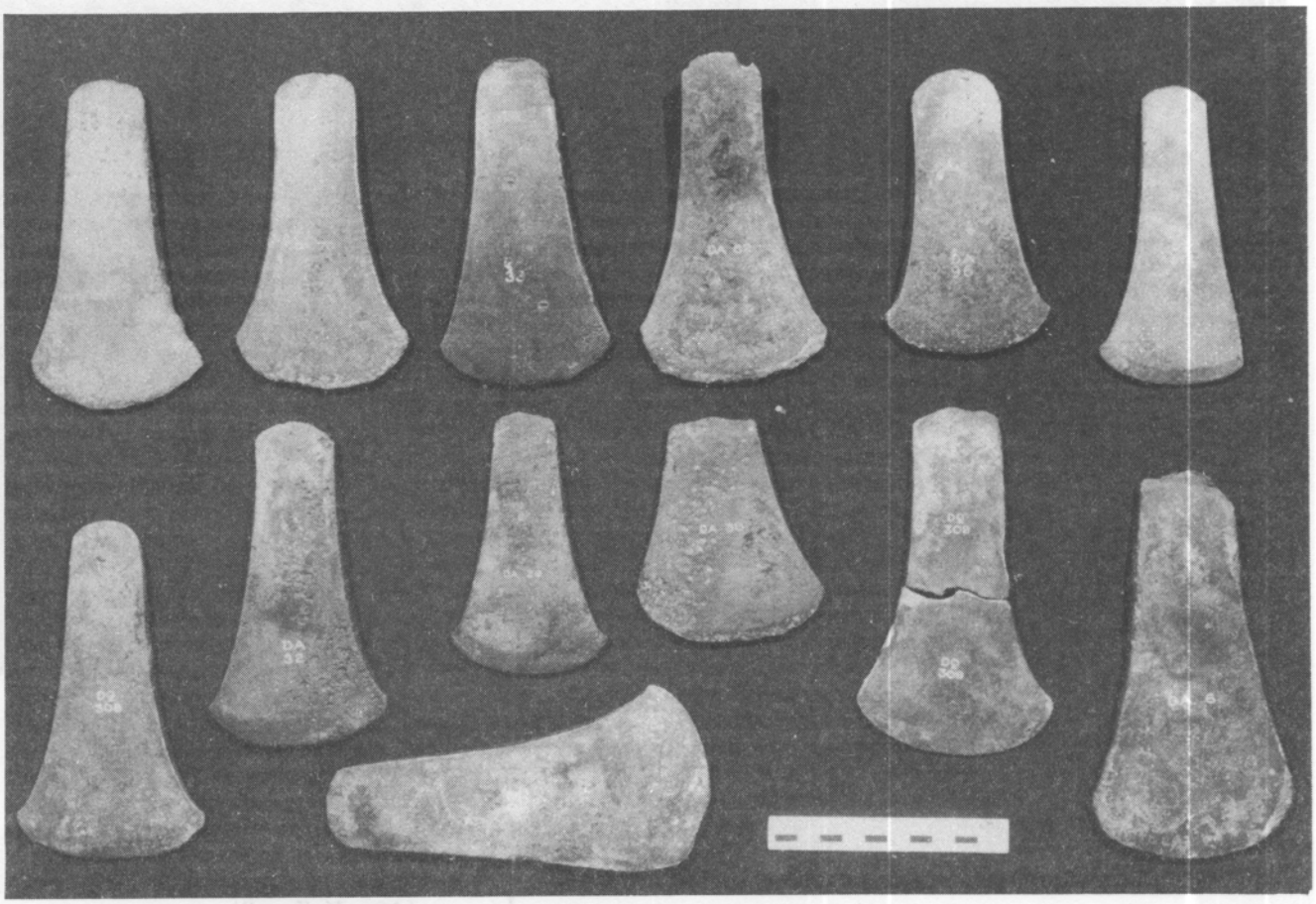

Fig 3 Tin-coated flat axes of Scottish origin. (Scale, cms). (Photo kindly provided by Dr H McKerrell).

Table 1

Tinned Axe Analyses

(after McKerrell)[6] (Atomic Absorption Analyses)

		% Sn	% As	% Sb	% Ag	% Cu
DQ 335	Surface	23	1.0	0.5	0.5	Rem.
Migdale	Internal	13	0.4	0.2	0.2	Rem.
DQ 308	Surface	25	2.1	1.0	0.6	Rem.
Rhynie	Internal	13	0.7	0.4	0.2	Rem.
DA 38	Surface	34	1.9	0.7	0.8	Rem.
Balnoon	Internal	9	0.9	0.3	0.3	Rem.
DA 32	Surface	32	1.5	1.0	0.5	Rem.
Edenkillie	Internal	12	0.7	0.5	0.3	Rem.
DA 6	Surface	45	2.4	0.5	0.9	Rem.
Ravelston	Internal	13	0.7	0.2	0.2	Rem.
DA 29 (?28)	Surface	26	0.7	0.3	0.4	Rem.
Camptown	Internal	13	0.3	0.2	0.3	Rem.
DA 62	Surface	41	2.4	1.1	1.2	Rem.
Abdie	Internal	9	0.6	0.3	0.3	Rem.

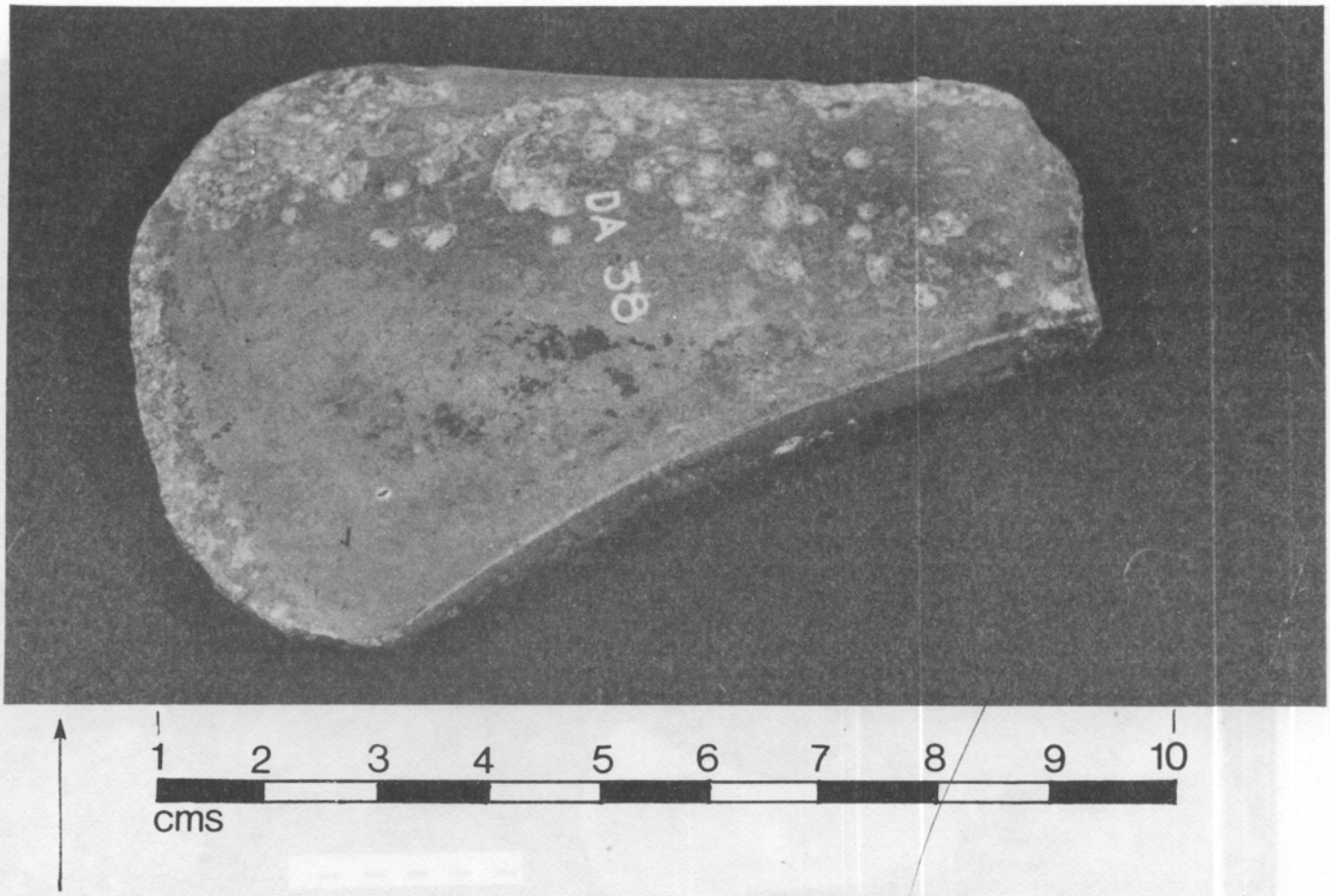

Fig 4 Flat axe from Fortrie of Balnoon, DA38. (After McKerrell).

Fig 5 Section through tin layer on above axe X84 (After McKerrell).

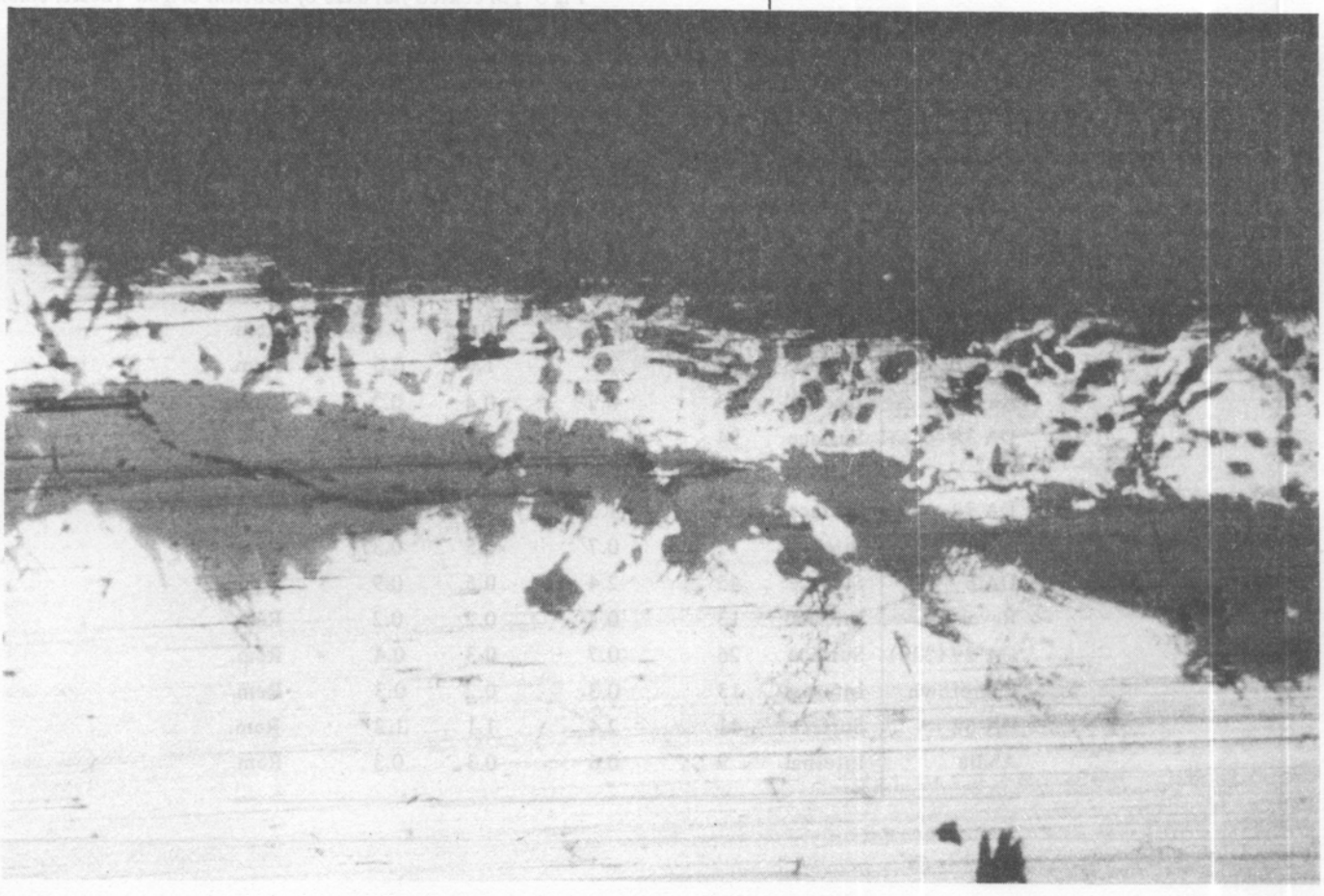

Table 2

Gairloch 'Ingot'. Composition %

(After Close-Brooks and Tate)[9] (Atomic Absorption).

	% Sn	% As	% Ag	% Pb	% Cu
Surface	67.5	3.8	1.3	0.7	Rem.
Internal	9.4	0.9	0.7	0.3	Rem.

No 1. The tin layer was very uneven and in the unetched state had dark cracks or grain boundaries in it. One area had a deep tongue-like penetration into the bronze. The micro-hardness of the tin layer was 12.6 HV (25g) showing that it has not dissolved much copper and is virtually impure tin. (Pure tin has a hardness of 5.0 HV). The tin layer was rapidly etched (Fig 6).

No 8. The tin layer was well-adherent on one surface but again was variable in thickness. Again the tin layer etched preferentially. The bronze was about one third eutectoid - the rest being the alpha solid solution.

No 10. The tin layer has grain boundary 'cracks' as in No 1. The hardness of the tin layer was 10.4 HV (100 g).

No 12 The coating was of variable quality with 'cracks'. The hardness of the tin was 9.1 HV (25g) and the bronze 154 HV1.

The etching was carried out in ferric chloride and in all cases the tin rapidly etched dark. This may have had something to do with the high tin content of the bronze which was in the range 16–18% Sn. There is no doubt that a true tinned surface is quite soft compared with the tin alloy surface referred to above. One would not expect diffusion of copper into tin at normal ambient temperatures ever to be responsible for the alloy content found in the Edenkillie axes, for example.

Alloying between Copper and Tin

Much is known about the reactions between copper and tin and lead-tin solders[13]. It is possible to form all the phases of the Cu-Sn system with the lead, when present, acting as a diluant as it does not dissolve in copper. The two intermetallic compounds are:

ϵ Cu_3Sn with 61% Cu by weight

η Cu_6Sn_5 with 40% Cu by weight

In the case of molten tin on solid copper,

0.001 mm (1μ m) of η forms after 1 sec at 232°C

0.006 mm (6μ m) of η forms after 30 sec at 285°C

0.001 mm (1μ m) of ϵ forms after 30 sec at 285°C

These layers are somewhat thinner with Pb-Sn solders. The delta phase does not form below 350°C.

But if the layers are held in contact and the temperature and/or time are increased, the interdiffusion of the Sn and the Cu will continue, finally terminating in a dilute bronze.

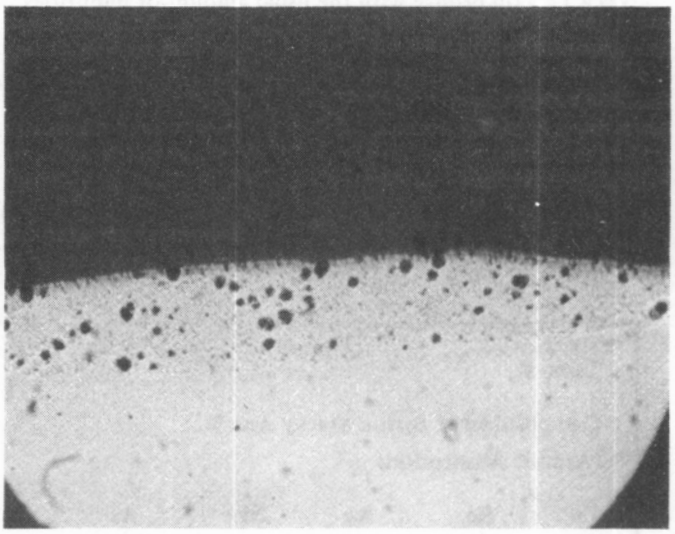

Fig 6 Tin coating on experimental dip-tinned bronze plate after 10 secs immersion at 320°C; the black spots are pores in the tin coat. X100.

In the case of a tinned bronze the tin layer would finally become a bronze layer. Thus, by heating the tinned surface for some time after tinning, we could get a similar structure to that of an inverse segregated layer. But there would be some difference. Diffusion leads to a more or less linear enrichment in copper with distance from the interface while inverse segregation gives a more or less uniformly dispersed alpha+ compound structure.

In the case of Anglo-Saxon jewelry from Sutton Hoo, Oddy[14] came to the conclusion that the tin plating on the helmet and shield fittings had been intentionally heated to produce higher melting point alloys with between 20-70% Cu to stabilise them against later adjacent mercury gliding. Panseri and Leoni[15] discuss the inter-diffusion of copper and tin. Diffusion of tin into copper, when the former is heated above its melting point of 232°C is very rapid and it is possible that the typical 30% Cu alloy could be made by diffusion during annealing. It is also possible that tinning around 300°C could anneal cold-worked bronzes.

One flat axe which appeared to have a patchy tinned surface is from Barton Stacey. Analysis of the inside showed that it

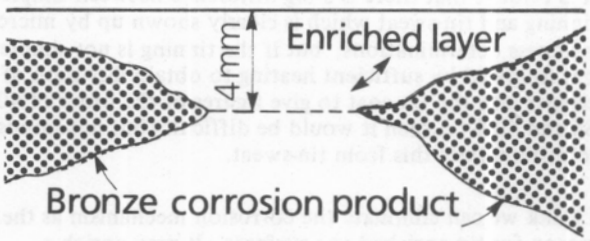

Fig 7 Enriched layer formation on Barton Stacey axe X250 (After Kinnes et al, Ref8).

was a 12% tin bronze with the usual amount of impurities (Table 3). Surface analysis by XRF and XRD showed the plated areas to contain about 25% Sn and 75% Cu probably present as the alpha + delta eutectoid [16] (Fig 7).There was no evidence of exudation of the tin-rich phase onto the surface from the matrix but the authors could see a dark layer of tin-rich 'threads' penetrating the grain boundaries of the interior from the surface. They suggest that the layer may have been formed by a cementation process during which diffusion of the copper into the tin took place, but certainly not as a result of tin sweat.

Table 3

Composition of Barton Stacey Axe %

(Atomic Absorption)

Cu	Sn	Ag	Ni	As	Fe
87	12.0	0.1	0.07	0.15	0.01

After Kinnes, Craddock et al [16].

It has been shown that even at 170°C the rate of solid state diffusion of copper into lead-tin alloys is sufficient after long times to embarrass the electronics industry and cause them to limit the operating temperatures [17]. But the penetration of copper is nothing like that obtained when tin is heated above its melting point.

One cannot imagine the simple tinning of an axe by dipping or rubbing being anything other than the final process, and one of the aims would be to reduce the time required so as to prevent annealing of a cold worked cutting edge. But a soft tin coating would soon be lost anyway. Therefore it is possible that the tinned axes were ceremonial or ritual and nobody would be very worried about an annealed cutting edge on such an axe. But the axes described earlier do not have simple tinned surfaces. They have alloy layers that must have been heat-treated after tinning.

Conclusions

Having started the discussion with three possible techniques by which tin enrichment could have been brought about we have now added a fourth, cementation.

It is evident that there is a big difference between simple tinning and tin-sweat which is clearly shown up by microhardness determinations; but if the tinning is not simple but followed by sufficient heating to obtain diffusion of the copper into the tin-coat to give figures of the order of 40% Sn and 60% Cu then it would be difficult (but not impossible) to differentiate this from tin-sweat.

I think we can eliminate the corrosion mechanism as the reason for tin-enriched axe surfaces. It may enrich a corroded bronze but does not form the tin-rich layers we found; but it is interesting that a pure tin coating can be anodic under certain conditions to a high tin bronze (15-18%); and a high tin bronze and intermetallic compounds cathodic to a low tin bronze. The latter would favour the retention of tin-sweat, a cementation layer, or a tin-copper alloy layer on a low tin bronze.

Diffusion between tinned surface and matrix could arise due to a normal homogenisation treatment which is necessary to remove the cored dendritic structure to render the edge easily sharpened by cold hammering. It would be interesting to know whether this has been done on 'tinned axes' or whether they have been left in an otherwise unfinished condition.

But surely surface tinning would be expected to be the last operation and the low temperature of tinning would not anneal a standard (10%) tin bronze although it might anneal an impure or arsenical copper, particularly if heavily worked.

It would appear then that we are left with inverse segregation, diffused tin plate, or a cemented layer, and the only way by which we can distinguish between them is to do more investigational work. This means experimental reproduction and the examination of more museum specimens.

Acknowledgements

I am indebted to Dr H McKerrell for the provision of much information and some of the photographs and to R E Clough for the dipping experiments. Dr Nigel Meeks kindly read through the original draft and made many useful suggestions which have been incorporated in the final version.

References

1 R F Tylecote. Metallurgy in Archaeology. London 1962 1962, p 156.

2 H Miles. Barrows on the St Austell Granite, Cornwall. Cornish Arch 1975, (14), 5-81.

3 J A Smith and S Macadam. Notice of bronze celts . . . which have apparently been tinned. PSAS, 1872, **9**, 428-43.

4 M G Spratling, R F Tylecote et al. An Iron Age Bronze Foundry at Gussage All Saints, Dorset. Proc 16th Int Symp on Archaeometry. Edinburgh, 1976, p 283.

5 N B Vaughan, Inverse segregation: A review. J Inst Met 1937, **4** (7), 377-400.

6 H McKerrell. (Personal communication, 1972).

7 H McKerrell and R F Tylecote. The working of copper-arsenic alloys in the Early Bronze Age and the effect on the determination of provenance. Proc Prehistoric Soc 1972, **38**, 209-218.

8 C S Smith. An examination of the arsenic-rich coating on a bronze bull from Horoztepe. In: S J Young (Ed), Application of Science in examination of works of art. New York, 1973.

9 J Close-Brooks and J M Coles. Tinned axes. Antiquity, 1980, **54** (212), 228-29.

10 J Close-Brooks. Personal Communication.

11 S Needham and I A Kinnes. Tinned axes again. Antiquity, 1981, **55** (214), 133-34.

12 H E Wulff. The traditional crafts of Persia. M I T Press, 1966, p 31.

13 G L J Bailey and H C Watkins. The flow of liquid metals on solid metal surfaces and its relation to soldering, brazing and hot-dip coating. J Inst Met 1951-2, **80**, 57-76.

14 W A Oddy. Gilding and tinning in Anglo-Saxon England. In: W A Oddy (Ed), Aspects of Early Metallurgy, London 1977, 129-134.

15 C Panseri and L Leoni. The manufacturing technique of Etruscan Mirrors. Studies in Conservation, 1957-8, **3**, 49-62.

16 I A Kinnes, P T Craddock, S Needham and J Lang. Tin plating in the Early Bronze Age: The Barton Stacey axe. Antiquity, 1979, **53** (208), 141-143.

17 D A Unsworth and C A Mackey. On the growth of compound layers on various metal bases plated with tin and tin alloys. (Int Tin Res Inst). Trans Inst Metal Finishing, 1973, **51**, 85-90.

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XPS depth profile analysis of the surface decoration on a Pre-Columbian gilded gold copper alloy pectoral

Katherine Gillies and David Urch

Abstract

The surfaces of a pre-Columbian tumbaga pectoral disc have been analysed principally by X-ray photoelectron spectroscopy, combined with argon ion etching for depth profiling, in an attempt to determine the technique by which they were decorated. Comparative data were obtained using a scanning electron microscope with an energy dispersive X-ray analysis system, and on experimental surfaces produced on a ternary alloy. The data indicated that surface compositional variation arising from ion etching was negligible for the etch conditions and samples used. The elemental concentration profiles, within the pectoral surfaces, constructed from XPS measurements showed relatively good agreement with SEM probe line scans over sample cross-sections. From the results presented it is concluded that the surface decoration of the pectoral disc was achieved by depletion gilding and either (i) selective burnishing or (ii) burnishing and selective chemical etching. The results were not conclusive, both methods being considered to produce very similar results. The study however illustrates that X-ray photoelectron spectroscopy combined with ion etching can provide reliable results as an archaeometric tool for depth profiling although the method is too time consuming for routine analysis.

Introduction

The principal metals which were exploited in the Andean region of South America in pre-Hispanic times were gold and copper, whilst platinum and silver were utilised to more limited extents. A gold/copper alloy, called tumbaga, was commonly employed in the manufacture of metal artifacts. This alloy varied widely in composition and could contain up to 25% of silver due to the natural occurrence of the latter with gold, rather than to deliberate addition. Both metal and alloy artifacts, whether cast or hammered, were invariably gilded by one of a number of different techniques (eg oxidation/pickling, salt cementation etc)[1,2]. This paper is concerned with the analysis of the surface decoration of a fragment of a pre-Columbian pectoral, made of tumbaga, which is 'depletion gilded', and illustrates the use of X-ray photoelectron spectroscopy (XPS), combined with argon ion etching, as an archaeometric technique. The pectoral fragment (3081) Fig 1 (Museum No 21222, Museo del Oro, Bogota, Colombia) comes from the Narino district in the Andean region of Colombia and was made during the Piartal period (800-1250 AD); it has been described fully by Scott in this Journal[3].

It is possible that the depletion gilding was effected by the oxidation-acid pickling method since Lechtman[2] has shown that very fine control would need to have been exerted with the cementation technique.

Decoration of both cast and hammered objects with geometric motifs was commonly carried out by making use of the colour contrast existing between gilded and non-gilded areas. Such a design appears on both surfaces of the pectoral 3081 but in this case the entire surface seems to have been gilded and the design appears as light gold

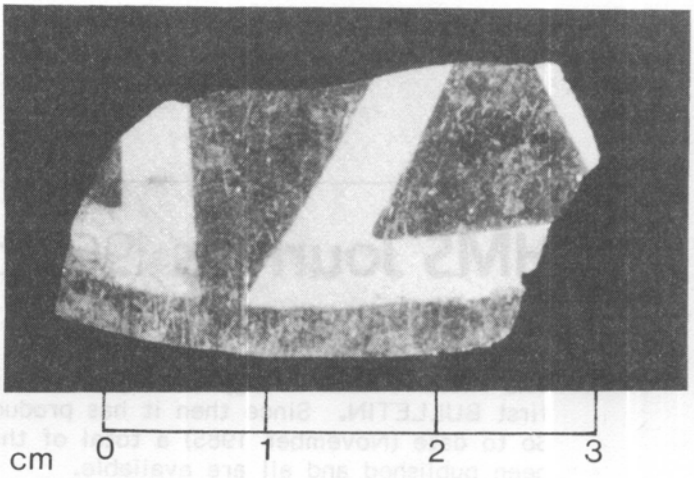

Fig 1 Pectoral fragment 3081

coloured matt areas against a darker gold coloured shiny background. It was the nature of these two different finishes and the technique(s) used in their production which were of particular interest.

Preliminary examination of a cross-section through the pectoral with an electron microprobe had revealed[3] that the enriched/depleted gilded zone was some 2 to 3 microns thick and thus the thickness of the surface decoration appeared to be on a scale which could be readily probed by XPS combined with argon ion etching and this was subsequently carried out. Complementary data were obtained using scanning electron microscopy with electron probe analysis. An experimental gilded alloy, produced by Scott, was also analysed for comparison.

Quantitative Analysis by XPS

Attempts to obtain quantitative analyses from X-ray photoelectron spectra peak intensity values, have so far been based either on calibration using standards with compositions approximating to those of the samples, or on elemental sensitivity factors derived from measurements on compounds with a range of compositions[4-6] or by the construction of a theoretical model.[7-10] Each one of these approaches is, however, beset with difficulties which together with experimental uncertainties (eg surface roughness, contamination) mitigate against the use of XPS for quantitative analysis. For this reason only semi-quantitative analyses of the pectoral and the experimental alloy were attempted, based on relative peak intensity measurements. These were sufficient to make a comparison between the matt and shiny surfaced areas of the pectoral and the alloy. Previous investigations[11,12] have shown that for pottery samples good semi-quantitative XPS analyses could be obtained by simply dividing relative peak intensities by the calculated atomic photoionisation cross-sections of Scofield[13] and normalising the sum of the resulting elemental concentrations within the sample to 100%. The resulting analyses having an estimated precision of $\pm 10\%$ but an absolute accuracy of only $\pm 50\%$. On such a semi-

empirical basis it was found that, in this work, improved estimates of concentrations were obtained by taking into account the variation of electron mean free path with kinetic energy. Electron mean free paths, calculated by Penn [14] for gold, silver and copper are very similar for any given energy. Thus the mean free path correction factors for photoelectrons of differing energies were assumed to be independent of sample composition. The corrected Au, Ag and Cu concentrations were normalised to 100%, as before, in an attempt to eliminate intensity variation due to differing sample roughnesses and sample positioning after argon ion bombardment.

Depth Profiling by Argon Ion Etching

One of the main problems commonly associated with the use of argon ion etching for depth profiling of metal or alloy systems is that differential sputtering of elements occurs [15-17] because the efficiency of removal of surface atoms depends upon their atomic mass and the strength and nature of the bonds with which they are held. In general, on ion etching, surfaces tend to become enriched in the heavier components [18] and also in the less abundant components. Differential sputtering of metal alloys can lead to cone formation, [19] material with a low sputtering rate remaining in spikes protruding from the etched surface thus causing a large increase in surface roughness. Surface enrichment/depletion can also result from radiation-enhanced diffusion. [20,21] After initial enrichment/depletion upon ion etching, however, a steady-state composition is eventually established in the surface region. Other effects which can occur include implantation of the bombarding ions within the specimen surface and an effective knocking in of heavy atoms within a light element matrix.

Sputtering of the binary alloy systems Ag-Au, Au-Cu and Ag-Cu with 1 keV argon ions has been shown, by the use of Auger electron spectroscopy, to result in preferential removal of silver in the Ag-Au system, the enrichment being larger in the topmost surface layer and decreasing with depth; no enrichment/depletion in the Au-Cu system; and a copper enrichment in the Ag-Cu system. [16] Kaiser [22] reports that after argon ion etching (10 mins, 10 μA/cm^2 3 kV at the discharge gap) a ternary alloy of composition $Au_{0.25}Ag_{0.38}Cu_{0.37}$ the XPS spectra showed a considerable increase in the intensities of the Au 4f and Cu 2p signals and a slight decrease in those of the Ag 3d, and that initial carbon and oxygen contamination had been removed. The Cu 2p signals displayed a relatively greater intensity increase than the Au 4f signals. An overall increase in peak intensities would be expected upon removal of surface contamination with a greater increase in the Cu 2p signals due to the relatively low kinetic energy of these 2p electrons. The possibility that ion bombardment of the samples considered in this paper might have affected the surface elemental concentrations was made the subject of particular attention as described below.

Experimental

XPS spectra were recorded using a Vacuum Generators ESCA 3 spectrometer, with an Al Kα (1486.6 eV) X-ray source operated at 10 kV, 20 mA, which gave experimental detection limits of th e order of 1%. The operating vacuum was better than 5 x 10^{-9} Torr. The irradiated target area was estimated to be centred over $\sim$10 mm^2 and samples of this approximate size were used thus maximising signal output whilst minimising specimen destruction. Four different areas of adjacent matt and shiny surfaces were separately depth profiled using XPS analysis in conjunction with argon ion etching. A Vacuum Generators AG2 ion gun was employed which was operated at $\sim$2 KeV with a gas pressure of $\sim$3 x 10^{-5} Torr to give a focussed beam of current $\sim$ 20 μA.

Full range scans were run periodically throughout profiling and the C 1s and 0 1s peaks monitored. The Au 4f, Ag 3d and Cu 2p peaks were recorded with a scan range and time of 100 eV/1000 secs and a 3 secs time constant. The relative intensities of these peaks were estimated from the areas under the main photoelectron peaks by multiplying the peak height, taken to the centre of a tangent to the background on either side, by the FWHH. Estimated elemental concentrations, derived from the correction and normalisation of the relative peak intensities as previously described, are plotted as a function of argon ion dose (μA.mins) to give depth profiles. Scanning electron micrographs and electron probe analyses were obtained with a Hitachi S450 scanning electron microscope (SEM) and a Link 860 fully quantitative analyser system employing a KEVEX silicon detector. Quantitative analyses were computed using a ZAF-4/FLS programme from standard spectra held on file. In addition to the pre-Columbian Narino pectoral, a modern sample, upon which an attempt had been made to simulate the matt and shiny finishes, was also examined by the same techniques. Scott produced and depletion gilded this sample, an Au-Cu-Ag ternary alloy of atomic composition 18.21% Au, 77.64% Cu, 4.20% Ag. The alloy was cast at 1150^{o}C and air cooled. The oxidation/pickling method of gilding was employed using oxalic acid to remove copper oxide formed by heating. Part of the gilded surface was then burnished with agate.

Results and Discussion

Visual Examination

Under the binocular microscope the experimentally produced matt and shiny surfaces were observed to closely resemble those of the pectoral as illustrated in Figs 2 and 3. The shiny areas, which appear dark in the Figures, are seen to be covered with numerous small scratches, orientated predominantly in one direction, a result of burnishing. No apparent height difference between adjacent matt and shiny areas on the pectoral was observed. On the pectoral some of the matt decoration appears to be partly 'worn away' (Fig 2) while some small matt patches lie with in shiny areas (Fig 2), this latter phenomenon occurring on the experimentally produced shiny surface also (Fig 3).

SEM examination of the pectoral and experimental alloy showed the matt areas to be rough and 'porous', and the shiny areas to be generally compacted and smooth, although scratched (Figs 4 and 5). Differences between the detailed features of the pectoral and experimental surfaces can probably be attributed to differences in the specific methods and tools employed in their production and in the bulk compositions. The order in which the two types of finish were produced on the pectoral surface could not be ascertained from the scanning electron micrographs. Talysurf traces across the pectoral surface confirmed that there were no height discontinuities at matt (rough)/shiny (smooth) junctions.

XPS and SEM Probe Depth Profiles

The only elements detected by XPS in the pectoral surfaces, apart from carbon, oxygen and nitrogen, which were principally present as contaminants, were gold, silver and copper. The depth profiles obtained (Figures 6-8) through the matt and shiny pectoral surfaces show a general similarity, ie an increase in the copper, and decrease in

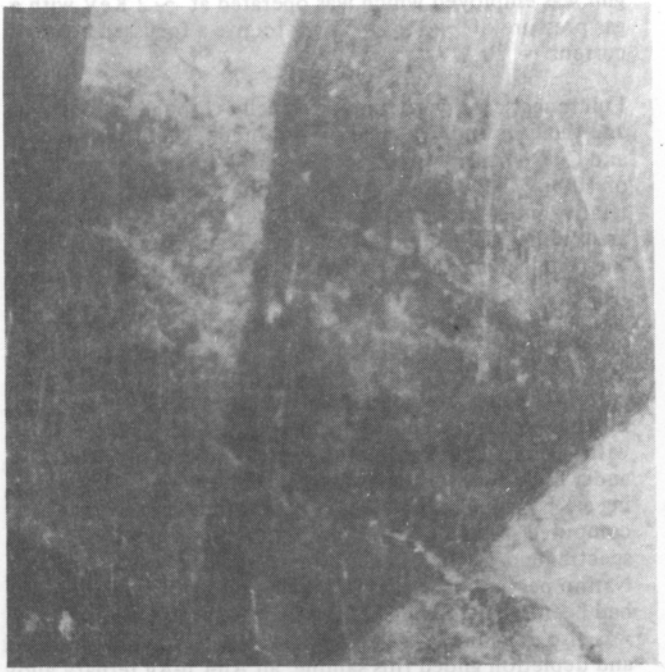

Fig 2 Optical micrograph of pectoral fragment

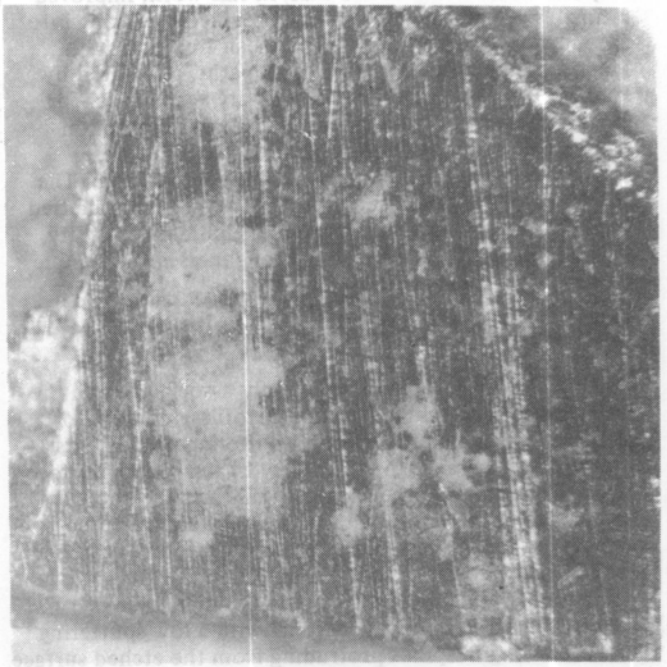

Fig 3 Optical micrograph of shiny surface of experimental alloy

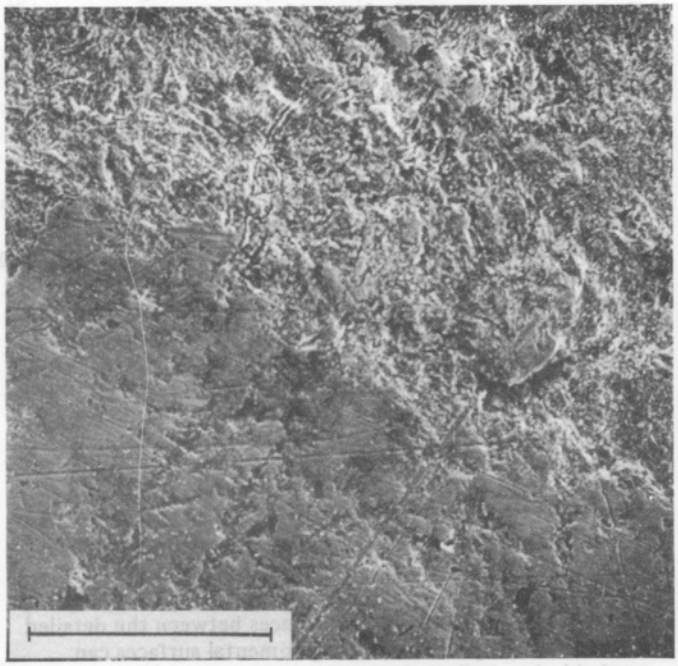

Fig 4 Scanning electron micrograph of pectoral surface
⟵⟶ = 50 μm

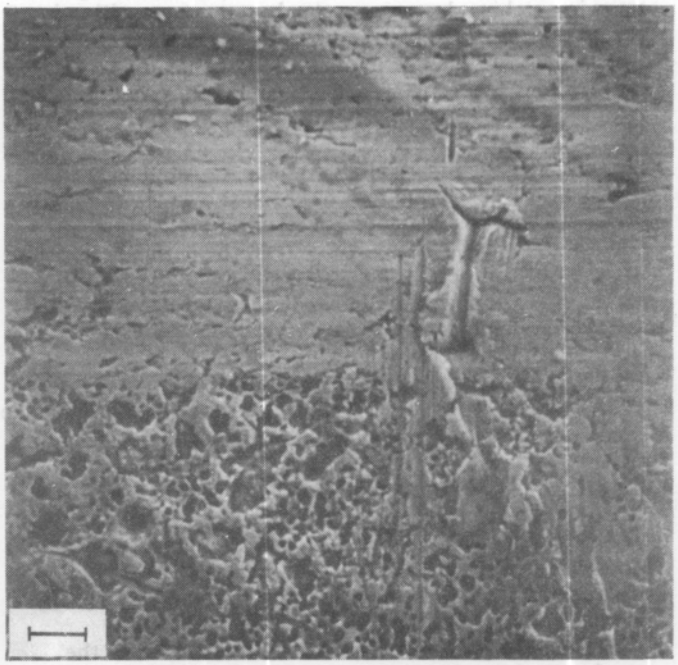

Fig 5 Scanning electron micrograph of experimental alloy surface
⟵⟶ = 5 μm

the silver and the gold concentrations with depth. Despite the lateral variation shown by these depth profiles, the main apparent differences between the two types of surface are that the concentrations of silver and gold are higher and those of copper lower in the matt than in the shiny surfaces, and that the absolute concentration changes are greater, within the depths profiled, for the shiny surfaces. The depth profiles in Figures 7 and 8 in particular, indicate that in the extreme surface regions of part of the pectoral the silver concentrations are higher in the matt than in the shiny areas, and that there is a superficial copper enrichment/gold depletion which is more marked in the matt areas.

XPS depth profiles through the experimental matt and shiny alloy surfaces are given in Figure 9. They show the same general characteristics as those obtained from the pectoral (Figures 6-8), ie an overall decrease in the Ag and Au, and an increase in the Cu concentrations with depth, with the average concentrations of Ag and Au being lower, and those of Cu higher, in the shiny compared to the matt surface. In particular, the Ag profiles in Figure 9 appear very

similar to those in Figures 7 and 8, while the Au profiles are comparable to those in Figure 6. The Cu profiles, however, exhibit less variation at the extreme surface of the alloy than at that of the pectoral. The apparently high concentrations of copper at the extreme surface of the pectoral shown by some of the XPS depth profiles may have resulted from superficial corrosion of the pectoral fragment during burial.

The relative increase in the copper to gold concentration ratio with depth through the pectoral surfaces profiled is consistent with the latter having been depletion gilded, although the corresponding decrease in the silver to gold ratio with depth is not. The absolute, as well as the relative, concentration gradients measured, however, could well have been affected by the analytical technique employed particularly by the ion etching as previously outlined. Before further interpreting these results, an attempt was thus made using the SEM probe to try to establish whether the XPS depth profiles reflected actual concentration gradients within the pectoral and experimental surfaces on either an absolute or a relative basis or whether they were dominated by effects produced by the analytical technique itself.

Elemental line scans for Au, Ag and Cu made with the SEM probe across the gilded regions of a polished cross-section of a fragment of the pectoral, are given in Figure 10. These depth profiles compare relatively well with those obtained by XPS/ion etching (Figures 6-8), the profiles through the matt and the shiny surfaced gilt layer again appearing very similar, and indicate that the XPS profiles extend to a depth of 1-2 μm. A fairly good correlation exists between the SEM probe and XPS profiles for copper and gold, the former verifying an absolute increase in the Cu and decrease in the Au concentrations with depth; a higher Au and lower Cu concentration in the matt than in the shiny surfaced gilt layer; and a steeper Cu concentration gradient in the shiny surfaced gilt layer. A similar correlation, also on an absolute basis, is observed between the SEM probe and XPS data for Ag in the matt surfaced gilt zone.

The SEM probe Ag profile through the shiny surfaced gilt zone, however, shows no decrease with depth which suggests that preferential sputtering of silver may have occurred during argon ion bombardment. However the SEM probe line scans were generally less sensitive than the XPS depth profiles due to the relatively large sampling area and depth (~ 3 μm^2 x 3 μm) and because the low concentrations of silver present meant the signal to background and noise ratios for this element were particularly high. Nevertheless, the XPS depth profiles do indicate that there is a relatively higher concentration of silver in the matt than in the shiny surfaced gilt layer as shown by the SEM probe depth profiles and spot analyses (Table 1). In order to try to elucidate some of the causes of the compositional variations displayed in the XPS depth profiles, a further experimental matt alloy surface was profiled, the sample being removed from the spectrometer and burnished with agate half way through the construction of the profile; the result is shown in Figure 11. From the constructed depth profile it appears that burnishing of the depletion gilded surface resulted in a Ag depletion/Cu enrichment, with compaction of the surface probably accounting for the subsequent relatively steeper concentration gradients, assuming an unchanged sampling depth. A significant change in the effective sampling depth could occur with a change in sample composition due to the variation of electron mean free path with kinetic energy.[14] This does not appear to be likely to occur with the alloy in question as values of electron mean free paths, calculated by Penn, are closely similar in gold, copper and silver for any given electron energy.

The XPS depth profile through the 'bulk' alloy surface (Figure 12) shows little variation in the Cu, Ag and Au concentrations with depth except for a superficial Cu depletion/Au enrichment which may have been a result of the method of sample preparation used. This profile suggests that argon ion etching was not responsible for the previously observed decrease in Au concentration with ion dose, however, elemental sputtering yields which predominantly determine the extent of enrichment/depletion of constituent elements as well as the steady state composition, vary to some extent with alloy composition.[16]

Estimation of Ion Etching Rate

The SEM probe line scans across the gilt layer of the cross-sectioned pectoral (Figure 10) indicate that the depleted/enriched zone is $\sim$3-4 μm thick. The effective sampling area of the probe spot analyses, given in Table 1 are probably centred over $\sim$ 2-3 μm. Thus the spot analyses centred $\sim$ 0.7 μm from the decorated surface edge are approximate average compositions of the gilt layer, while those centred at $\sim$ 4.3 μm, closely approach the composition of the bulk alloy. These averaged analyses have been used in a rough estimation of the rate of sputtering under the ion bombardment conditions used. From Figure 12 it can be seen that the XPS estimated elemental concentrations, for the 'bulk' experimental alloy, agree relatively well with the batch composition. If it is assumed that a similar correspondence exists between the XPS estimated elemental concentrations within the gilt layer of the pectoral and the SEM probe analyses, then it appears from a comparison of the analyses in Table 1 with the depth profiles in Figures 6-8, that the latter extended over not more than half the depth of the gilt layer and probably over less than half. The sputter rate for gold, given by Vacuum Generators, using the AG2 Ion Gun operated at 10 KeV to give a beam current of 200 μA focussed onto $\sim$1 cm^2 by a voltage of 8 KeV, is 3.5 Å per μ A.min. These etch conditions will produce a higher sputter rate than a 2 KeV beam focussed over a similar sized area as used in this work. From the data of Czanderna [19] which lists sputtering yields for Au, Cu and Ag for various ion energies, a 2 KeV AG2 ion beam may be expected to produce a sputter rate of $\sim$2Å per μA min. for all three metals. The approximate total argon ion dose used in profiling was 8000 μA mins and assuming a 2Å per μA min sputter rate, this would give an estimate profile depth of 1.6 μ which is in relatively close agreement with that estimated on the basis of the SEM probe analyses.

Conclusions

The close similarities in composition depth profiles of both the matt and shiny areas indicate that the aurification of the pectoral was achieved by depletion gilding rather than by the addition of a surface layer of gold. That sharper changes in composition with depth are observed in the shiny rather than in matt areas, is to be expected since burnishing of a depletion gilded surface will lead to compaction. However, it is consistently found that the matt areas show a **lower** percentage of copper than the shiny areas suggested that the matt areas had been subjected to more, severe depletion procedures than the shiny areas. This may have been achieved by the burnishing of the whole artifact following the first stage of depletion gilding followed by a second depletion stage on those areas that were to become matt: the shiny areas, being masked off. Whilst this con-

Figures

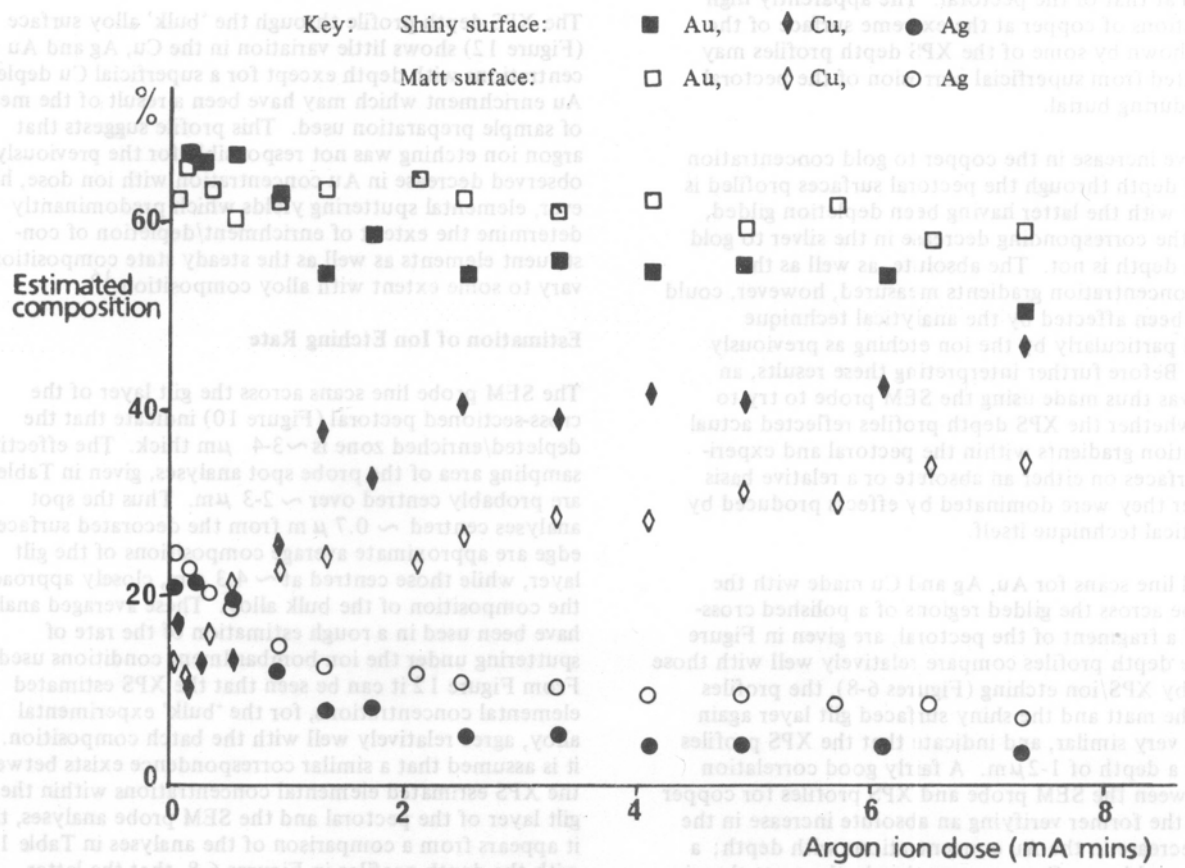

Fig 6 XPS depth profiles of pectoral surfaces 1

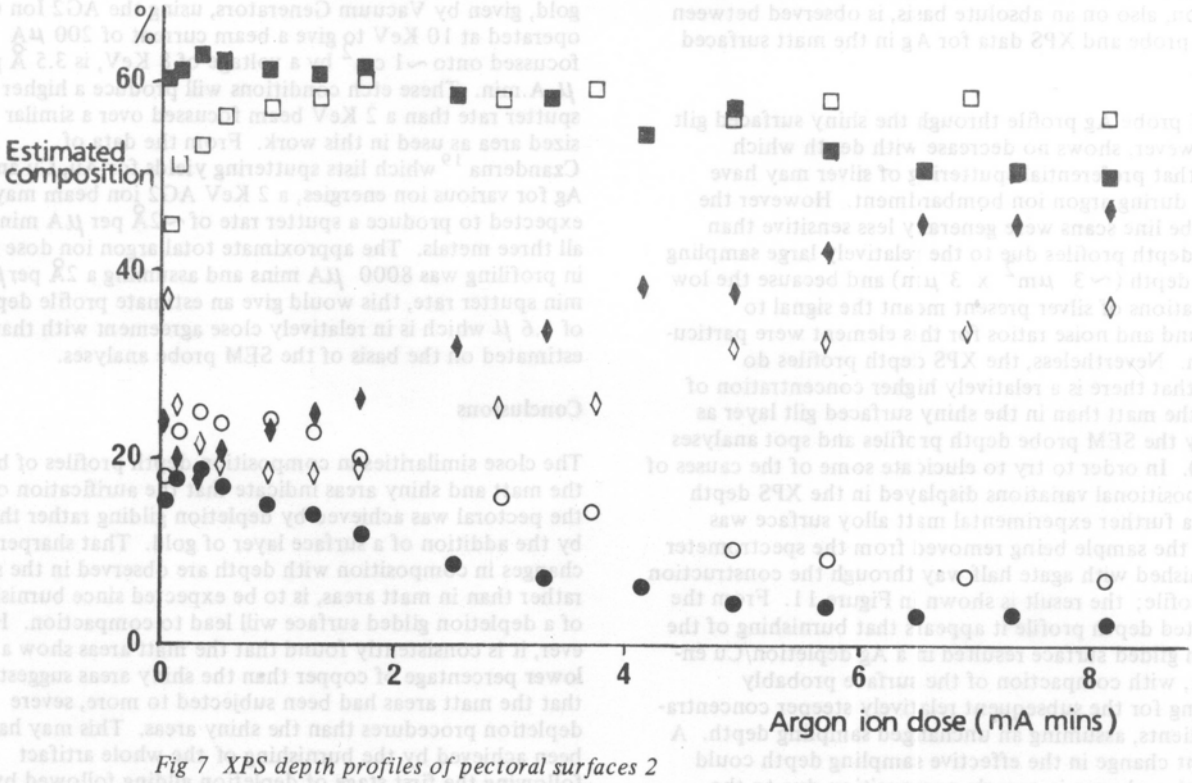

Fig 7 XPS depth profiles of pectoral surfaces 2

Table 1. Averaged SEM Probe Analyses* of a Polished Cross-Section Through the Pectoral Fragment

Distance of Spot Analysis Centre from Given Surface

	0.7 μm		4.3 μm		
Atomic % of Element	Shiny	Matt	Shiny	Matt	Area Analysis of Bulk
Au	33.9	40.9	6.6	8.1	6.9
Cu	63.8	54.5	91.3	90.0	91.4
Ag	1.9	4.4	1.7	1.61	1.8

* Data for spot analyses based on total of twelve analyses

clusion is consistent with that drawn by Scott based on extensive SEM investigations it is not a conclusion that could be drawn with confidence just from the ESCA results since selective burnishing also produced very similar results in the matt and shiny areas of the artificial specimen to those observed in the pectoral itself.

In this study XPS combined with argon ion etching has proved to be a useful technique for characterising the extreme surface decoration on the pectoral fragment. This method of analysis provides information on a scale several orders of magnitude greater than does the SEM probe which has found many applications as an archaeometric technique. XPS with ion etching for depth profiling is a relatively time consuming and expensive method, is very surface sensitive and provides results which must be interpreted with caution due to possible effects arising from the technique of analysis itself; as such it is not suitable for routine archaeometric work. The technique is useful in archaeometry in specific instances for example, in the examination of very thin decorative layers, superficial corrosion or for the detection of elements of $Z < 13$, providing semiquantitative analyses and relative elemental depth profiles.

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References

1 H N Lechtman, in **Science and Archaeology**, ed R H Brill, Massachusetts Institute of Technology, 1979, p 2-30.

2 H N Lechtman, in **Application of Science in Examination of Works of Art**, ed W J Young, Museum of Fine Arts, Boston, 1973, p 38-52.

3 D A Scott, **J Historical Metallurgy**,1983, **17** (2), 99-115.

4 C K Jorgensen and H Berthou, **Chem Soc Faraday Discussions** No 54, 1972, 269.

5 C D Wagner, **Anal Chem** 1972, **44** (6), 1050.

6 C D Wagner, **Anal Chem** 1977, **49** (9), 1282.

7 W J Cater, G K Schweitzer and T A Carlson **J Electron Spectrosc, Relat Phenom**, 1974, **5**, 827.

8 M Janghorbani, M Vulli and K Starke, **Anal Chem** 1975, **47** (13), 2200.

9 C J Powell and P E Larson, **Appl Surf Sci** 1978, **1** (2), 186.

10 M P Seah, **Surface and Interface Analysis** 1980, **2** (6), 222.

11 K J S Gillies, Ph D Thesis, University of London, 1982.

12 K J S Gillies and D S Urch, **Archaeometry**, 1983, **25**, 1, 29.

13 J H Scofield, **J Electron Spectrosc Relat Phenom** 1976, **8**, 129.

14 D R Penn, **J Electron Spectrosc Relat Phenom** 1976, **9**, 29.

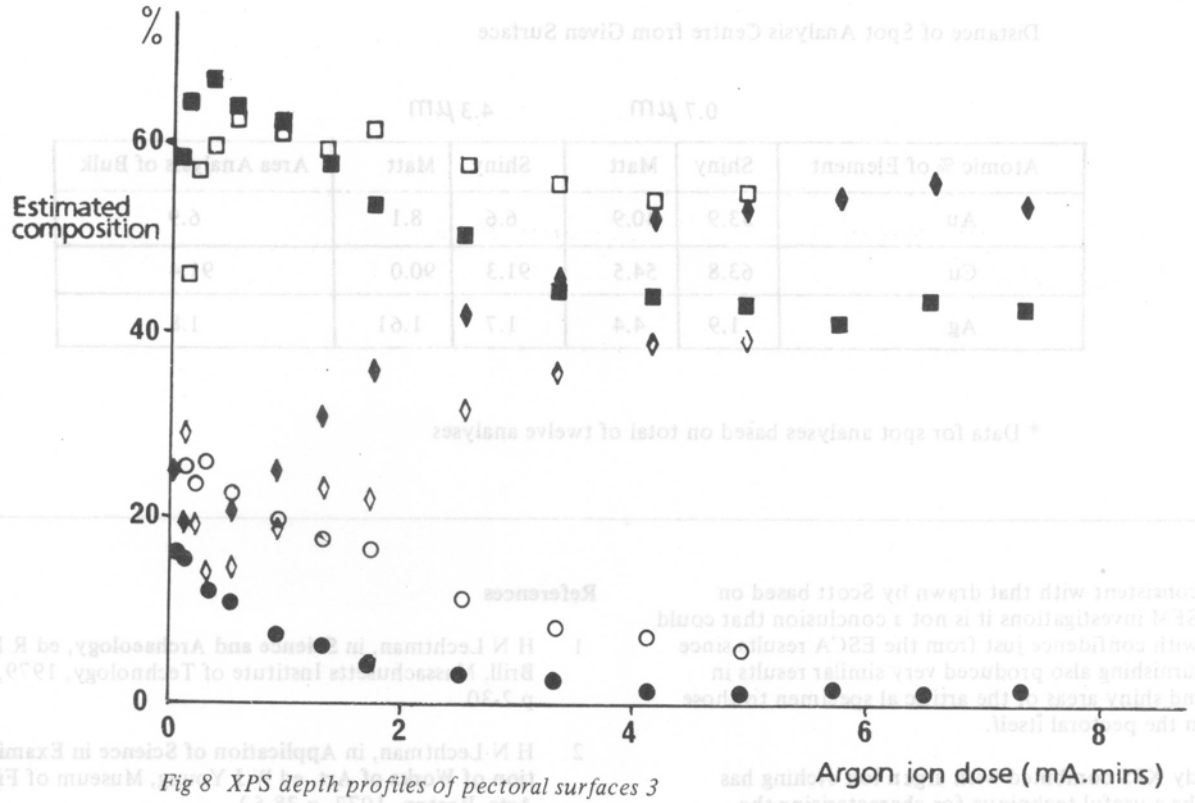

Fig 8 XPS depth profiles of pectoral surfaces 3

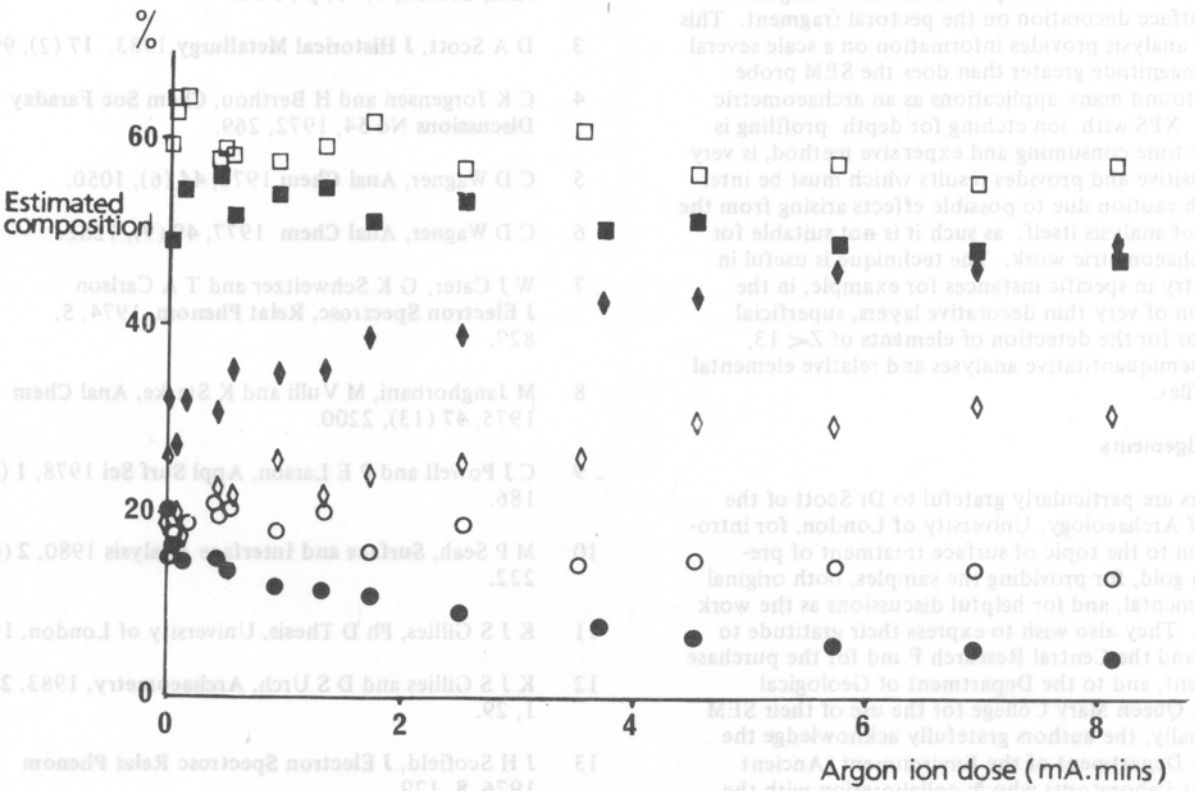

Fig 9 XPS depth profiles of experimental matt and shiny alloy surfaces

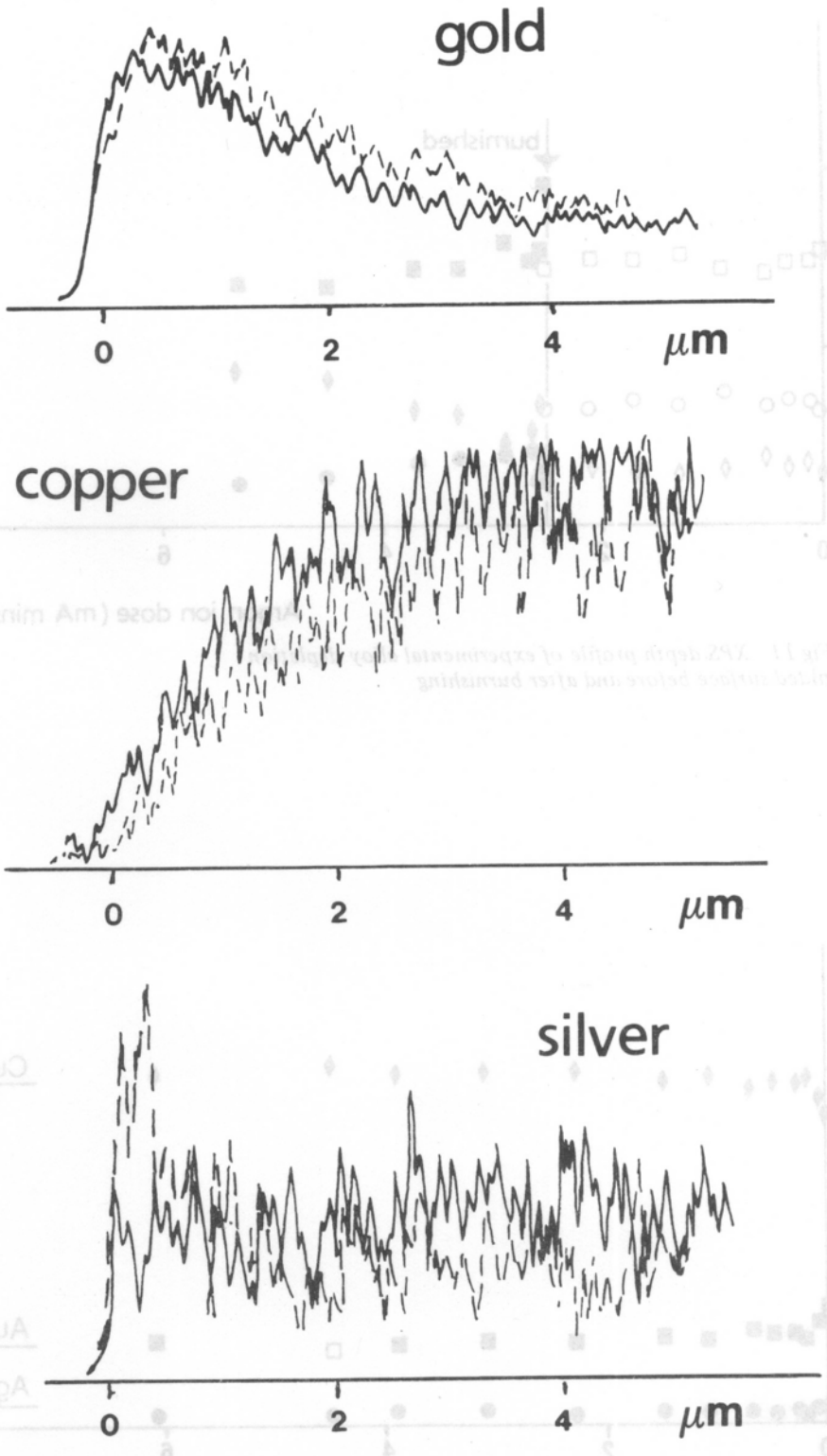

Fig 10 SEM probe line scans of polished cross-section through gilt layer of pectoral; —— shiny surface, - - - - matt surface

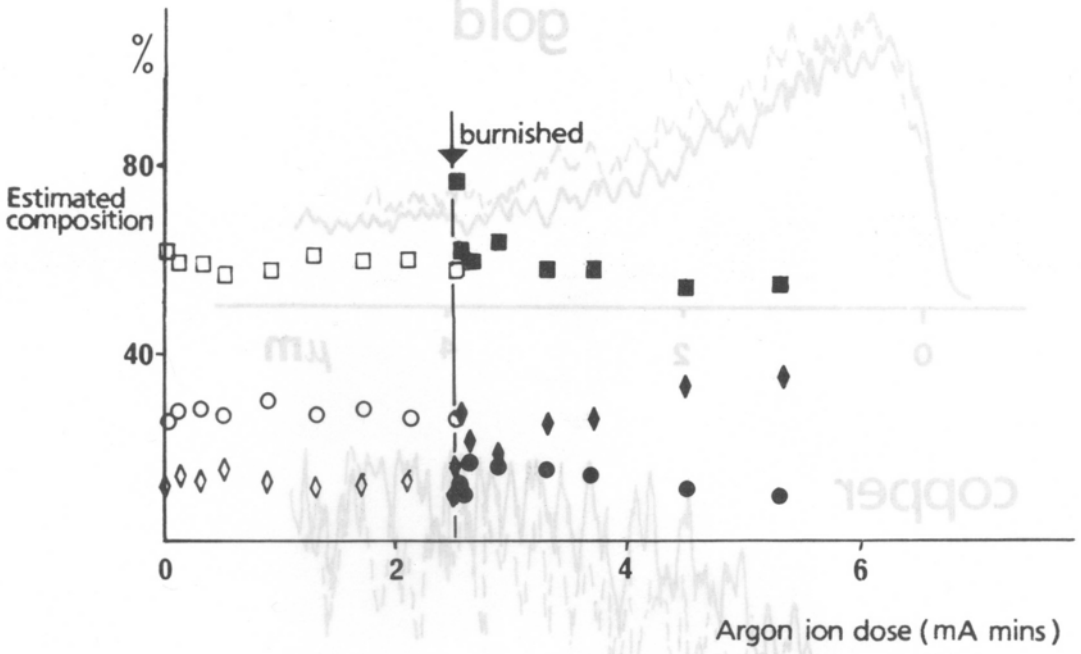

Fig 11 XPS depth profile of experimental alloy depletion gilded surface before and after burnishing

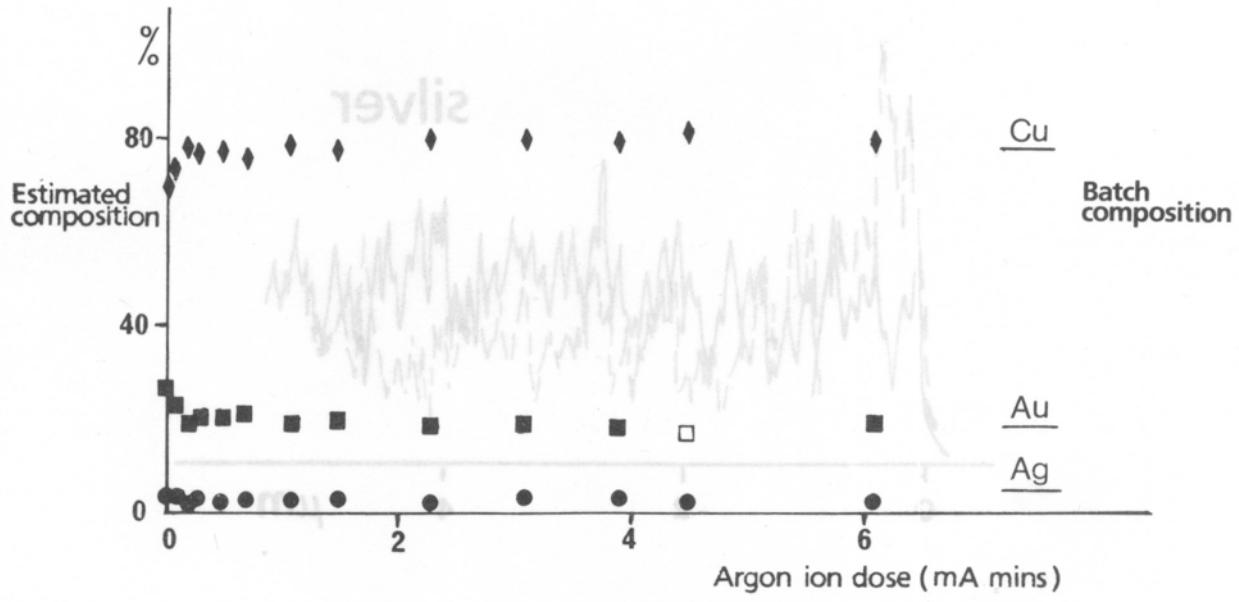

Fig 12 XPS depth profile of 'bulk' surface of experimental alloy

15 P Braun and W Farber, **Surf Sci**, 1975, **47**, 57.

16 W Farber, G Betz and P Braun, **Nucl Instrum Methods** 1976, **132**, 351.

17 R Kelly, **Nucl Instrum Methods** 1978, **149**, 553.

18 Z L Liau,W L Brown, R Homer and J M Poate, **Appl, Phys Lett** 1977, **30** (12), 626.

19 A W Czanderna, in **Methods of Surface Analysis**, ed A W Czanderna, Elsevier Scientific Publishing Co, New York, 1975, p 1-37.

20 P Blank and K Wittmaack, **Radiat Eff Lett** 1979, **43** (3), 105.

21 W F von der Weg, D Sigurd and J W Mayer, in **Application of Ion Beams to Metals**, eds S T Picraux, E P Eer Nisse and F L Vook, Plenum Press, New York, 1974, p 209.

22 R Kaiser, Dissertation Technische Universität Wien, 1975.

Biographies

Katherine J S Gillies

B.Sc (1978 - University of Bristol), PhD (1982 - University of London). Thesis 'The application of X-ray photoelectron spectroscopy in Archaeology'. Post-doctoral research with Dr Cox, York University (1982-84), 'Medieval glass'. Present position, IBM Laboratories, Winchester. Research interests:- archaeometry, inorganic chemistry, scientific computing.

David S Urch

B Sc (1954), PhD (1957) London University. Post-doctoral research with Professor Wolfgang, Yale University (1957 – 59), 'chemistry of recoil tritium atoms'. Lecturer in Physical Chemistry (1960 - 72) Birmingham and London Universities: Reader in Physical Chemistry, Queen Mary College (London University) 1972 - present. Research interests: – electronic structure of molecules and solids studied theoretically and experimentally. Techniques used include X-ray emission and photoelectron spectroscopy, Auger spectroscopy etc. Also archaeometry and chemistry of particles produced by nuclear transformations.

Percy's Metallurgy

In March 1984 Historical Metallurgy Society members received a leaflet setting out the Society's 'Percy Plan'.

The **Iron and Steel** volume was to be published in September 1984 in time for the Birmingham Alloys Conference.

Fuels, Fireclays, Copper, Zinc and Brass would (if sales indicated that the plan was viable) follow in 1985.

And succeeding years would, hopefully, see facsimile copies of **Lead** and **Silver and Gold** available.

Iron and Steel was produced and of the original print order less than a dozen remain at the end of 1985.

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Fuels, Fireclays, Copper, Zinc and Brass was originally published in 1861 and ran to 635 pages. This new edition contains all the material printed in the John Murry edition, reproduced as a facsimile from the original text and illustrations, plus a new introduction by Dr Kenneth Barraclough.

Prehistoric and medieval iron production

Reaction processes in the production of iron ores in low shaft furnaces

Nils Bjorkenstam

General Conditions of Iron Production

Obviously, the first efforts at extracting metal from ferrous ores were made at a very early stage of history. The poor success, or possibly, complete failure of the then known methods of extracting other metals was connected with a difference in oxygen affinity between iron and other metals known at that time. Apart from gold, the earliest-known metals (silver, copper, tin, lead, antimony and zinc) have a closer affinity to sulphur than to oxygen and usually occur in the form of sulphide ores. Roasting converts these ores into oxides, after which the metals can easily be reduced by heating them with charcoal. This is because the oxides of these metals have a higher melting point than the metal itself, which in turn is relatively low. Ferrous ores in their natural state occur mainly as oxides or can be turned into oxides by roasting. However, all iron ores contain a certain amount of gangue, with the result that their melting point is lower than that of pure iron oxide. Using the small amount of charcoal input and the weak blast sufficient for the production of other metals, all that really happens is that the ore melts and accumulates at the bottom of the furnace without any iron being precipitated or, at best, with very insignificant quantities of an extremely low-carbon iron.

For far too long now, interest has focussed solely on primitive iron production, to the detriment of studies concerning the real, industrialised and still practiced method – the blast furnace process – whose origins can now be firmly traced back to the Middle Ages in Europe. The contemporary development of the blast furnace into a high productive and exceedingly energy-efficient unit is based on scientific laboratory studies of partial reactive processes and modern thermochemistry, and of course the same also goes for the development of various methods of reducing iron ores in their solid state to sponge iron. In a modern blast furnace, the oxides of the iron ores pass through all the sub-reactions included in the reduction process until practically all iron ore has been reduced. With this ideal process in mind, it should be easier to study and understand similarities and dissimilarities in progresively lower shaft furnaces, both continuously and intermittently used. A general outline will therefore be given here of the modern blast-furnace process, after which four experiments in smaller furnaces, which included a study of the transformation of the charge during the process, will be viewed in relation to present-day knowledge concerning the reaction involved in the reduction of iron ores.

Iron production cannot be said to have started until it was possible to produce iron in larger quantities and of a quality superior to cold-hammered bronze. This took place in the eastern Mediterranean countries between 1200 and 900 BC.[1] Experience had then shown that a surplus of charcoal was needed in relation to the oxygen content of the ore and that this was a **sine qua non** of efficient production, since the ferrous oxides had to be reduced partly via the carbon monoxide of the gaseous phase. What then happens is that the precipitated iron absorbs carbon, which reduces the melting point of the iron and makes it possible to achieve a carboniferous, hardenable end-product.

The Blast Furnace Process

The blast furnace can be described as a resistance reactor in which the downward-moving charge meets a hot rising reduction gas, formed in the blast zone. On its way down through the shaft, the charge passes through a series of chemical reactions ending with the formation of pig iron and slag. The ferrous ore is reduced through a number of partial reactions, the equilibria of which at various temperatures are illustrated in the diagram shown in Fig 1.

The partial reactions are usually divided into two main groups:

Indirect reduction, in which the ferrous oxides of the ore are reduced by CO or H_2 and the end products are CO_2 and H_2O.

Direct reduction, in which the oxides of the ore are reduced and C is consumed. This may take the form of an intermediate direct reduction, in which the gas reduction is followed by a reaction between carbon in the charge and the CO_2 and H_2O formed, or else a true direct reduction, in which molten iron oxides come into contact with carbon in the stack.

The reduction process can be described as a sequence of reactions from hematite (Fe_2O_3) via magnetite (Fe_3O_4) to wüstite (FeO) and iron. In fact these reactions are partially simultaneous in the stack and on a micro-scale – in the individual lumps of ore – they are always simultaneous in certain temperature zones. Linder[2] has compiled a schematic account of this kind concerning the reaction process in a modern blast furnace, and the following description is based on his essay:-

Drying the charge

Moisture and water of crystallisation accompanying the ore, charcoal and other charge ingredients are emitted in the uppermost zone of the stack. At 200° - 300° all water is eliminated.

The pre-reduction zone

Even with low CO contents, Fe_2O_3 is reduced to Fe_3O_4 and this happens so quickly that it is probably unaffected by the nature and origin of the ore. This reaction starts as 300° and can be taken as completed at 700°.

The gaseous reduction zone

With rising temperature, Fe_3O_4 is reduced to wüstite and iron. As soon as wüstite has been formed, it is reduced to iron in the conditions prevailing in all furnaces with a charcoal surplus in the charge. It has been known for a very long time that the reduction of magnetite proceeds via the wüstite phase to metallic iron and penetrates towards the centre of the piece of ore, producing concentric layers of the various phases. Wiberg[3] and Edstrom[4] have independently shown that this outer ferrous scale is carburised in proportion to the tempera-

ture of the ore during reduction. Thus it is possible to have an outer, carboniferous scale of iron at the same time as the core of the piece of ore still consists of Fe_3O_4 and the intermediate layer consists of wustite.

Rising temperature increases the gaseous reduction of iron to the point where the charge begins to melt. At 900° the CO_2 and H_2O generated begin to react with the carbon of the charge and at 1100° all the CO_2 and H_2O have changed into CO and H_2. Thus on average at 1000° the reduction, which until now has been completely indirect, becomes an intermediate direct one. This carburisation of the gas is highly endothermic and predominates in the 1000°-1200° range.

The direct reduction zone

Thus at the 1000° level, more or less carboniferous iron has been partially reduced but a considerable proportion still remains as wüstite. The amount of iron increases with rising temperature, but at the same time molten FeO-rich reduction products occur. A successive re-solidification and dilution is now to be expected, because the reaction whereby molten wüstite in contact with charcoal is reduced to iron is highly endothermic. No major rise in temperature can occur, therefore, until most of the iron oxide has been reduced and the heat, the molten phase, approaches the composition of the blast furnace slag.

The blast zone

In a modern blast furnace, the charge sinks down into the blast zone which is heated to about 1500°. The temperature here can now vary from the 1500° of the preheated coke up to a theoretical flame temperature exceeding 2000°. Obvious as it may seem, it is still worth pointing out that even very small furnaces from which molten slag is drawn off have to operate at a high temperature in the blast zone. These slags, it is true, are FeO-rich and have a relatively low melting point, 1100°-1150°, but in order for them to flow out of the furnace the temperature must be slightly higher, 1200° - 1250°. Owing, however, to heat losses to the surrounding walls, the temperature here falls rapidly and the charge has to be heated above this level in the blast zone. Thus the temperature of the preheated charge in low furnaces with slag tapping is probably between at least 1300° - 1350° and the theoretical flame temperature.

At a temperature of 1200° the slag in a blast furnace is partly molten, and at this temperature iron in its solid state can absorb 1.7%C. At temperatures exceeding 1200°a slag of low FeO content becomes molten and pig iron containing 3.5-4%C is precipitated.

Both in coke blast furnaces and in smaller charcoal-fired blast furnaces, a higher silicious content has been observed in the pig iron formed above the blast zone than in the pig iron collected in the hearth. Both in the USSR and in

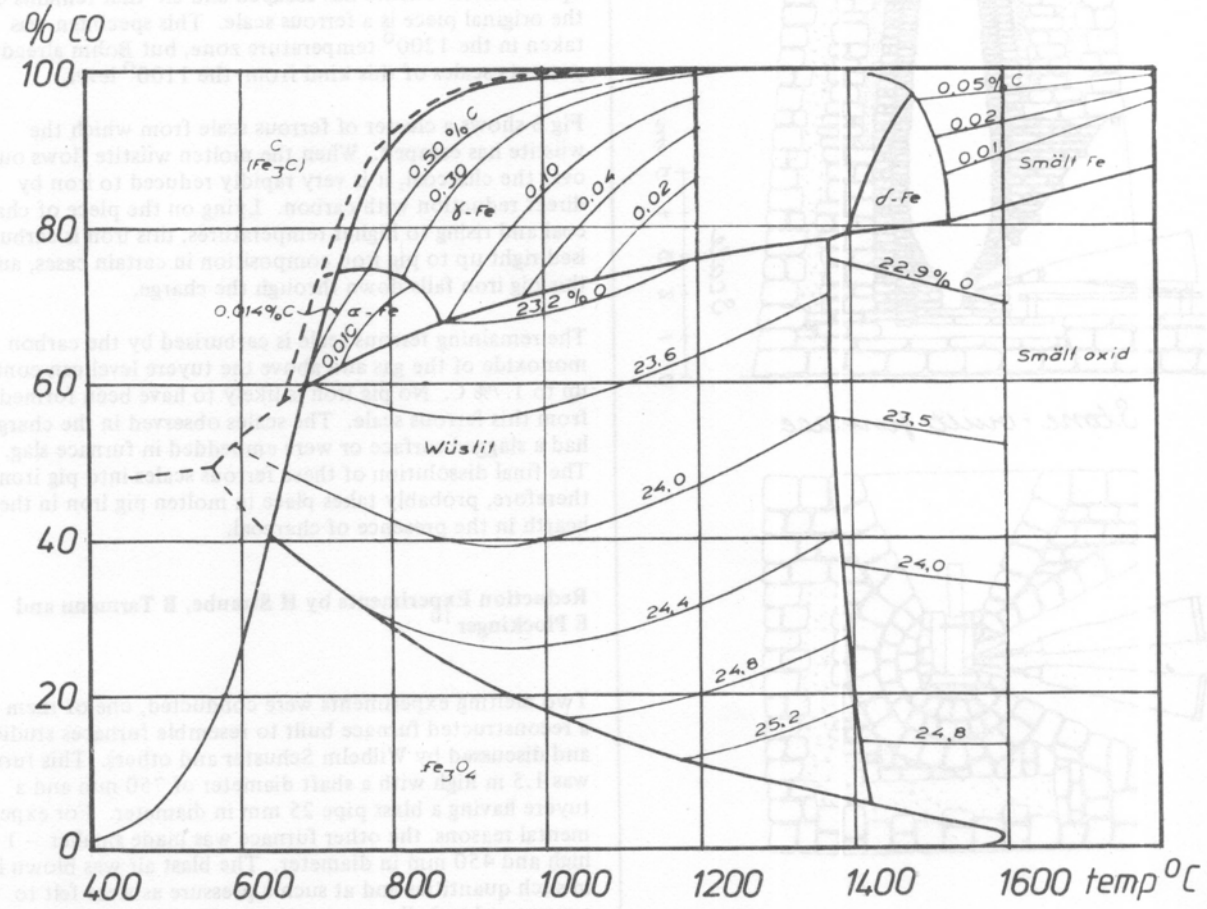
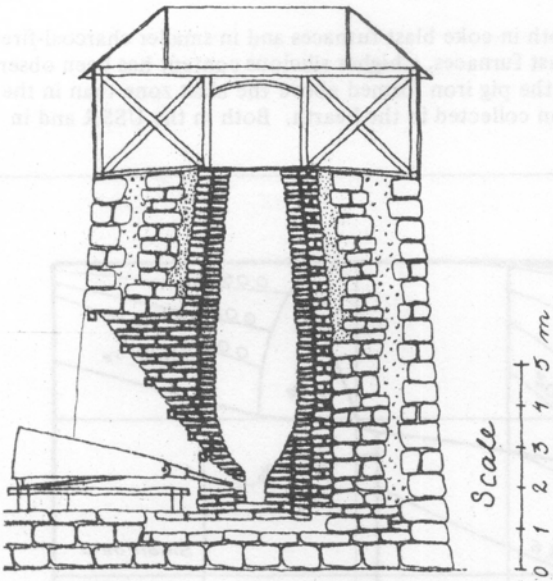


Fig 1 Fe-C-O system at 1 atm pressure

Japan, blast furnaces have been cooled while in operation and a study made of the change undergone by the charge. Here again, very high silicious contents have been found in the pig iron reduced above the blast zone and, at the same time, low silicon content in the produced iron. The silicon reduction of slag FeO is probably the reason for the extremely low FeO contents which can be achieved in blast furnace operations. Another interesting recent observation concerns the role played in the process by alkaline compounds. These greatly accelerate the reduction of wüstite and SiO_2, even in the very small quantities present in all charges. The natural refractory materials used in the earliest Swedish blast furnaces always contained alkali, and this may actively have contributed to the formation of pig iron here.

Ivar Bohm's Study of the Blast Furnace Process

A typical Swedish blast furnace of the 19th century is shown in Fig 2. Bohm made a study in 1927 of the process in an experimental blast furnace only 6 metres high[8]. This study involved banking the furnace while it was fully operative.



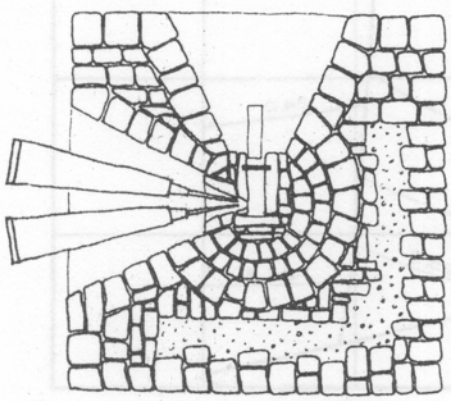


Fig 2

The blast was turned off and all access of air prevented, after which the furnace was left to cool. Specimens of unaffected ore and unaffected charcoal could now be extracted down through the successively transformed charge to the finished slag and pig iron. The various partial reactions were already known at that time, and the general pattern of the reaction agrees with what was previously stated.

Fig 3 shows how metallic iron is precipitated on the surface of the grains. This specimen was taken halfway down the stack, at a point where the temperature was 900 - 1000°. The process then described by Bohm corresponds exactly to that subsequently described by Wiberg[3] and Edstrom [4,6].

Fig 4 shows a piece of ore in which the wustite was melted; this too comes from halfway down the stack. The reaction of the wüstite with CO penetrating the surrounding ferrous scale has resulted in a cavity, due to the wüstite being consumed and yielding iron, thus increasing the thickness of the ferrous scale. Wiberg[3] experimentally heated grains of ore to 1000° in CO and obtained grains of the same appearance as those in Fig 4, a ferrous scale surrounding the wüstite and showing cavities. At this temperature the iron contains 0.8% C, and Wiberg estimated the pressure of the gas in the cavity at 40 atm. Pressures of this magnitude of course, explode the scale, whereupon the remaining wüstite escapes.

Wüstite reacts with the ore gangue and the melting point declines, so that a silicious wüstite may already be molten at 1100°. Fig 5 shows how a piece of ore has burst, whereupon molten wüstite has escaped and all that remains of the original piece is a ferrous scale. This specimen was taken in the 1200° temperature zone, but Bohm already presents scales of this kind from the 1100° level.

Fig 6 shows a cluster of ferrous scale from which the wüstite has escaped. When the molten wüstite flows out over the charcoal, it is very rapidly reduced to iron by direct reduction with carbon. Lying on the piece of charcoal and rising to higher temperatures, this iron is carburised right up to pig iron composition in certain cases, and this pig iron falls down through the charge.

The remaining ferrous scale is carburised by the carbon monoxide of the gas and above the tuyere level can contain up to 1.7% C. No pig iron is likely to have been formed from this ferrous scale. The scales observed in the charge had a slagged surface or were embedded in furnace slag. The final dissolution of these ferrous scales into pig iron, therefore, probably takes place in molten pig iron in the hearth in the presence of charcoal.

Reduction Experiments by H Straube, B Tarmann and E Plockinger [10]

Two melting experiments were conducted, one of them in a reconstructed furnace built to resemble furnaces studied and discussed by Wilhelm Schuster and others. This furnace was 1.5 m high with a shaft diameter of 750 mm and a tuyere having a blast pipe 25 mm in diameter. For experimental reasons, the other furnace was made smaller – 1 m high and 450 mm in diameter. The blast air was blown in in such quantities and at such a pressure as were felt to correspond to bellows operations. The intention was to obtain a lump of metal typical of the bloomery process, and so the furnaces were taken off blast while consuming the remaining charcoal.

A study of the charge remaining in the furnaces after they had been taken off blast revealed that the reduction of the ore to iron had begun in strata about one-third of the way up the stack. This iron was carburised further down in the stack, and above the tuyere there was an iron rich in carbon which had been partly or wholly melted.

Wilhelm Schuster's Reduction Experiment

Schuster was the first to break with the dogma that iron ore was reduced to lumps of iron in the solid state without ever entering the molten state during the process. During his lifetime he experienced all the adversities and opposition which new thinking provokes.

The basic idea underlying Schuster's experiments was the absolute necessity of trying to establish the completely unknown factor – the amount of air which could have been blown in per unit of time – instead of relying on previous assumptions that small amounts of blast air must have been blown into prehistoric furnaces so as to obtain an end product in the form of a lump. He therefore took as his starting point the work done by a postman when steadily climbing a staircase at a rate of one 11 cm riser per second. This makes it easy to estimate the amount of air which, when the same work is done by somebody treading bellows, is forced through a blast tube 35 mm in diameter, which was the size commonly occurring in the furnaces which Schuster had excavated.

Schuster's furnace had a stack height of 1.6 m and one tuyere. He opted for a stack diameter of only 400 mm, because the wider furnaces he had excavated must have been heavily eroded at the time they were abandoned. Subject to these conditions, cold air achieves a velocity of 50-60 m/sec rising at 1700° in the hearth to 440-500 m/sec. At this high temperature the reaction between atmospheric oxygen and the charcoal in the charge proceeds very rapidly via CO_2 to Co – in 1/1000 sec – and is thus completed in a distance of 0.4 m. In this way the blast zone comprises the entire furnace space. As the experiments proceeded it was established, by means of optical measurements, melting cones and gas analyses that temperatures of 1700° and over were attained.

Studying the transformation of the charge in the stack, Schuster found that an early precipitation of thin ferrous foils had taken place during the indirect CO reduction. Further down in the stack, wüstite and iron carburised to the composition of pig iron, occurred simultaneously, and the latter was subsequently decarburised in the FeO-rich slag, so that the end result was a carboniferous lump.

Hans Hagfeldt's Reduction Experiments[12]

Two laboratory experiments were conducted in a low, wide furnace (400 mm high and 425mm in diameter). The amount of air blown in was relatively high by comparison with other similar experiments. The charcoal was finally crushed (3-15 mm). The carbon content of the iron from the first experiment varied between 0.07 and 2.20% (4.36%) The carbon content rose from the blast tube and into the furnace. In the second experiment the carbon content was consistently low, but this experiment had to be discontinued because of a refractory slag. In neither case had the reduced iron flowed into a continuous lump. It should be noted that in these experiments the furnace was taken off blast after the final charges made up of charcoal only. Above the tuyere zone there was a drop of iron containing 4.36% C. Outside the pieces of metal and, at a distance from the tuyere, there were mainly pieces of charcoal held together by slag and foil-like ferrous scale.

The iron production experiments studied, viewed in relation to experimentally established reactive processes

Until Schuster and Straube showed that during the reduction process reduced iron passed through a stage as molten pig iron even when the end product was a more or less low carbon lump or iron, it was implicitly believed that all reduced iron remained in the solid state throughout the process. This interpretation still forms the basis of many iron production experiments. Its advocates assume that the partial reactions proceed to equilibrium in each temperature zone (cf Fig 1) and that at about 1200° it is only possible to have precipitated iron in the solid state with a maximum of 1.7% C.

It is above all Schurmann [13] and Osann [14,15] who have argued recently that the production of all iron is a kind of sponge iron process. Osann avers that no iron can be carburised until all wüstite has been consumed and that pig iron does not occur until the slag has become entirely molten and has run off the iron above the blast zone.

Wiberg's and Edstrom's studies have shown that this is quite wrong. These studies are fundamental and are used internationally for the study and development of the blast furnace process and sponge iron production. As regards modern works, mention should above all be made of von Bogdandy and Engel[16], The Reduction of Iron Ores, 1971, with no less than 759 references, and the chapter entitled Physical Chemistry by Ross et al[17] in Direct Reduced Iron published by the Iron and Steel Society of AIME in 1980. The theoretical argument in both these works is very much based on Wiberg's and Edstrom's writings, and both of them, for example, make use of Wiberg's photographs.

Bohm's observations and conclusions agree entirely with the reactive process in the reduction of iron ores as described in the above-mentioned literature.

Straube and his co-workers assume that the pig iron formed during the process results from the iron foils first precipitated – the ferrous scale or parts of ferrous scale on the surface of the pieces of ore – having absorbed carbon from the gaseous phase to such an extent as to form molten drops of pig iron. It is highly improbable, however, that the iron foils should have been capable of existing without any slagging at all during the time needed for carburisation to the pig iron stage. Although wüstite formation has not been observed, the formation of pig iron in these experiments must also have proceeded in the manner shown by Bohm. The pictures of the reduced metal (Straube [10], Figs 10, 18 and 20) bear considerable resemblances to Bohm's.

Schuster has concentrated particularly on temperature conditions in the furnace. Apart from showing that very high temperatures are bound to occur in the combustion zone, he shows by means of gas flow measurements and temperature measurements that considerable differences of temperature occur on the horizontal plane in the stack of furnaces having only one tuyere. This alone can account for the simultaneous existence of molten wüstite and carboniferous iron. He assumes that the iron foils melt and while in the molten state are carburised to pig iron. This explanation is incorrect. As is well known, volumetrically every shaft furnace for the production of iron can be deemed charged with charcoal only. The space occupied by the ore corresponds to no more than the cavities between the pieces of charcoal. As soon as molten wüstite occurs, it inevitably strikes heated charcoal.

The iron production experiments dealt with here took place

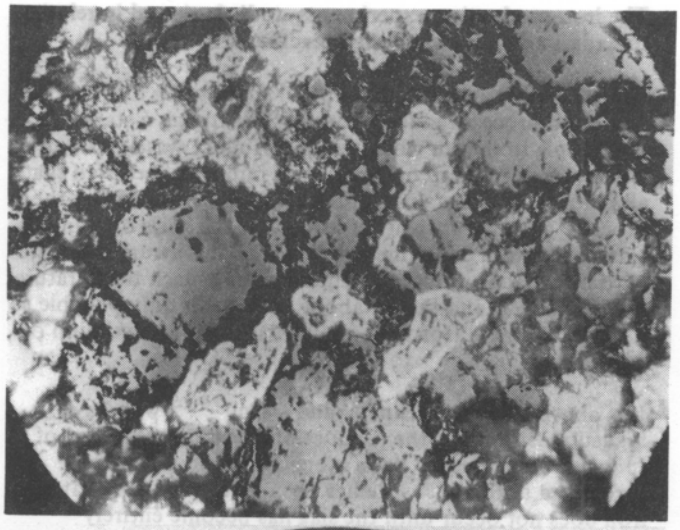


Fig 3 Partially reduced ore grain from the 3 m level, 500 x. Metallic iron at the grain surface.

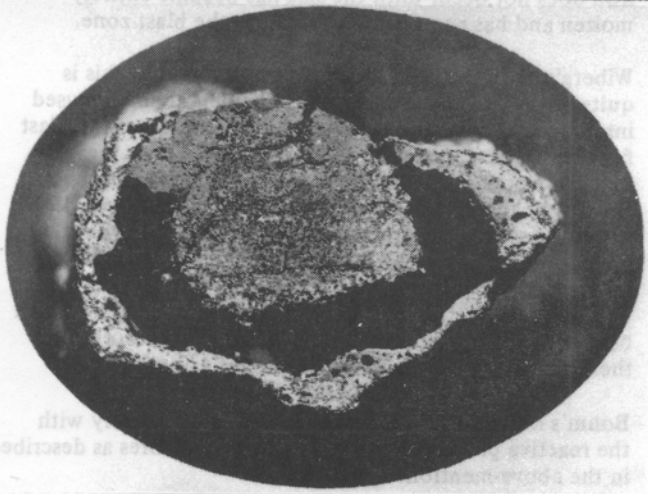


Fig 4 Ore specimen from the 3 m level, showing the cavity between shell and core, 2.5 x.

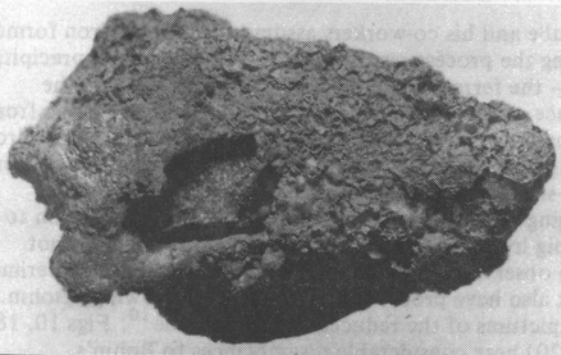


Fig 5 Ore specimen from the 3 m level, 1.8 x. The cavity between shell and core is easily seen.

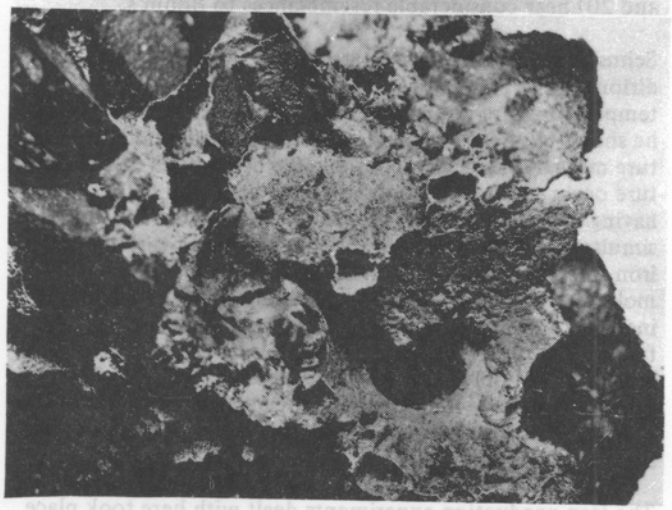


Fig 6 Surface of a lump of ore from the 3.3 m level, 1.8 x.

in a relatively small blast furnace for the production of pig iron, and also in three lower furnaces where the aim was to produce a ball of iron having a carbon content not exceeding that of hardenable steel. All these cases, of course, are subject to the same theoretical conditions, and they all involve the same reactions during the reduction of the iron from its ores. With a lower stack, the zones for the various partial reactions are compressed and the available time for reduction is reduced. The height of the furnace, however, is not the factor deciding whether the product will be a pig or a lump. The essential, crucial difference is that between continuous and intermittent operation of the furnace.

Continuously Operated Furnaces.

The prime characteristic of a blast furnace is that it is operated day after day in highly reducing conditions, which is bound to result in pig iron. Thus the advent of the blast furnace must be viewed in connection with the introduction of the water-wheel for industrial purposes, which means that furnaces of this kind must have appeared not later than the 13th century. Recent archaeological excavations have in fact shown furnaces of this kind to have existed since the medieval period.

In Sweden, a furnace only 3 m high with one tuyere and a water-powered blast has been excavated. This furnace produced pig iron which was refined in 8 hearths to low carbon iron or steel, which were then cut up into Osmund-type pieces. The slag is of the blast-furnace type, with very low FeO content. The remaining quantities of slag suggest that the furnace was operated for more than a century. The furnace ruins have been dated to the mid-14th century. Previous furnaces occupied the same site, possibly as early as the 12th century (Magnusson [18]).

During excavations in Mark, in Germany, a furnace with a water-powered blast which must at least intermittently have produced nothing but pig iron has been dated to the 13th century (Sonnecken) [19].

Intermittently Operated Furnaces

Every furnace, of whatever size, which is at full heat and charged with charcoal and is then slowly charged with ore will of course at this stage of things work in exactly the same way as a continuously operated furnace, and reduction will describe the same pattern as described by Bohm.

This process will continue as long as ore continues to be filled without reducing the amount of charcoal. As soon as one stops adding ore and, subsequently, adding charcoal and the charcoal in the furnace begins to be consumed, oxidating conditions develop in the furnace. The slag becomes FeO-rich and the carboniferous iron which has been formed is decarburised. In high shaft furnaces, enough pig iron is formed previously for a considerable proportion to remain in the hearth, but in the centre a ball is formed ranging in carbon content from soft iron to steel (the Stuckofen).

As every furnace engineer knows, the pig iron teemed when a furnace is taken off blast contains less and less carbon and the slag becomes progressively blacker and richer in oxide. The bear – ie the slag-coated iron remaining in the furnace – now has a carbon content clearly below that of pig iron. Morton and Wingrove [20] have a drawing showing ball iron formation in a coked blast furnace taken off blast in 1917. The final discharge in modern blast furnaces very much resembles the teeming of a steel furnace.

Experiments conducted by Tylecote et al [21] have not been dealt with here because no data have been available concerning the transformation of the charge as the experiments proceeded. These experiments, however, are highly important because they show that the carbon content of the bloom can be controlled by modifying the ore/charcoal ratio of the charge. No less than 28 experimental heats were produced in a furnace about 2 m high and 30 cm in diameter. One of these experiments, involving a high charcoal/ore ratio, yielded pig iron. Thus, as Tylecote [21] points out, pig iron can very well be produced even in very low shaft furnaces. The slag, however, is highly viscous unless self-fluxing ores are used. Self-fluxing ores have been used at Lapphyttan, but so have mixed silicious ores and basic ores, a procedure which remained common in Sweden well into the 19th century.

It has not been uncommon for archaeological excavations to yield individual blooms of iron with a carbon content varying up to that of pig iron. Mostly however, furnace slag is all that remains at the furnaces. Inga Serning [22] investigating prehistoric furnaces, has established in a couple of cases that the iron must have been carburised during the process and absorbed by the slag in its molten state.

References

The preceding text is a summary of the author's thesis published in 'Jernkontorets Forskning, Serie H No 27, 1983', where a more detailed list of references is included.

1 J C Waldbaum. From bronze to iron; Studies in Mediterranean Archaeology, 1978, Vol 54, Goeteborg.

2 R Linder. Termokemiska berakningar over masugnsprocessen. Jernkontorets Annaler, 1960, Vol 144.

3 M Wiberg. Om reduktion av jarmalmer med koloxid, vate och metan. Jernkontorets Annaler, 1940, Vol 124, p 179 et seq.

4 J O Edstrom. The mechanism of reduction of iron oxides. Journ Iron & Steel Inst 1953, Vol 175.

5 J O Edstrom. Solid state diffusion in the reduction of hematite. 'Jernkontorets Annaler, 1957, Vol 141.

6 J O Edstrom. Reaktionsforlopp vid kulsintring och jarnmalmsreduktion. Jernkontorets Annaler, 1958, Vol 142. pp 416-436.

7 J O Edstrom and G Bitsianes. Solid state diffusion in the reduction of magnetite. Journ Metals, 1955, 7.

8 I Bohm. A study of the blast furnace process. Jernkontorets Forskning, 1982, Serie H No 22.

9 H Straube. Untersuchungen über die römerzeitliche Stahlherstellung im Gebiet Noricum. Interner Druck. Museum zu Allerheiligen. Schaffhausen, Schweiz, 1973.

10 H Straube, B Tarmann, E Plockinger. Erzreduktionsversuche in Rennöfen norischer Bauart. Mitteilungen der Edelstahlwerke Gebrüder Bohler & Co, A G, 1964.

11 W F Schuster. Das alte Metall- und Eisenschmelzen, Technologie und Zusämmenhange. Technikgeschichte in Einzeldarstellungen. Verein Deutscher Ingenieure, 1969.

12 H Hagfeldt. Reduktionsforsok i blasta. Examensarbete vid The Royal Institute of Technology, Stockholm, 1966.

13 E Schurmann. Die Reduktion des Eisens im Rennfeuer. Stahl und Eisen, 1958.

14 B Osann. Rennverfahren und Anfänge der Roheisenerzeugung. Verein Deutscher Eisenhüttenleute. 1971. Fachausbericht 9.001.

15 B Osann. Direkter Ablauf des Rennverfahrens oder Ablauf über das Zwischenprodukt Roheisen? Die Versuchsschmelzen und ihre Bedeutung für die Metallurgie des Eisens und dessen Geschichte. Interner Druck. Museum zu Allerheiligen, Schaffhausen, Schweiz, 1973.

16 L von Bogdandy, B J Engel. The reduction of iron ores. Scientific basis and technology, Berlin, 1971.

17 H U Ross, M McAdams. Direct reduced iron. The Iron and Steel Soc of AIME. Chapt 3, part 2, 1980.

18 G Magnusson. Lapphyttan i Norberg. En medeltida hyttanlaggning. Kulturminnesvard 2/82. Riksantikvarieambetet, Stockholm, 1982.

19 M Sonnecken. Forschungen zur spatmittelalterlichen fruhneuzeitlichen Eisendarstellung in Kierspe, Markscher Kr. In: Ein Beitrag zur Entwicklungsgeschichte des Eisenhuttenwesens in Westfalen. V D Eh Fachausschussbericht 9.006. Dusseldorf, 1977.

20 G R Morton, J Wingrove, Slag, cinder and bear. Bull Historical Group, 1969, Vol 3, No 2.

21 R F Tylecote, J N Austin, A E Wraith. The mechanism of the bloomery process in shaft furnaces. Journ Iron &Steel Inst May 1971.

22 I Serning. Forhistorisk jarnhantering i Dalarna. Jernkon Jernkontorets Forskning, 1973, Series H, No 9, pp 19-49.

Nils Bjorkenstam

Graduated from the Royal Institute of Technology in Stockholm 1938. Research engineer and assistant professor at the Institution for the Metallurgy of Iron at the Royal Institute of Technology 1938-1941.

Has worked for Uddeholm Co 1941-1979. 1954-1969 as general manager Hagfors Steelworks and as member of the board of directors in Uddeholm Steel Group 1970-79. A member of the Historical Metallurgy Group of the Swedish Ironmasters Association from 1966. Chairman since 1979.

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HM Tower Armouries: Wrought iron cannon project

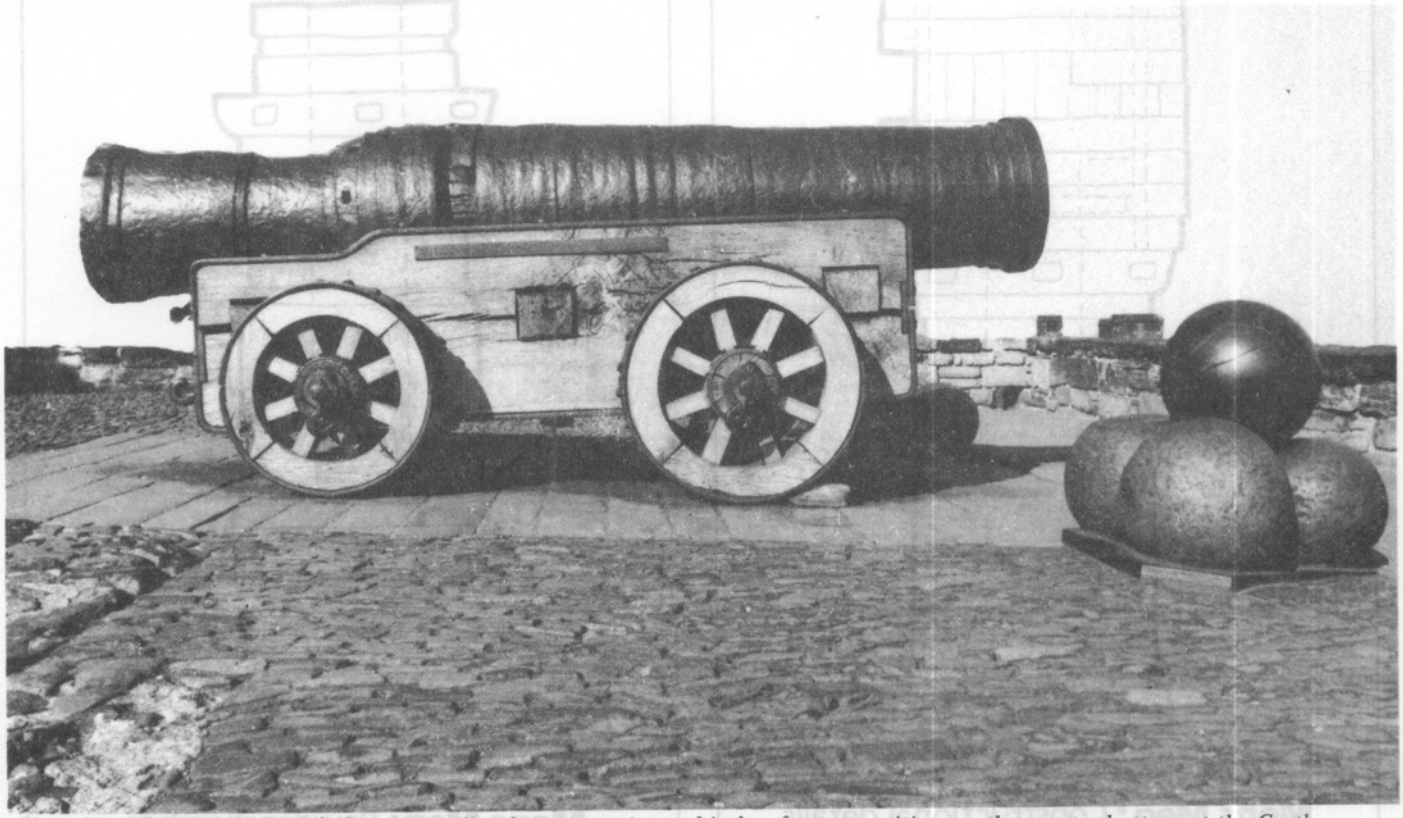
R Smith

One of the major products of the iron industry in the 15th and 16th centuries were cannon. Although much has been written about their construction and manufacture, very little work based on the examination of surviving examples has been published. The purchase, in 1980, by the Armouries of a large gun from Boxted in Suffolk sparked off an interest in these masterpieces of the medieval iron industry. This particular gun, formerly called the Eridge Mortar had disappeared from view, but not from notice, in the late 18th century, and was rediscovered at Boxted in the late 1970s. One commonly repeated 'fact' about it was that, although its barrel was made in the conventional medieval manner from wrought iron staves and bands, it had a cast-iron breech. In 1982 a small sample of the powderchamber was taken for metallurgical analysis and found to be of wrought iron. This led to a re-examination of the current ideas on medieval cannon construction in general, and a closer look at this gun in particular. Visual examination, both external and internal, and the ultrasonic probe provided little new information. Fortunately, at this time, we were offered the use of the X-ray facilities of the non-destructive testing laboratory at the Royal Armaments Research and Development Establishment at Fort Halstead in Kent. This laboratory owns and runs a 12MV linear accelerator made by Radiation Dynamics of Swindon, Wilts. This work has resulted in a research project into early iron guns which has included the X-raying of Mons Meg, the large siege gun from Edinburgh Castle.

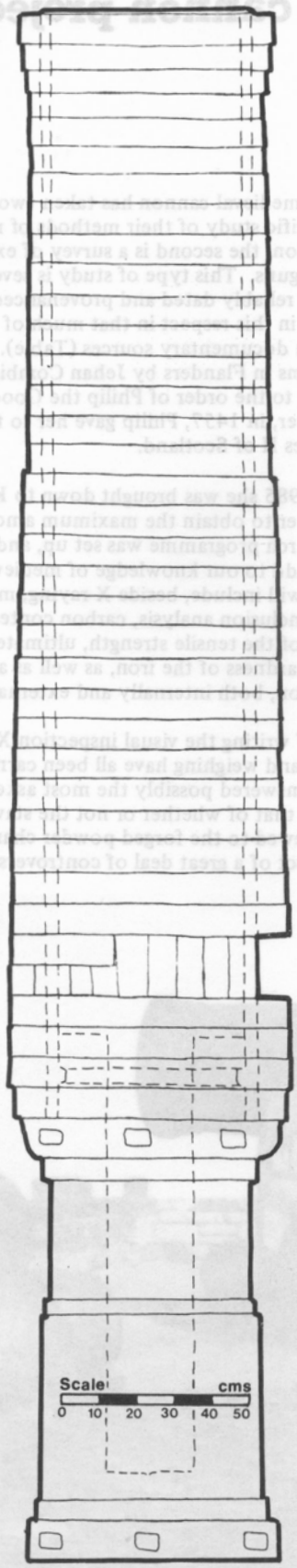
This study of medieval cannon has taken two forms. The first is a scientific study of their methods of manufacture and construction, the second is a survey of existing medieval iron guns. This type of study is severely hampered by the lack of reliably dated and provenanced pieces. Mons Meg is unique in this respect in that much of its long history is known from documentary sources (Table). It was made in 1449 in Mons in Flanders by Jehan Combier, a leading arms manufacturer, to the order of Philip the Good of Burgundy. Eight years later, in 1457, Philip gave her to the husband of his niece, James II of Scotland.

In February 1985 she was brought down to Kent to be X-rayed. In order to obtain the maximum amount of information a research programme was set up, and it is hoped that this will add to our knowledge of medieval iron technology. This will include, beside X-raying, metallurgical analysis, slag inclusion analysis, carbon contents analysis, measurement of the tensile strength, ultimate tensile strength and hardness of the iron, as well as a thorough visual inspection, both internally and externally.

At the time of writing the visual inspection X-raying, measurement and weighing have all been carried out. The X-raying has answered possibly the most asked question about the gun that of whether or not the stave and ringed barrel was screwed to the forged powder chamber. This has been the subject of a great deal of controversy. The two



Mons Meg, Edinburgh Castle's famous medieval cannon, pictured in her former position on the mortar battery at the Castle, is the centre piece of an extensive programme of research being carried out by the Armouries of the Tower of London into the construction of early iron guns. (Length 4.04 m).



Mons Meg: Constructional details

Table **A Chronology of Mons Meg**

1449 Mons Meg made at Mons by Jehan Cambier, master gunner, for Philip the Good, Duke of Burgundy. Gun tested outside Mons.

1453 Mons Meg moved from Mons to Ducal Palace at Lille, 61 stone balls ordered for her.

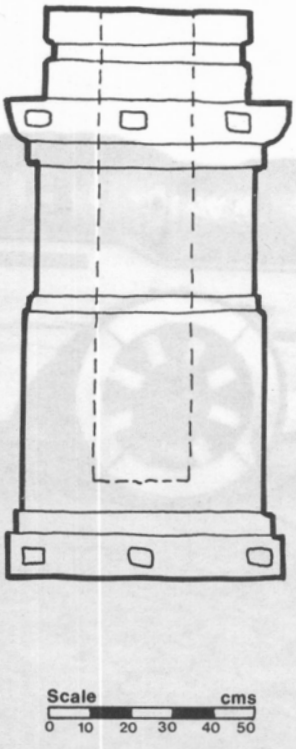
1457 Philip the Good sends Mons to the husband of his niece, James II, as a gift. She and another gun set sail from Sluys with powder and balls.

1489 First recorded mention of Mons in the Scottish records when she was part of the siege train sent to the siege of Dumbarton under James IV.

1497 Siege of Norham Castle by James IV in support of Perkin Warbeck. Mons prepared and tested prior to the siege and set off from Edinburgh Castle. Her 'cradle' collapsed at St Leonards and workmen had to build a new cradle, decorated with a painted cover. After the siege, she returned via Dalkeith.

1501 Mons had a wooden shelter built for her and the other guns in Edinburgh Castle.

1558 Mons fired salute in honour of Mary Queen of Scots' marriage to the Dauphin of France. Workmen were sent out to retrieve the stone ball, which landed over a mile away.



Mons Meg: Powder chamber

1571 Mons Meg used by Queen Mary's supporters in Edinburgh.

1633 Mons Meg thought to be unfit to fire royal salute at the coronation of Charles I in Scotland.

1660 Mons Meg fired to celebrate the Restoration of the Stuarts under Charles II.

1680 Mons Meg fired to salute James, Duke of York, the future James II. The gun burst.

1754 Mons Meg brought to England under the Disarming Acts which followed the Jacobite Rebellion. She was sent to the Tower of London.

1822 Sir Walter Scott attempted to have Mons returned to Edinburgh.

1828 Society of Antiquaries of Scotland request the return of Mons to Edinburgh. George IV gave his permission.

1829 Mons Meg shipped from Tower to Leith and returned to Edinburgh Castle.

1835 Mons' old carriage collapsed.

1836 New iron carriage made at Woolwich for Mons, with plaques recording her 'battle honours'. The model for this carriage is in the Armouries and will be lent to Edinburgh Castle in March 1985. She was placed on the Mortar Battery.

1934 New carriage made for Mons Meg, based on the sixteenth century carving in the gatehouse.

1980 Mons Meg taken to Bathgate to be X-rayed by North British Steel. She was moved to new permanent home in the French Prisons. Following scientific tests she was painted orange.

are in fact joined together by a tongue and groove arrangement. A rectangular groove has been cut into the side of the powder chamber in that part which fits into the barrel. Each barrel stave has a lug, or tongue, which fits into the groove, the whole being bound together by the external rings. I have found this type of construction on three other medieval wrought iron guns.

Over the next few months it is hoped that the remaining analyses will be completed and a detailed account of how Mons Meg was made will emerge. This work will then be related to our other work on undated and unprovenanced pieces to try and build up a comprehensive picture of this branch of medieval iron technology.

The second part of this work, the survey of existing examples of medieval wrought iron guns, is intended to help us to identify the various products of the industry, to evaluate both its diversity and its extent. It will also be used to decide the direction of future work, to help us ask the right questions and hopefully to indicate how or where the answers might be obtained.

Acknowledgements

I would like to thank a number of people for their assistance and co-operation in the course of this project. Firstly Mr T Band, Mr N Smith, Iain McIvor and Chris Tabraham of the Scottish Development Department for allowing me to bring Mons south of the border. To Alan Armstrong and his staff at Edinburgh Castle. To the director, Dr T P McLean, of the Royal Armaments Research and Development Establishment for permission to use their marvellous facilities and to Dr A Moore, Chas Hunt, Brian Radcliffe and Brian Bourne of RARDE. To Mike Cooper of Avery Ltd for arranging to have Mons weighed and to John Wiley and his crew for setting up the scales. To Bob Drewery for the loan of video equipment to inspect the inside of the gun. And to the Trustees and staff of the Armouries; especially to Ruth R Brown for continued support and for compiling the chronology of Mons Meg.

Postscript

The arrival of Mons Meg at the Tower of London on March 7th was a much publicised event which was witnessed by Charles Blick who reports:-

'She arrived by barge at The Tower Wharf at 7.30 hrs and was piped in by an escort of Royal Scots pipers. She was weighed and registered 6040 kg (5.93 tons). When her examination is complete she will be returned to the French Prison at Edinburgh Castle where she has been kept since 1981 after years of exposure to the weather on the Castle ramparts.

Mons Meg is one of the finest and largest surviving examples of Medieval heavy artillery. It is unique as it is the only piece of its type to have a documented history. There is no reference to such guns in Agricola nor in Biringuccio as they had been replaced by bronze guns by the 16th century and cast iron guns were only slowly being introduced. She was said to be capable of firing a 330 lb granite shot 2000 yards.

The rupture of the breech rings occurred in 1681 when one ring and another half ring burst off killing a man and exposing the longitudinal staves which are no longer smoothly in contact as they are in the rest of the bore.

It is hoped to estimate her maximum range by computer simulation and to draw comparisons with other medieval cannons of unknown provenance including the two in Britain, the Boxted Bombard in the Armouries, and the Bodiam Mortar from the Rotunda in Woolwich'.

We are indebted for this information to Mr Nick Norman, the Master of the Armouries; to Mr R Smith, Conservation Officer and Ian Eaves, Conservation metallurgist; and to Peter Lenoel of McAvoy, Wreford, Bayley Ltd.

Number 46235, LMS steam locomotive City of Birmingham: Metallurgical notes

Brief History

No **46235** 'City of Birmingham' entered service in July 1939 as the first of ten streamlined engines built in 1939 and 1940 at a cost of £9,437 each. 'City of Birmingham' was painted Maroon with Gold bands and was the first of the Class to be built with a double chimney. During the Second World War the engine's livery was changed to the austerity scheme of black without lining.

In April 1946 the 'City of Birmingham' was the first streamlined Coronation Class locomotive to have its streamlining removed and to be fitted with smoke deflectors. The smoke box with a tapered upper portion, fitted to suit the streamlining, was retained for several years and provides a means of dating early postwar photographs.

'City of Birmingham' was withdrawn on 12th September 1964 after covering over 1,650,000 miles. The locomotive was offered to the Museum and was delivered to the site in July 1966.

Overall Design Considerations

Previously untried and experimental materials were not utilised, and no material was built into the engine which had not already been incorporated in some form on other modern locomotives belonging to the same railway. On the other hand, the design of so powerful an engine within the allowable axleweights was not achieved without very particular thought being given to the metallurgical side, even within the limitations imposed. The problem thus resolved itself into one of restricting as much as possible any unavoidable weight increase as compared with the previous 4-6-2 type locomotives, and so designing and constructing the engine that in spite of the considerable and sustained demands made upon it, it should at all times be equal to its task, and able, therefore, to maintain the reputation of the service in respect of speed and punctuality.

The various savings in weight total over five tons, and as the locomotive is up to the limit of weight at present allowed by the company's engineering department, unless this saving had been possible a very considerable reduction in the size of the boiler and capacity of the engine would have been necessary.

2% Nickel Steel Boiler Shell

The boiler shell is constructed of 2 per cent nickel steel. The physical properties and analysis called for in the material used for the boiler and outer firebox shell, is as follows and were made at Colvilles Limited.

Analysis	Per cent
Carbon	0.2 - 0.25
Silicon	0.1 - 0.15
Manganese	0.5 - 0.7
Sulphur	0.04 max.
Phosphorus	0.04 max.
Nickel	1.75 - 2.0

Physical Properties

Maximum stress	34-38 tons per sq in
Yield point	17-19 tons per sq in
Elongation	22-24 per cent on 8 in gauge length
Reduction in area	50 per cent min
Ratio of yield point to maximum stress	50 per cent min

A saving of over two tons was obtained in the construction of the boiler shell and firebox by the use of the nickel steel, the empty weight of the boiler, including mountings, being 28 tons 3 cwt 2 qr. This represents a most valuable gain, as it permits of a boiler being used of the maximum diameter which can be mounted between the coupled wheels and within the loading gauge, and it is to be noted that the boiler centre is placed 9 ft 6 in above rail level.

Deoxidised Arsenical Copper Firebox Plate

The inner firebox is of copper, and it is specified that the plates shall contain not less than 99.2 per cent of copper; not less than 0.30 per cent nor more than 0.50 per cent of arsenic; not more than 0.05 per cent of antimony nor more than 0.01 per cent of bismuth. The tensile strength called for is a minimum of 14 tons per sq in with an elongation of not less than 35 per cent measured on a length of 8 in.

The material used for the smokebox, smokebox door, and ashpan, parts of which are subject to the corrosive action of hot ashes. These parts are made of copper-bearing steel, the specification calling for a steel having 0.30 to 0.35 per cent of copper, and not more than 0.06 per cent of sulphur or phosphorus. The tensile strength of this material is 28-32 tons per sq in., and no difficulty is experienced in fabricating it by welding, as in the case of the ashpan. The use of this steel is based on the findings of the Research Committee of the Iron and Steel Institute, which have indicated its increased resistance to corrosion, as compared with mild steel.

Cast Iron Cylinders

The mixture used in the manufacture of the cylinders was comprised of 50 per cent cylinder scrap and 50 per cent special low phosphoric pig iron. The analysis of a typical cylinder mixture is as follows:-

Carbon	3 - 3.3 per cent
Silicon	1.2 - 3 per cent
Manganese	0.8 - 0.9 per cent
Sulphur	0.1 per cent max
Phosphorus	0.5 per cent max

The cupola melting of this metal was carefully controlled, and the tapping and casting temperatures carefully watched by means of a Cambridge disappearing filament pyrometer. The cylinders were cast at a minimum temperature of 1250°C. The metal for the piston valve liners, piston heads, and piston rings, is of similar material, and the same method

of control was adopted for these details. In addition to the cylinder castings themselves, test bars were also cast; these were of the LMSR standard rectangular specimen for transverse breaking load, approximately 3 ft 6 in long by 2 in by 1 in, the centres for breaking being taken at 36 in. The specification for these bars is: breaking stress minimum 30 cwt, with minimum ½ in deflection. From the bar a hardness survey is made of the cross section, the Brinell numbers generally being in the neighbourhood of 220-230. Test bars are also cast integrally with the cylinder for tensile and transverse tests, the transverse centres in this case being 12 in. The maximum stress obtained is in the region of 15-16 tons per sq in .

Nickel Chromium Molybdenum Steel (Vibrac) Coupling Rods.

The coupling rods are of Vibrac steel, of fluted section made at the Vickers Works of English Steel Corporation Limited. A saving in weight of 412 lb on the set of four rods was obtained, compared with the previous engine, but it must here be stated that the length between the outer centres has been reduced from 15 ft 3 in to 14 ft 6 in, the weight per engine of the coupling rods, complete, being 908 lb. These rods are also illustrated. The lighter weight of the revolving parts is naturally reflected in a reduction in the balance weights carried in the wheels, and to sum up the effect of the Vibrac steel, and the re-design made possible, it may be stated that a total saving in weight of approximately 1000 lb was obtained in the reciprocating and revolving parts. The steel named gives a breaking strength of 50-60 tons per sq in, with an elongation of 20 - 25 per cent, and a value of over 40 lb in the Izod impact test.

The steel is of the well-known nickel-chromium-molybdenum type, which is forged and heat treated with a test bar attached. The heat treatment consists of oil quenching from a temperature of 840°C, followed by tempering at a visible red heat from 650-670°C, in order to relieve the hardening stresses, and the rods are subsequently allowed to cool in air from the tempering temperature. As this steel contains certain proportions of molybdenum, it is free from temper brittleness. It has been found, when certain details are quenched from the tempering temperature, that on machining there is a release of stresses which causes warping in the detailed part, and this has been obviated by the method described. This steel, which has high tensile values, is admirably suited for the stresses occurring in locomotive coupling and connecting rods. It is interesting to note that in machining these rods, the increased tensile strength made it necessary to reduce the machining speeds and feeds by about 20 per cent, as compared with the practice in plain carbon steel components.

Acid Steel 0.5% C Loco Tyre

The coupled wheel tyres of the engine are of acid steel, 6 ft 2¾ in inside diameter before machining in quenched and tempered condition and made by Steel Company of Scotland. A typical test result of this material is given below:

	Specified	Actual
Breaking strength, tons per sq in	50/55	53.37
Elongation, per cent	18/15	21
Contraction of area, per cent	-	33.4
Carbon	-	0.52
Silicon	-	0.298
Manganese	-	0.72
Sulphur	0.04 max	0.031
Phosphorus	0.04 max	0.028

In addition to the foregoing, falling-weight and impact tests are called for in LMSR specifications. In the former, every tyre selected for test is to be placed in a running position, with the tread resting on a block of metal of not less than 5 tons weight, supported on a rigid foundation; it must withstand, without fracture, blows from a falling weight of one ton, the weight being allowed to fall freely from heights of 10, 15, 20, 25 and 30 feet, until the deflection of the tyre corresponds to that given by the formula

$$\frac{(D-3\,S)^2}{45T^2}$$

where:-

D = internal diameter of tyre
T = thickness at middle of tread
S = depth of snip

In a representative actual test on these lines, 14 successive blows were withstood without fracture, the final deflection being 12¼ in. The impact test is made on a standard Izod test piece, 10 mm square, cut as close to the surface of the tread as possible. The results of this test are taken for information only, and are not specified beforehand. On actual test, a figure of 4 ft lb represents an average result.

Silicon Mangangese Leaf Springs

The ribbed silico-manganese steel used for the manufacture of the springs, was received from the contractors in long bars in the 'as rolled' condition, and complied with the undernoted specification as regards composition:-

C	Si	Mn	S	P
per cent	per cent	per cent	per cent	per cent
0.5 - 0.6	1.8 - 2.0	0.7 - 1.0	0.04 max	0.04 max

The spring plates were cold sawn to length, and the longer plates drilled to take the spring link, the shorter ones being speared at the ends. After heating to approximately 850°C, they were bent to the required camber, and cooled to below 600°C. For heat treatment, two town gas-fired furnaces were used, each equipped with a recording pyrometer for temperature control. After soaking at 890°C - 900°C for about 15 min, the plates were quenched in linseed oil. Thereafter they were tempered in a furnace standing at 800°C for 4 min for 5/8 in plates, and 3 1/3 min for ½ in plates. A hazel stick was used on the plates after withdrawal, to ensure proper temperature conditions by showing heavy sparking; or alternatively, the temperature of the surface of the plate was checked by a contact pyrometer to come within the range 450°C - 500°C.

Bearing Metals for Axle Boxes

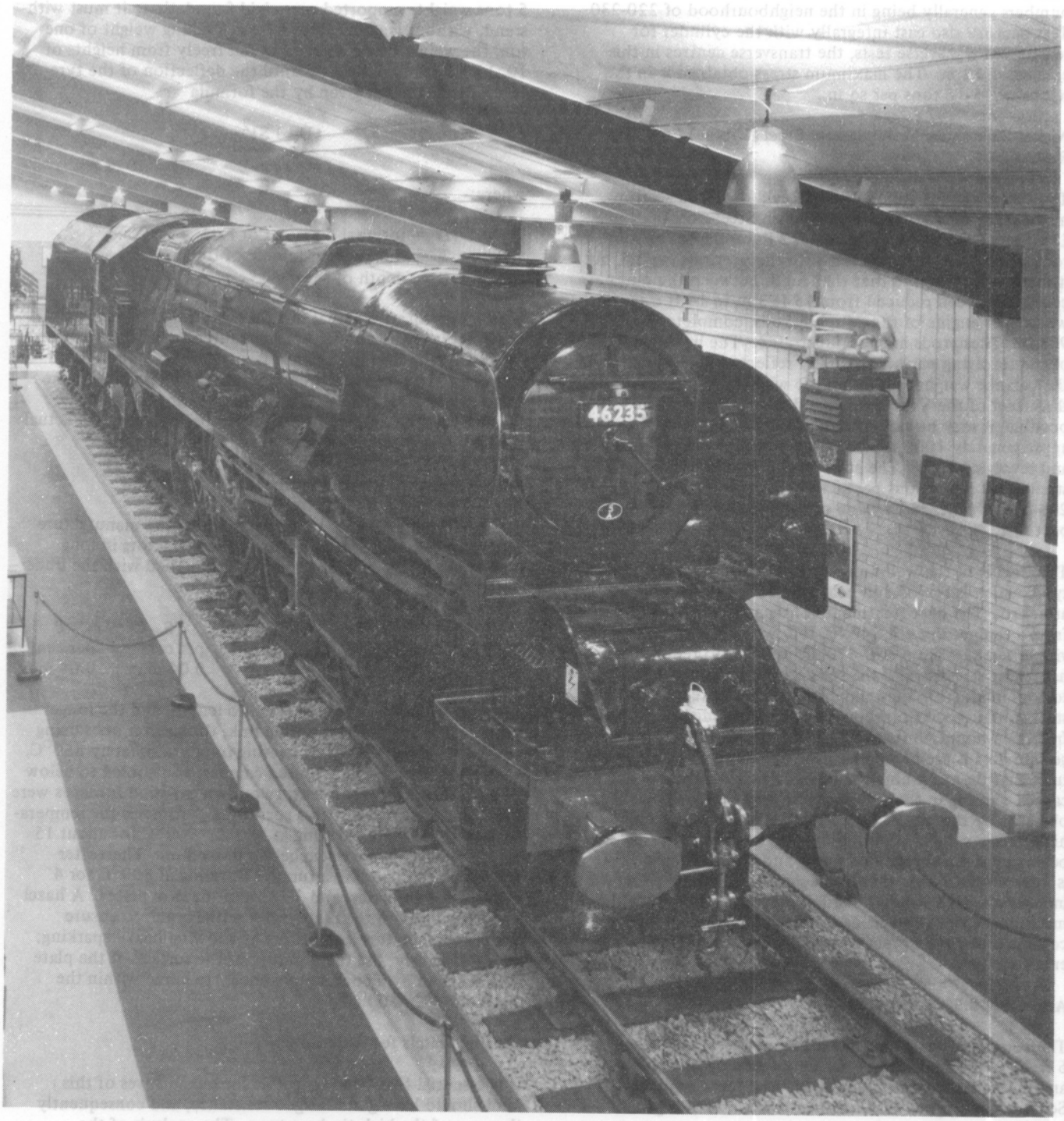
It is essential that bearing metals for locomotives of this kind should have good fatigue resistance, and consequently they are of the high-tin base type. The analysis of the metal used on the big and little ends of the connecting rods and the axlebox bearings, is as follows:-

Tin	85 per cent
Copper	5 per cent
Antimony	10 per cent

The tinning medium used is an alloy of the following composition:-

Tin	59.0 per cent
Antimony	9.5 per cent
Copper	3.0 per cent
Lead	28.5 per cent

46235 dominates the Locomotive Hall at Birmingham Museum. In fact the Hall was built around the 'City of Birmingham' which weighs 125 tons and was moved into its final position by another exhibit, 'Busy Bee', a Burrell Steam Tractor.



The noted reproduced above were prepared by Professor Alexander for visitors to the Birmingham Museum of Science and Technology on Saturday 22nd September 1984. In the following pages there are metallurgical comments on exhibits in the Birmingham Museum and in the Museum of British Road Transport in Cook Street, Coventry, which was visited on the same day.

Alloys and the Motor Trade: 1900 - 1950

Non-Ferrous Castings in Automobiles

The foundries in the Midlands have always been connected with production for the motor trade and many examples of their work will be seen in exhibits in the Museum, although on Saturday morning we are highlighting the 1923 Austin Seven and the 1935 Austin Lichfield. One of the largest Midland foundries entered the field almost by chance. In 1900 Birmingham Aluminium Casting Company had been engaged in brazing tubes for bicycles and they also developed a process for holding the tubes together by casting aluminium around the joints. One of their employees, Hugh James Owen, happened to see a French motorcyclist whose machine had broken down; he helped him with the repair and afterwards they got into conversation. The Frenchman, a Monsieur Clement, confided that he was about to produce petrol engines in Britain and wanted a source of aluminium castings. Mr Owen at once said 'I'm your man', took him to the works, and got the first order for motor trade aluminium castings. Monsieur Clement went on to establish the Clement-Talbot Company, which later became Sunbeam-Talbot Ltd.

In 1912 Birmingham Aluminium investigated the gravity die casting process and soon after that they started manufacture of aluminium alloy pistons, a very specialized part of the industry that has accounted for millions of gravity die castings in many parts of the world. The use of the light alloy piston helped to make possible the high speed motor engine. Aluminium alloy pressure die casting was developed in about 1927.

During the First World War the production of casting companies was directed to the making of machine gun parts, fuses and aircraft components. The following reminiscence is hardly metallurgical but those who are familiar with the Birmingham Repertory Theatre may like to know that actors from the old theatre dedicated voluntary Sunday work to Birmingham Aluminium. Sir Barry Jackson and the dramatist John Drinkwater both worked in the gravity die casting foundry on Sunday. They received pay and all the actors pooled the money and voted on which charity should receive the proceeds.

The two Austin cars which are exhibited at the Museum indicate the growth of non-ferrous castings during the period directly after the First World War. The Austin Seven is produced mainly from steel, cast iron and a few items in brass. The Austin Lichfield manufactured in 1935, shows how in the intervening twelve years more use was made of non-ferrous metals. So far as I can ascertain the Lichfield has an aluminium cylinder head and probably a few more engine components.

It is easier to see that by 1935 the Austin cars had begun to use zinc alloy die castings. If you look at the Austin Seven it will be seen that bodywork fittings were mainly of brass but by 1935 several zinc alloy die castings were involved. For example at the sides of the bonnet there are some little ventilator handles which my Company, Fry's produced in 1935. We also produced the winged badge at the front of the radiator.

Early in the 1930s Wilmot Breeden of Birmingham, Josiah Parkes of Willenhall and the Wolverhampton Die Casting Company were becoming involved in making car door handles, the locks for the handles and a wide range of other car body fittings. They began with Austin, Morris and Standard, but later widened their scope to other cars at home and abroad. I have said something about this development in the paper on zinc alloys to be given later.

In the 1920s the carburettors of most cars were cast in gun-metal, but in the early 1930s the Zenith Carburettor Company developed the use of zinc alloy die castings and the increasing sophistication of carburettor design made it more and more important to get the benefit of the die casting process because the many small holes could be cast with accuracy.

During the later 1930s the Morris/Austin cars began to use SU carburettors but soon they changed to aluminium alloy. As will be told in the paper on zinc alloys, there were serious problems with alloy contamination in the early 1930s. Some companies whose housekeeping was not very good allowed their zinc alloy to become contaminated and the castings cracked. Others, who had suspected that zinc alloys needed to be absolutely contamination-free, succeeded in making more reliable die castings. However in the early 1930s the SU Carburettor Company had some unfortunate experiences with cracked zinc alloy and they changed to aluminium alloy – and still use the same type of material.

Before the 1939 war many of the aluminium castings produced were of a fairly impure aluminium silicon alloy. During the war, when it was imperative to use scrap material wherever possible, two diecasting alloys were developed, both of which could be made from crashed aircraft, factory scrap and the many pots and pans that were handed in following the appeals of Lord Beaverbrook. LM4 (known at first as DTD 424) was developed for gravity diecasting, containing 4-6 per cent silicon, 2-4 per cent copper and several small amounts of allowable impurities. For pressure diecasting LAC112, later classified as LM2, contained 9-11 per cent silicon and 1-2 per cent copper. Both these alloys could be made from scrap and both proved satisfactory for the gravity and pressure die casting processes – and with some slight amendments in their composition and a somewhat tighter control of impurities both are used at present.

Arthur Street

Nodular or Spheroidal Graphite Iron. 1947

Until 1947 all machinable engineering cast iron components which could be used in their as-cast condition were characterised by having a structure containing carbon in the form of graphite flakes which could easily be seen under the microscope. This structure resulted in the well-known brittleness of cast iron and its relatively low strength, as

well as the grey fracture appearance from which grey iron takes its name. Increased strength and ductility could be obtained in cast iron at that time by adjusting the composition so that in the as-cast state components were hard and brittle, and before use a prolonged heat treatment was necessary to remove iron carbide and develop a graphite structure consisting of clusters of graphite in a nodular form.

In 1947 the discovery was made that small amounts of cerium or magnesium of the order of 0.04 per cent, together with graphitising inoculation with ferrosilicon, could cause the graphite present in the as-cast state in engineering irons to assume a compact nodular or spheroidal shape, conferring strength and ductility on otherwise ordinary grey cast iron. This new kind of cast iron paved the way for the commercial production of nodular graphite or spheroidal graphite cast irons having at least twice the strength of ordinary grey iron, with ductility up to 30 per cent measured on a test bar in the as-cast state.

Widespread use of these irons, variously known as nodular irons, SG irons or (in the United States) ductile iron followed rapidly. Early applications included agricultural machinery, automobile components, and outstandingly, crankshafts for passenger cars, adopted first by Ford and later by other manufacturers. The magnesium process has become the most versatile and widely used.

Subsequently production of these irons rose to 10 per cent or more of total engineering iron production in most developed countries, and in addition to growing applications for many engineering purposes have found application in cast iron water and gas pipelines.

H Morrogh was the British inventor of the cerium process which resulted from classical painstaking and logical research. K D Millis, A P Gagnebin and N B Pilling developed the magnesium process in the laboratories of Inco at Bayonne, New Jersey, USA, in the course of research aimed at finding substitutes for expensive or strategic alloying elements.

Ian Hughes

Museum of British Road Transport – Coventry

Of the many exhibits at the museum available for viewing, four vehicles were selected for a detailed metallurgical study of selected cast engine components in an attempt to cover the theme of the 20th Annual Conference. The 1910 Maudslay car and the 1948 Maudslay coach together with the 1897 and 1950 Daimler cars represent the beginning and the end of the period under consideration at the conference.

An example of an aluminium alloy, bronze and cast iron component from each car was sampled by drilling and the drillings analysed by x-ray fluorescence techniques. The carbon content of the cast irons was determined by wet analysis.

Commentaries on the results together with a short history of the Muadslay and Daimler car companies are presented here prior to visiting the museum. Additional information can be

The Maudslay Company

The Maudslay Company was set up in Coventry at Parkside in 1902 by Cyril C Maudslay, a great-grandson of the outstanding engineer, Henry Maudslay. Henry was an exceptional engineer who worked with Brunel remodelling the Royal Navy's block making plant. He later founded the Maudslay, Sons and Field Company where marine engines for the British Navy were manufactured. It is interesting to note that Maudslay employed as apprentices James Naismith and Joseph Whitworth. With many years of naval development and design experience it is not surprising that Maudslay cars were built to last and were also easy to service. The design of the engine on the 1910 Maudslay car is attributed to Alex Craig (who also designed engines for Lea Francis and Hillman) and it is designed in the Maudslay naval tradition. Only the best materials were used and easy maintenance was achieved since (a) the camshaft is secured by four nuts, undo these and the camshaft can be swung back on its hinges to allow access to the valves; (b) a piston can be changed in 15 minutes; (c) the Maudslay Company were the first to replace the chain drive by a live rear axle, and on this model the differential and rear axle driving gear can be removed from the car without the use of jacks.

All wonderful ideas but hardly necessary, since the components were so massively over-designed in both materials and dimensions that failure was extremely remote. However, aluminium was introduced to cut down weight.

The Maudslay Company had been manufacturing buses since 1905 and after World War I they concentrated almost exclusively on commercial vehicles. The motor car manufacturing was finally closed down in 1926 in order to concentrate on the manufacture of lorries and large passenger vehicles, where their reliability and hill climbing potential contributed significantly to their success in the thirties and forties.

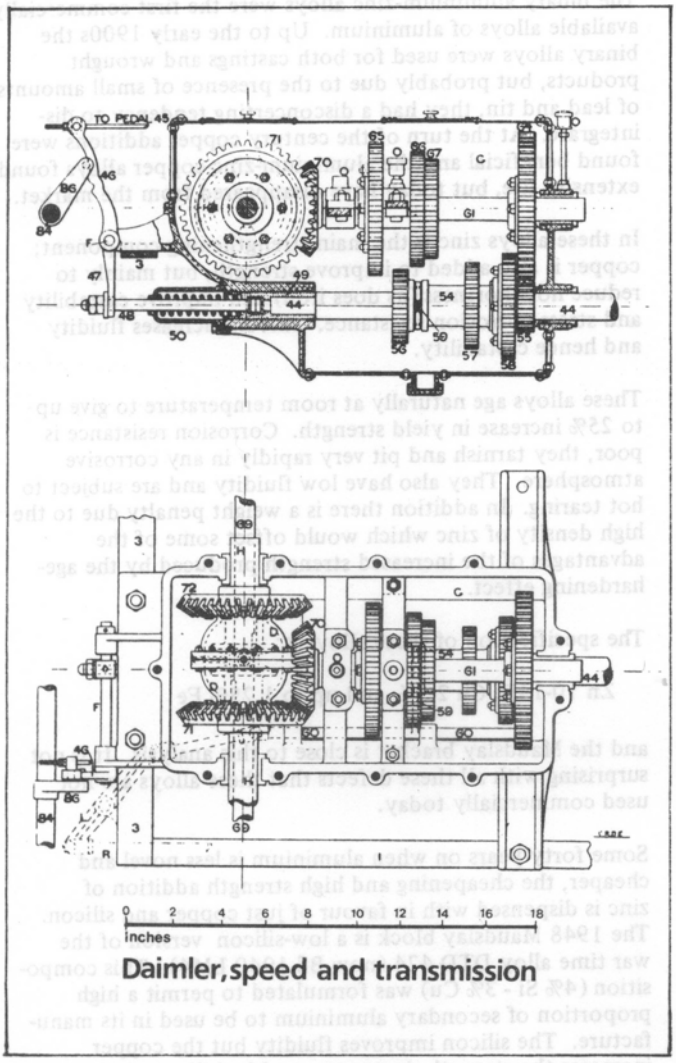
In 1951, Maudslay were absorbed by the AEC group but the name still survives as part of the Rockwell group at Alcester where heavy commercial vehicle driving axles are produced.

The Daimler Company

There is some doubt as to who built the first car in Britain using the internal combustion engine for the power source, but there is no doubt that the first British motor car to go into mass-production was the Daimler.

The Daimler Company originated from the visit of a young mechanical engineer, F R Simms, to an engineering exhibition at Bremen in the 1880s. At this exhibition, there was a passenger trolley propelled by an internal combustion engine. Simms realised the potential of the small power unit and he approached the inventors Daimler and Maybach and secured the patent rights of the Daimler engine for the United Kingdom.

On the 16th May 1891, the first Daimler engine arrived in this country, and by 1893 after many setbacks the engine had found numerous applications. This success stimulated Simms into setting up a private company called the Daimler Motor Syndicate with an initial capital of £6000. The major difficulty at this time was the Red Flag Act and when Parliament repealed this Act in 1896 allowing a speed of 12 mph, it gave the green flag to the British Motor Industry. It was around this time that Lawson, Hooley and Rucker purchased the Daimler Motor Syndicate from Simms. This led to the production of cars in an old cotton mill on Sandy Lane, Coventry and by November 1897 quantity production of Daimler cars was well under way.



Daimler, speed and transmission

The 1000 mile time trials in 1900 had an important effect on the company's future. The success of Daimler vehicles in this event persuaded the Prince of Wales (later King Edward VII) to buy Daimler. This led to the now famous association of Royalty and Daimler cars which lasted for fifty years.

In 1910 the BSA group acquired the controlling interest in Daimler and in 1931 they also acquired the Lanchester Company. In the following year the Daimler fluid fly wheel became a feature on all Daimler vehicles.

In 1960, Daimler was acquired by Jaguar. In 1966 the group merged with BMC and two years later the giant BL group was created. The Jaguar/Daimler company is an independent group within BL and the Daimler name still survives as a prestige marque. Recently Jaguar has 'gone private' and is no longer part of BL.

Comments

Bronze

The Bronze samples illustrate the changes in composition of these alloys which took place from 1900 onwards.

At the turn of the century the favoured composition for bronze castings for engineering uses, mainly for bearings, was 90% copper and 10%tin, sometimes with small amounts of zinc or lead being added at the expense of copper.

The 1897 water pump is of this composition – specifically the alloy designated 'Admiralty Gun Metal' of nominal composition 88% copper, 10% tin and 2% zinc, which was found to be reasonably resistant to corrosion by sea water and similar media. Zinc was added to improve its castability.

In the next few decades lead was added for applications involving the need for easy machining (such as these) and, as tin became proportionally more expensive than lead or zinc, and also in the two World Wars in short supply, alloys of lower tin content with more zinc and lead were demonstrated to be quite suitable for many engineering applications with the nominal 'three fives' alloy, Viz 85% copper, 5% tin, 5% zinc, 5% lead – also designated 'Leaded Gun Metal' – becoming popular. By 1950 in UK, three alloys, based on 3%, 5% and 7% tin, had been standardised and the most recent issue of the relevant British Standard Specification – No 1400 – 1973 – lists only two ranges, Viz.

Designation	Tin	Lead	Zinc
LG2	4.0 - 6.0	4.0 - 6.0	4.5 - 6.0
LG4	6.0 - 8.0	2.7 - 3.5	1.7 - 3.2

with a note indicating that recent research work and ex-

Bronze Components

Exhibit Description	Date	Chemical Analysis (%) Cu	Sn	Zn	Pb	Fe	Ni	Ag	Sb	As
Bronze Water Pump – Daimler	1897	84.42	11.19	2.51	0.20	1.12	0.03	0.01	0.01	0.53
Bronze Valve Cover – Maudslay	1910	84.96	6.58	6.77	1.20	0.08	0.07	0.01	0.05	0.28
Universal Camshaft Coupling – Maudslay	1910	86.02	7.71	2.08	2.95	0.33	0.06	0.02	0.69	0.18
Induction Manifold – Maudslay	1948	84.21	6.67	3.69	4.52	0.33	0.19	0.02	0.30	0.27
Oil Filler Cap – Daimler	1950	86.63	7.80	3.27	1.75	0.40	0.17	0.01	0.11	0.02

perience has shown that the majority of applications could be met by these compositions.

Cast Iron Components

Exhibit		Chemical Analysis %			
Description	**Date**	**C**	**Si**	**Mn**	**P**
Cylinder block – Daimler	1897	3.4	3.1	-	1.0
Exhaust manifold – Maudslay	1910		2.9	1.3	1.4
Exhaust manifold – Maudslay	1948	3.4	1.6	0.3	-
Thermostate housing – Daimler	1950		1.8	0.6	0.1

Comments

The 1897 Daimler cylinder block has a composition common of the time with its high silicon and phosphorus. Silicon strengthens the ferrite and promotes the formation of graphite and can therefore be used to control the production of a machinable grey iron. The silicon content is varied according to casting thickness, a thin section would require a high silicon to avoid the formation of a white iron. Phosphorus renders the metal very fluid due to the formation of a low melting point constituent which aids the feeding and running of thin sections. For the production of sound castings in heavy sections, the phosphorus content should be reduced to less than 0.3% to avoid shrinkage porosity.

The 1910 Maudslay exhaust manifold also contains a high phosphorus level again to improve the fluidity of the iron and enable thin sections to be easily cast.

The silicon content of the 1948 Maudslay exhaust manifold is low compared to that normally used for such applications.

The 1950 Daimler thermostat housing has been manufactured from a modern high-grade 'cylinder' iron, with the low phosphorus ensuring freedom from shrinkage porosity, in thick sections. The analysis is typical of cast iron currently being produced to BS 1452 Grade 260, a common alloy used for a variety of vehicle parts.

Aluminium Components

Exhibit		Chemical Analysis %			
Description	**Date**	**Zn**	**Cu**	**Si**	**Fe**
Bracket – Maudslay	1910	13.6	5	2.2	1.8
Engine block – Maudslay	1948	-	3	2.1	1.4
Induction manifold – Daimler	1950	-	3.2	3.2	0.5

Comments

The binary aluminium-zinc alloys were the first commercially available alloys of aluminium. Up to the early 1900s the binary alloys were used for both castings and wrought products, but probably due to the presence of small amounts of lead and tin, they had a disconcerting tendency to disintegrate. At the turn of the century copper additions were found beneficial and the aluminium-zinc-copper alloys found extensive use, but today have disappeared from the market.

In these alloys zinc is the main strengthening component; copper is also added to improve strength, but mainly to reduce hot shortness (as does iron) and improve castability and stress corrosion resistance. Silicon increases fluidity and hence castability.

These alloys age naturally at room temperature to give up to 25% increase in yield strength. Corrosion resistance is poor, they tarnish and pit very rapidly in any corrosive atmosphere. They also have low fluidity and are subject to hot tearing. In addition there is a weight penalty due to the high density of zinc which would offset some of the advantages of the increased strength produced by the age-hardening effect.

The specification of these alloys is:

Zn 10-14%, Cu 2-3%, and up to 1.25% Fe

and the Maudslay bracket is close to this analysis. It is not surprising with all these defects that these alloys are not used commercially today.

Some forty years on when aluminium is less novel and cheaper, the cheapening and high strength addition of zinc is dispensed with in favour of just copper and silicon. The 1948 Maudslay block is a low-silicon version of the war time alloy DTD 424 (now BS 1940 LM4). This composition (4% Si - 3% Cu) was formulated to permit a high proportion of secondary aluminium to be used in its manufacture. The silicon improves fluidity but the copper increases the strength, improves machinability but reduces ease of casting, corrosion resistance and ductility. Such alloys are in widespread use for automotive castings but have casting properties inferior to those of the pure but more expensive aluminium-silicon alloys.

The 1950 Daimler induction manifold is again a version of LM4 but the slightly higher silicon content of this alloy over the 1940 Maudslay block would give increased fluidity and hence better castability.

Acknowledgements

The author would like to thank Mick Bullivant, Sam Temple and Sam Apsley for helping to prepare the commentaries on the alloys, and the Department of Applied Physical Sciences for the chemical analysis.

Ron Blackwell

Transformer core steels

In 1831 Faraday achieved his ambition of converting 'magnetism into electricity': the experimental device consisted of two coils of wire wound onto an iron ring: switching on the current in the first coil induced a current

in the second: he had invented the transformer. The core of the modern transformer is the equivalent of Faraday's iron ring ie a 'soft' magnetic material for transmitting the induced magnetic field produced by the primary winding to the secondary windings. This requires a material of high magnetic permeability ie the ability to carry the highest possible density of magnetic flux, yet it must also have the least resistance to changes in the magnetic flux when the magnetic field is reversed: its residual magnetism or coercivity must be extremely low: ie it must be magnetically soft as opposed to a permanent or 'hard' magnetic material.

The efficiency of a modern power transformer is about 99.6% much of which has been brought about by developments in soft magnetic materials. In 1885 the first commercial transformer was built by George Westinghouse using for the core the softest magnetic material then available, wrought iron: subsequent analysis showed that it contained: 0.046%C, 0.05% Si, 0.036%S, 0.019%P, 0.059%N. By 1900 the efficiency had improved by using Swedish charcoal-iron, but the first major improvement that reduced core losses by almost threefold was in 1900 by Barratt, Brown and Hadfield following their investigation into iron-silicon alloys. It is reported that the adoption of these new alloys saved the electrical industry some $340 million in its first 17 years of use. The discovery of the silicon irons seems to have been initiated by chance since Hadfield was actually investigating the abrasive possibilities of iron silicon alloys. Undeterred by this initial failure he persevered with the iron silicon alloys but found severe processing problems: being killed they exhibited excessive piping and shrinkage: the ingots were extremely brittle (silicon raises the ductile-brittle transition temperature) and as a result the cost of the steel was very high: development of the alloy took seven years and it was not until 1906 that the first material was sold.

In 1900 Hadfield chaired a meeting of the Faraday Society on the magnetic properties of alloys. Having carefully laid claim to have already published a considerable number of papers on magnetic properties, he discoursed on the non-magnetic properties of iron manganese alloys, before introducing a paper by Professor Gumlich on iron silicon alloys. Gumlich, to whom much of the credit should be given, determined that 4.5% Si was the optimum level of addition and also showed that silicon had marked influences on the A1 temperature. The problem with Gumlich's alloys was that they contained 0.2%C but he claimed that thinner sheets (presumably decarburised), containing 4.5% Si had the best magnetic properties.

The next thirty years were a period of slow development. The major improvements stemmed from a reduction in the impurity contents, particularly carbon, and a consequent decrease in coercivity. Gumlich had recognised that a high electrical resistivity was required to suppress eddy currents; this together with the improved understanding of magnetic alloys led to the development of essentially binary alloys of approximate composition Fe - 4% Si, silicon providing the necessary magnetic and electrical properties.

Developments in physics following the stimulus of the First World War led to the investigation of the magnetic properties of iron-silicon single crystals. In order to grow single crystals it was necessary to stabilise iron in the ferritic form by keeping carbon low and exploiting the ferrite stabilising effect of silicon. These developments coupled with progress in x-ray diffraction and magnetic measurements showed that iron silicon is magnetically anisotropic ie specific crystal directions eg<100>and<110> can pass more magnetic flux than others; the problem was how to construct a large enough perfect single crystal to take advantage of this effect in a transformer. In 1933 Norman Goss went one better than this by patenting a process for producing polycrystalline silicon steel which had the overall magnetic characteristics of a single crystal but the advantage of being poly-crystalline thus giving it the higher resistivity necessary for reducing eddy-current losses. Goss found by trial and error that certain combinations of heat treatment and cold rolling on a 3.5%Si steel resulted in strip of high magnetic anisotropy. Unfortunately Goss misinterpreted his X-ray results and claimed that the improvement was not as a result of preferred orientation in which the individual crystal magnetic properties were aligned. This caused some puzzlement among the contributors to the discussion of his paper who expected, correctly, that a strong preferred orientation should have been present. Ruder of General Electric provided a very accurate analysis of what had actually occurred predicting the 'Goss texture' exactly. He also queried Goss' claim to having produced a fine grained steel and showed micrographs resembling the typical secondary recrystallised large grain structure familiar today. Goss did however determine the process route for encouraging the growth of the 'Goss' texture, even if his explanation was in error, and the result was a reduction in core loss to a third of the 1900 value and a tenth of the 1885 value. The savings in electrical power production as a result of the work of these pioneers is incalculable.

Michael Wise

Extracts from a Notebook of personal recollections

David Flather

The first paragraph was written by Kenneth Barraclough who is responsible for the presentation of the extracts. He also wrote the final comments at the bottom of page 205 and at the top of page 206.

David Flather was a member of a notable Sheffield family of engineers and steelmakers whose activities had roots early in the nineteenth century and who, early this century, were pioneers in the production of precision drawn steel bars. He was born in 1864 and towards the end of his long career he became a pioneer in the field now known as Industrial Archaeology as a founder member of the Society for the Preservation of Old Sheffield Tools, now past its Golden Jubilee as the Sheffield Trades Historical Society. He left a notebook of personal recollections and it is from this valuable document that these extracts are taken, by kind permission of his family.

I left School in June 1880, having made no achievement or little real profit of the six years I spent there. I had, however a strong leaning to Science and Literature – both of which have been of value in my life. Perhaps Chemistry and Physics were the chief subjects in which I was interested. On leaving School my father made arrangements for me to spend some years as a 'pupil' at the works of John Brown. In the interval between leaving School in June and commencing work in September I attended classes in Chemical Analysis given by A H Allen, the Borough Analyst, and also attended lectures in Chemistry at the Firth College – given by Andrew Carnelly – and on Crystallography by Hilary Bauerman.

On 20th September I started my career at Atlas Works. It had been arranged that I should first spend a year in the Steel Department of which Mr Henry Machen was Manager. I was not to receive any salary but, although nominally a Junior Clerk, I was given complete liberty to wander round the works and to visit every department in order to acquire a general knowledge of the many branches of the Steel Trade.

I took ample advantage of that privilege and was especially interested in the Crucible Steel Department, the Converting Furnaces and the Bessemer Department. I also found much interest and instruction in the Forges and Rolling Mills and Puddling Furnaces; in fact, I found in every branch much to learn and much was of the utmost value in my later life.

As it will be gathered by the foregoing, my duties as a Junior Clerk in Mr Machen's office were very small. It was generally engaged in the writing out of orders for the Sheffield Rolling Mills and for the 'South Forge' Rolling Mill, checking the delivery notes, etc. The South Forge was engaged chiefly in rolling small rails for colliery purposes and small diameter rounds and square bars, all produced by the Bessemer Process and cogged down to billets in the North and South Forges. (I might add here that my father bought considerable quantities of Bessemer bars for resale and billets which he had rerolled by the Hallamshire Steel and File Co.)

I gathered a good deal of information on my frequent visits to the Crucible Department and with my talks with the head melter and after a few months I was entrusted by Mr Machen with the job of wrapping up the packets of 'physic' for the melter. It should be noted that the making up of the 'physic' was only done by Mr Machen himself.

Each packet of physic weighed about one pound and consisted of (1) lump charcoal, (2) sal ammoniac (3) spiegeleisen and occasionally an alloy that I now know to have been ferrochrome.

There was very little work done in the converting furnaces at that time but I did have one opportunity of seeing a single heat prepared and fired. It was a most interesting and useful experience.

I spent much time in the Bessemer Department and acquired a good deal of knowledge from Mr Richards (Manager) and 'Tom Adams' as he was called – the real manager of the shop. His full name was Tom Adams Freeston.

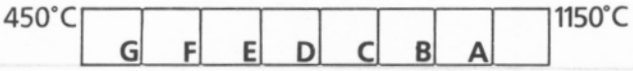
I spent a great deal of time in the Steel Warehouse where I had chance to examine the steel bar fractures – for all finished bars, in addition to being measured for size, were 'ended', that is, the ends nicked and broken and then carefully examined by the head warehouseman, Tom Kelk, who, like all the old steel men, could judge the 'temper' of the bars as closely by sight of the fracture as could any analytical chemist.

It was during my many visits to the Steel Warehouse that I made some observations, theories and experiments that formed the foundation of my later success. Having seen the preparations for melting of crucible steel, which consisted in breaking up the 'blister' steel by a heavy hand hammer and that the blister steel – that being bar iron in the condition in which it existed when it had been 'converted' – was of extreme brittleness, I could not quite understand why the same bars which, instead of being broken up, were sent to the Rolling Mill or Forge and reduced by heating and stress so as to lose its brittle nature and become intensely strong. I at first attributed this change to the closing up of the 'grain' by mechanical work; in order to test out this idea, I took a piece of blister steel intending to forge it down by hammering; for some forgotten reason, my experiment was interrupted after I had heated the steel to forging heat and therefore the trial piece was laid aside without being put under the hammer. The following day, intending to complete my experiment, I first tried to break a piece off one end to examine the fracture; to my surprise, I found it impossible to break it without first nicking the end; when I did succeed in making a break I found that the steel had lost its coarse crystalline and brittle structure and become fine grained and tough. So that by heat alone this great change had resulted without either mechanical working or by quenching in water.

The result of this experiment led to a second effort but this time I had an ascertained fact to guide me. Taking another piece of blister steel I broke off a piece about 18" long, first making and preserving a fractured specimen of each end.

I then inserted one end of the test piece in a smith's hearth and heated it so that the front end came to a white welding heat (probably about 1150°C) the remainder being a steadily

graduated 'colour heat' down to the back end which was a very dark red or 'black hot'. At that time there was no pyrometer or means of measuring the heat – but as I remember it the temperature passed from 1150°C and uniformly down to 450°C or below. The piece was then withdrawn from the fire and allowed to cool in the air. The test piece was then nicked at the points A to G and the fractures shown as follows:



A Very coarse crystalline but not like the original
B Crystalline and Brittle
C Finely crystalline and tougher
D Very fine crystalline
E Inclined to be fibrous, crystalline
F Coarse crystalline and brittle
G Practically unchanged blister steel structure

This experiment gave me the absolute truth that the coarse crystalline brittle structure of the blister steel can be altered or refined by heat alone without being submitted to mechanical work or by quenching in water and that the finest structure can be obtained by heating to a full cherry red (800°C).

Later I made a third experiment which consisted of heating a length of blister steel to a low cherry red (about 720°C) and quenching in water; this on fracture showed a uniformly very fine slaty crystalline structure of intense hardness, in fact it was like hardened razor steel.

In January 1882 I was moved to the Laboratory in the Blast Furnace Department, of which Mr Thomas Blair was Manager. There were two Blast Furnaces, one being used for the production of Forge and Foundry Iron and the other for Spiegeleisen. A third furnace was built in 1882 and was mainly used for making Ferromanganese.

The Laboratory was a small building on the ground floor opposite No 1 Furnace. It consisted of a balance room, a working laboratory and a porch. The latter was fitted with a hand drill for sampling and mortars for crushing coke, coal and ore for sampling and analysis. A steam heated still produced ample supplies of distilled water. Air under pressure from the blowing engine was used for the blowpipe and ignition purposes and gas supplied from the company's gas works.

The Chief Chemist was Ernest Wheatcroft who had started as a 'gate boy' at the works but who had been helped by Mr Richards and Mr Blair to study chemistry and to equip himself for the post. Wheatcroft used to receive from Mr Blair many samples which were analysed for Robert Hadfield. I might explain that at that time Hadfields had no laboratory. It is to me a great memory to know that I made many analyses of steels which Hadfield produced, being his famous Manganese Steel. About 1884 Wheatcroft went to Hadfields and established their own laboratory and I was given charge of the Blast Furnace Laboratory.

While I was working under Wheatcroft at the Blast Furnace Laboratory I was at first put to checking analyses of special materials which had already been analysed by Wheatcroft. Amongst these was a long series of iron ore, cast iron, slag and steel, the result of the first trials for making Basic Bessemer by the Thomas and Gilchrist Process. The trials were made by Bolckow, Vaughan and Company, Middlesbrough, and they all were the results of Blow No 59 and dated 23rd April 1879. I will not load my story with any details of the results as they are all fully recorded in the Transactions of the Iron and Steel Institute. There is, however, one point of personal interest. When analysing a sample of the slag resulting from Blow 59 I found it contained about 30% of lime and 3.85% phosphorus (= 8.81% P_2O_5) and it occurred to me that such a material should be specially valuable as a dressing or manure for agricultural land and I told Mr Ellis who was largely interested in farming. He was rather impressed by the idea and I believe made what would be the first trials of Basic Slag for the purpose of fertiliser.

There are some further matters of special interest passed through my hands during this time, but I might say that while I was in semi-charge of the Blast Furnaces I had most to do with the production of Ferromanganese and in that capacity had to inspect and analyse the cargoes of Spanish manganiferous ore and in the course of this work I made a really fine collection of crystals and minerals but unfortunately these were destroyed in the fire (at the laboratory during distillation trials on tar oil – this is described earlier in the notes.)

About this time (1884) the company decided to centralise all chemical work by erecting a special building in which the whole of the analysis should be done. Mr P G Pochin, son of one of the Directors was given charge of the laboratory and staff but he was actually a passenger. The most important work was done by Charles Phillips and I was his second. E T Barker was next under me, and then Ashbury, son of the Cashier, and later, after I left, my old friend A Scott Davy was employed. When Pochin was discharged, another Director's son, Stephen Burridge, was made head of the Laboratory, but he was also a failure and Phillips continued to be the actual head.

On 16th December 1886, I terminated my work at John Brown and Company Limited in order to join my father, Mr W T Flather, in his business.

The above extracts come from a time of great change in the Sheffield steel trade. The 'Old Sheffield Methods' of cementation and crucible steel melting were, apart from the special tool steel trade, being supplanted, first by Bessemer steel, and then from 1880 onwards, by the acid Open Hearth Process particularly for the production of engineering forgings. John Brown and Company always seem to have been in the forefront of changes. They had installed puddling furnaces and pioneered the production of puddled steel in Sheffield in the late 1850s; they had taken up the Bessemer process in 1861 and by 1865 were supplying something of the order of 50% of the steel rails used world-wide. The installation of the blast furnaces which figures in these notes came in 1872 and was accompanied by the acquisition of iron ore mines in Spain and of collieries and coking plants in South Yorkshire so as to make the Bessemer operation an integrated one on the Sheffield site; the provision of ferromanganese was part of this idea. John Brown was the only firm in Sheffield which went this far and the blast furnaces appear to have continued in operation until about 1911.

The growth in importance of the role of the analytical

chemist was also something quite recent when the young David Flather joined John Brown and Company. Only in the larger works was there a chemist in the 1870s; we know of them in action at Firths, Vickers and Browns by about 1876. The taking in of samples from other works by John Brown as described in these notes is thus a fascinating aspect when techniques were becoming more complex. No longer was steel simply an alloy of iron and carbon whose carbon content could be accurately estimated by the appearance of the fracture of materials whose history was clearly known and where the sulphur and phosphorus contents were controlled by the simple means of purchasing pure Swedish iron as raw material – although this was still true for a fair proportion of the steel produced in Sheffield.

The other interesting feature is the willingness of a firm such as John Brown and Company to encourage the enquiring mind of a youngster such as David Flather and the use made of such facilities by the recipient.

Letters to the Editor

Re Coalbrookdale, The Old Furnace, Ironbridge.

From Keith Gale.

Dear Sir,

I feel that the contents of Charles Blick's note on 'Early Blast Furnace News', 1985, Vol 19, Part 1, p 134 about the slightly mysterious hole in the furnace lining at the top of the bosh calls for comment.

Many years ago I told Fred Williams that I could not accept that it was a tuyere, for one very good reason; there was no means of access for changing it.

When you have worked on a blast furnace you know how often a tuyere had to be changed. Easy access was essential, which is why the old masonry structures always had such large access arches built into the brick or stonework at normal crucible tuyere level. There is no way of getting at the 'hole' in the lining of the Coalbrookdale furnace except: (a) from inside the stack or (b) by breaking out a mass of brickwork over the tymp. Both are obviously impossible on a furnace in blast.

With luck a tuyere might last several years. On the other hand its life could be only a few months, weeks, or even days. So inaccessibility seems to me to be a conclusive factor.

To back up my opinion I met the then manager of Lilleshall Priors Lee furnaces at Coalbrookdale and asked him the simple question 'Could you work a furnace with a tuyere in that position?' The answer was equally simple: 'No. How did they change the tuyere?' he asked. Moreover, if the hole was the **only** tuyere, as some people suggested, it was much too high up to be of any use. The burden below it would 'freeze'. That was the opinion of an experienced blast furnace manager.

The 'hole' connects with an annular passage round the furnace and this has been the cause of some of the confusion. Annular passages were an essential feature of masonry furnaces. They were simply moisture 'drains' and they had a number of apertures open to the air in the sides of the outer masonry. I believe that if the Coalbrookdale furnace linings were opened out, several of these passages would be found.

In blowing in a new or relined furnace there was a lot of moisture to be drained out. Failure to take this out carefully could split the masonry. So a coal fire was lighted on the hearth, with the tuyeres and forepart open and the heat was gradually increased to dry out the mass of masonry. Steam drifted out of the 'weep' holes and when this stopped it was a fair guess that the masonry was dry. The process could take a month or more.

So what was the function of the 'hole'? I suggest that it had none and the fact that it connected with the annulus was purely coincidental. I cannot offer any explanation except that somebody knocked it in to see how thick the lining was. This is not so silly as it might sound. The 'new' furnace nearby had its lining taken out to reline cupolas during the war, when firebricks were difficult to get.

As far as I know, my explanation is the only one based on practical operating experience. I shall stick to it unless a better one is forthcoming.

Yours sincerely, W K V Gale

From Dr Barrie Trinder

Dear Sir,

I notice in your early Blast Furnace News in JHMS 19.1 that you have included some observations from Dr Arthur Raistrick on the old furnace at Coalbrookdale. About the aperture in the lining of the furnace at the junction of the stack and the top of the bosh there must remain some doubts. It is not possible however to accept that there was no other aperture in the furnace because it is clear from the excavations carried out in 1981-2 that the present bottom of the furnace is considerably above the original working bottom. We would hope in due course to excavate the interior of the furnace but this must of course wait until adequate resources are available to do the job properly. About the use of the furnace for smelting iron ore after the casting of members for the Iron Bridge there can be no doubt, it is abundantly clear from a host of documentary sources that the furnace was still being used for smelting

until about 1818. Dr Raistrick knows these sources very well and I am surprised at his suggestion. It is true that the company was finding smelting at Coalbrookdale less and less economic and at least one lengthy paper was produced on this subject in about 1981. It only goes to prove that the furnace was still being used for smelting at that date. There must also remain a degree of agnosticism about whether the ribs for the Iron Bridge were actually cast in the iron works. The bulk of evidence suggests that possibly they were although it is not conclusive and one or two sources as well as the experience of many practical iron founders suggest that the ribs may have been cast from an air furnace near to the site of the bridge. There is certainly no conclusive evidence to show that the old furnace was used as a melting furnace for making the ribs. The 1777 date on the beams obviously suggest an enlargement at the time when the bridge was being built but there is nothing to suggest that on the assumption that the casting took place in the upper furnace complex, the iron was not melted from one of several air furnaces in the vicinity. All of this must remain a matter for doubt and speculation but it is important that we do not accept probabilities as certainties.

Yours sincerely, Barrie Trinder

Book reviews

Amina Chatwin: Cheltenham's Ornamental Ironwork — A Guide and History. *Reproduced from Metals and Materials. Published by the author at 6 to 7 Montpellier Street, Cheltenham and available at £5.00 including postage.*

The re-opening of the old wells in 1783 coupled with the visit to the town by George III in 1788 'to take the waters' probably established Cheltenham as a fashionable Spa. Its development was particularly rapid towards the end of the 18th and during the early 19th Century, attracting many who were seeking a place of retirement after long periods abroad. Among other famous architects, Decimus Burton and J B Papworth played important roles in the development of the town, with the latter recommending the use of cast iron in 'rural residences' as being more economical than wrought iron.

Compared with many examples of ornamental ironwork in other Regency towns, that in Cheltenham is often of delicate and exquisite design and this is shown to perfection in this delightful book by Amina Chatwin. Miss Chatwin takes her readers with skill through the periods of change from the early wrought iron with its simple designs to the later more elaborate wrought work, to the introduction of cast balconies in a variety of designs leading finally to the period of heavy and very often ornate cast iron. It is particularly pleasing in a work of this nature to find the author taking the trouble to explain the differences between wrought and cast iron in a way which should enlighten even the most uninitiated of her readers. It is obvious from this fascinating work that a tremendous amount of painstaking research has gone into this compilation. The author's style is superbly readable and not a word is wasted. The book will surely be welcomed as a most valuable addition to the architectural history of Cheltenham and hopefully will add weight to all those interested in preserving so important a part of the town's heritage.

L J Stewardson

J D Light and Henry Unglik: A Frontier Fur Trade Blacksmith Shop; 1796-1812. *Parks Canada, Ottawa, Canada* **$***8.95. (Available in French or English), 130pp.*

This is a pleasant surprise – an excavation at Fort St Joseph Ontario has yielded a number of close dated tools and slags which have been well investigated and reported by a competent metallurgist. They show the survival in an unusual environment of a traditional blacksmithing technique which has been mainly responsible for the repair and maintenance of axes, files and animal traps. The second author has produced a detailed metallurgical report on the axes and slags which give details of structure of metal and the smithing hearth bottoms which have been contaminated by chunks of iron and brass used for brazing. This is a very useful report for all involved in the interpretation of iron working remains and is strongly recommended.

If one has any criticism it is of the degree of reduction in some of the tables which require a lens to read them.

R F Tylecote

K C Barraclough: Steelmaking before Bessemer, *Metals Society, London, 1984:* Vol 1, Blister Steel, the Birth of an Industry, ISBN 0 904357 53 8, 273 + xx pp, 10 plates (Book 297).
Vol 2, Crucible Steel, The Growth of Technology, ISBN 0 904357 64 3, 387 + xix pp,15 plates (Book 309).

These two volumes together are based on Dr Barraclough's thesis for his PhD degree, but this bald statement falls far short of conveying the immense amount of energy, interest, research (and sometimes luck), together with the sheer determination that must have been necessary to continue over so many years collecting the data and from it piecing together the fascinating story that is presented here. As it unfolds, we are aware of gaps in the records that tantalise by demanding hypothesis when with a little more luck the critical facts might so easily have survived; but without the monumental effort that Ken Barraclough has put into this 'magnum opus' a great deal of what is presented here could well have been lost forever and much more might never have been collated.

Each volume stands by itself in dealing with a recognisable part of the development of the steel industry before the bulk steelmaking processes introduced as a result of the work of Bessemer, Thomas and Siemens changed its scale and direction in the manner both familiar and already well-documented, so of necessity there is some overlap in the treatment and some repetition if both volumes are read in sequence but in the main this is well limited to what is required to allow the reader of either volume to follow the argument presented in that part of the work. And the account of how a 50 ton ingot was cast at the Krupp works late in the 19th century shows how an inherently small scale process could be large-scale when needed. Most of the detailed account deals with the indigenous industry, so that volume 1 is much concerned with the North East, particularly around Tyneside, while Volume 2 deals with the gradual emergence of Sheffield and its rise to world leadership; but this is too simplistic a view of both the growth of the industry and the scope of these books, as each also deals with parallel work elsewhere in

Britain, in Europe and America, and even further afield.

The background to steelmaking and to the cementation process is dealt with in volume 1 and the story of how a process originally discovered in continental Europe was developed in this country until even in Europe it became known as the English process is followed by a remarkably complete account of its rise and fall in this country and a brief account of what is known about developments in the rest of the world, all presented in a very readable manner although it is thoroughly annotated. This occupies just over half the book, the rest being devoted to 37 appendices that expand the information given in the general account, sometimes on matters of considerable importance and sometimes on fine points of detail. The proof reading seems generally to have been very efficient, but the caption to Fig 12 refers the reader to, inter alia, Fig 12 and Plate 3; this should read Fig 13 and Plate 2. A 10-page bibliography and a comprehensive index complete the volume.

Volume 2 follows a similar pattern, devoting five chapters to Huntsman and the other British developments that made Sheffield a synonym for high-quality steel, and a sixth to the overseas competition that gradually developed competence and finally prevailed by succeeding in making a local product that could stand comparison with Sheffield steel even though it rarely, if ever, bettered it. Lore, technology and science as applied to the crucible process are examined and presented with knowledgeable comment from a practising steelmaker of a later period, and if the critical advantage at the beginning was probably the availability of suitable clay, later it seems to have been the way in which the steel-making team was organised so that skill and technique were learned and passed on as necessary, and the fierce pride in the ability to do a skilled job better than the opposition which accounted for much of Sheffield's eminence. 26 appendices, a 15-page bibliography, and a good index complete this volume, and while the academic metallurgist might deplore the omission of the peritectic region from the iron-carbon phase diagram present in Fig 5 (which is identical with Fig 3 of volume 1), he must concede that it is largely irrelevant to the content of the book and does not affect the argument there presented in any way.

The author is to be congratulated on recognising the gap in the records that these volumes now fill, and for presenting his facts so comprehensively and in so interesting a fashion. These must surely be standard reference books for years to come.

D Maxwell

D J Rowe: Lead Manufacturing in Britain. A History.
Croome Helm, London, 1983, £30; A5 Hardback. 425pp.

This is a history of the companies that were to become the Associated Lead Manufacturers Ltd. It follows their vicissitudes over the last 200 years and it was this anniversary that led to its commissioning.

To metallurgists, as distinct from chemical engineers, this book will come as a bit of a surprise. Lead is, or was, as useful as a chemical as it was a metal, and in 1855-59, 28 - 33,000 tons were sold annually as white or red lead, while 41 to 46,000 tons were sold as sheet, pipe or shot. The picture altered in 50 years to give twice as much metal as pigment and gradually, as lead oxides fell from favour, the ratio increased still further although lead pigments were still being made in quantity in the post-second world war years. It is this change that led to the industries vicissitudes, and its capacity for adjustment that led to its survival. By the 1960s lead pigments had declined to 20,000 tons while the use of lead in petrol had increased to the same amount. It is odd that society replaced one toxic compound with another. But for a while ALM had interested itself in the less toxic titanium dioxide as a paint base.

The book opens with a short survey of the early history up to the 18th century and then goes on to consider the formation of the first of the constituent companies, Walkers, Fishwick & Co. It is interesting to learn that the Walkers were the sons of Samuel Walker of Rotherham, that early pioneer, after Huntsman, of crucible steel, and that they combined with Fishwick of Hull to start a white lead works in Newcastle.

Perhaps one should state at this point what the problems were. White lead is the basic carbonate ($2\ PbCO_3.Pb\ OH_2$) which was made by corroding thin metallic (Blue) lead sheet by the 'stack' process in which the lead was exposed to the vapour of acetic acid at a slightly elevated temperature, described by Pliny. This temperature was achieved by decomposing manure or tanners bark.

So, although the plant requirements were not costly nor complicated, considerable capital was tied up, as the corroding process took 3 weeks. After this the oxide had to be scraped off the residual lead sheet and ground finely. This latter process needed power which was a problem. First, windmills were used and then horse gins as the power requirements became greater. Much unskilled labour was needed for filling the stacks and dismantling them, and this work was dangerous and could lead to early death.

Since the main market was in London, a works was established at Islington and after many amalgamations the associated companies were to have widely distributed works to serve their clients. These amalgamations gave rise to a lot of duplication of salesmen as it was supposed that old customers had to be provided with products from the old companies.

With such a heavy product, local supply points were essential and customer loyalty an asset. Much of the body of the book is devoted to the rise and growth of the various companies. The policy was aggressive and the picture of the late 19th and 20th centuries is one of cartelisation and take-overs. On the whole, technical development was by licensing arrangements with foreign firms and few developments were made in Britain. It is extraordinary how good management was achieved. Various members of the constituent firms seem to have been in the right places at the right time so that both the necessary level of technical and business management was maintained.

Since the toxic nature of lead was a problem we have a chapter on industrial lead poisoning and the measures taken to prevent it.

The book is provided with a useful number of statistical tables as an appendix. By 1970 the main products of the industry were cable sheathing, batteries, lead tetraethyl, and sheet and pipe, with pigments taking only 1/10th of the total output – a big change in 200 years.

A competent and useful book for those interested in lead as a chemical and business history. It should open the eyes of those inquiring into the history of lead as a metal, to another aspect of the subject.

R F Tylecote

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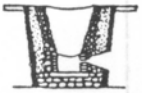

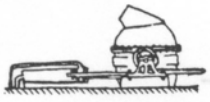

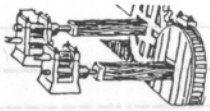

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1984 SYMPOSIUM PROCEEDINGS

THE CRAFTS OF THE BLACKSMITH
edited by B. G. Scott and H. Cleere

The 7th Symposium of the Comité was held at the Ulster Museum in Belfast from the 17th-20th of September 1984. The theme of the papers was the Crafts of the Blacksmith. The subjects covered ranged from the blacksmith in literature to the identification of smithing slags, from the metallographic study of early iron artefacts to the excavation of ironworking sites.

The Symposium Proceedings, which are being published with the assistance of the Ulster Museum, will include

K. Bielenin
Iron smithing areas on furnace sites in the Holy Cross Mountains of Lesser Poland.

H. Cleere
The role of the iron trade in the early economy.

R. Clough
Observations on the bloomery smelting process.

P. Crew
Bryn y Castell Hillfort, Ffestiniog - a late prehistoric ironworking centre.

N. Cuomo di Caprio and A. Storti
The mining statute from Massa Maritima (Grosseto), Italy: an early XIVth century act of the miners' corporation.

R. M. Ehrenreich
The study of iron technology in the Wessex Iron Age.

J. Gömöri
The three components of the early Hungarian blacksmith's art (vasvero-tarkany-kovacs).

P. Kresten
The mineralogy, chemistry and properties of ancient slags.

J. Lang
The technology of the Celtic sword.

J. G. MacDonnell
The study of early iron smithing residues.

R. Maddin
The blacksmith's art in the mid-1st millenium B.C.

G. Magnusson
Blacksmiths in Jämtland and Härjedalen in north-east Sweden.

E. Nosek and A. Mazur
The oxidation of iron-carbon alloy at low temperatures.

P. Ottaway and J. G. MacDonnell
Anglo-Scandinavian period knives from 16-22 Coppergate, York: typology and technology.

E. Photos
Ironworking in Macedonia: a preliminary report.

J. Piaskowski
A procedure for standardising the presentation of the results of metallographic examinations of early iron objects.

J. Piaskowski
Proposals for standardising criteria for determining fabrication processes in early iron and steel technology.

R. Pleiner
Problems in the standardisation of metallographic examinations of archaeological ironwork.

R. Pleiner
Investigation of Early La Tène period knives from Bohemia.

L. S. Rozanova (Khomutova) and M. V. Sedova
The art of metalworking in the ancient city of Suzdal.

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Andreas Hauptmann: 5000 Jahre Kupfer in Oman; Vol 1: Die Entwicklung der Kupfermetallurgie vom 3. Jahrtausend bis zur Neuzeit. *'Der Anschnitt', Beiheft 4, Bochum, 1985, 137 pp. A4 format (Price not stated).*

This is the report of the German archaeometallurgical expedition to Oman which has examined more than 150 copper working sites over the last 20 years. The work has been carried out by a team from the Bergbau Museum, Bochum, with a foreword by their archaeologist Gerd Weisgerber.

The exploitation of the Omani copper deposits occurred in three principal phases:- Early Bronze Age (3rd millennium) – then in the Umm-an-Nar period (3rd-2nd millennium) and finally in the Early Islamic period (9th - 10th century AD). This is similar to the exploitation in other desert regions and the gaps probably represent the periods of regeneration of the fuel resources after the previous inhabitants had completely removed the vegetation and left. It is estimated that it took 22-25 million mature acacia trees for the operations in the 9-10th centuries.

The estimated production was:-

Bronze Age (3rd-2nd mill BC)	2000 - 4000 t copper
9 - 10th cent AD	48000 - 60000 t
Middle Islamic to recent	3000 - 3700 t
Total	53000 - 67700 t

This exceeds the output of any other known site in the Middle East and clearly this must have been the ancient MAGAN that we hear so much about.

The ores are not unlike those of Cyprus – chalcopyrite with an original copper content of 2 - 2.5%. Outcrops have rich secondary mineralisation with malachite, brochantite and crysocolla reaching as high as 30%.

The smelting technique in the earliest period was very primitive, with fayalite-type slags containing up to 30% copper which was released by crushing. The copper product was in the form of Cu prills, cuprite and Cu-Fe oxides. During the Umm-an-Nar period the clay-built furnaces had a height of over 0.4 m and were 0.5 m dia. They used rich secondary ores dressed to give a charge of 30% Cu. Iron oxide was used for fluxing and the product was matte and copper. This was crushed and the copper remelted to form ingots. What happened to the matte is not known in this period but by Islamic times standard roasting and reduction treatment was applied to concentrates of the order of 20-30% Cu. How the beneficiation was done is not stated, and it is unlikely to have been done by washing. Perhaps some sort of winnowing was used. As the mineral was chalcopyrite in this period, quartz was added as flux. This was smelted in shaft furnaces with a height of 1.5 m with provision for tapping. The product of the first stage was 5-6 kg of matte and 20 - 50 kg of slag. The matte was roasted and good roasters can still be seen not unlike those found on the Wertime expedition to Iran in 1969 which had probably been used into the 20th century. These were 2 x 1.5 m oval shafts built into banks of at least four in a row. The matte was oxidised to copper metal by many stages of furnacing as described later by Agricola. This process was standardised all over Oman. At Mallaq, 20,000 t of slag were produced from 12 furnaces.

This is a very extensive piece of work and the conclusions are supported by full mineralogical, metal, matte and slag analyses which leads to a full discussion. The whole work is up to the Bergbau's Museum high standard of production. Criticism is confined to the furnace reconstruction which probably suffers from too little field evidence. It is unlikely that a shaft furnace with a diameter of 0.5 m would work satisfactorily with only one tuyere especially with the sort of primitive bellows that were used. No evidence of pot bellows was found so we must assume that they were bag or concertina-type bellows.

R F Tylecote

G A Wagner and Gerd Weisgerber: Silber, Blei und Gold auf Sifnos; Praehistorische und antike metallproduktion. *'Der Anschnitt', Beiheft 3, Bergbau Museum, Bochum, 1985. 242pp. A4 format with 10 maps and 8 colour reproductions. (No price stated).*

Siphnos is one of the Cyclades, an important group in the early culture of the Aegean. The work described in this report was carried out by the Max Planck Institute in Heidelberg with the full support of the Mining Museum in Bochum. It comprises a field study of the geology, the mines, and the smelting debris found on the Island, no excavation was carried out. The Bergbau Museum was responsible for the archaeological and mining research. In all, 15 authors have made contributions to this report which is dedicated to the late Professor Wolfgang Gentner.

The group found evidence of a number of phases of lead-silver mining which appears to have been the main production of the Island until the 19th-20th centuries when iron ore was mined in a big way and exported from small quays on the coast. Much of the easily visible evidence today relates to this phase. The first phase began in Early Bronze Age I, the Cycladic Culture, and consisted of surface working with open trenches and shallow shafts, sometimes inclined. The levels were back-filled, apparently for religious reasons, ie to propitiate the deities.

Pine chips were used for lighting as in the MBA Mitterberg mines of Austria. The mined rock was finely broken with round hand-held hammerstones and anvil stones and there seems to be no signs of grooved hammerstones for mining. This aspect will require more extensive work.

The next phase was in the First Millennium BC (mainly the 6th-5th centuries) and has written support from classical writers. These workings were much damaged in the 19th-20th centuries. The mining technique in this phase was by hammer and chisel and latex impressions were taken of the chisel marks seen in the rock. Heavy iron picks were also used and some form of scraper.

Very little slag now remains on the Island. What there is has a variable composition. The lead content of the ores reached 83.9% and the maximum of the other elements was:- Sb 23.6%, Zn 30.9%, Cu 37.5%, As 6.8%, Ag 7130 ppm, and Au 2.05 ppm. The slags, all from Agios Sostris contained from 1.1 - 19.3% Pbo, and 7.6 - 68% FeO, and were like those from Laurion. The thermoluminescence dates on these slags gave a range of 2970 BC to 750 BC and therefore do not represent the latter phase of lead/silver production. It is probable that the slags from this latter period were shipped to Laurion to be resmelted, or else all the smelting was done elsewhere after the 8th century because of fuel shortage. It seems that copper was smelted at one time as three slags from Platy Gimlos contain copper in the range 1.57 - 4.28%.

Litharge was found at Kapsalos and this proves that silver extraction took place at some time on the Island. The analyses show 3.1%Sb but very little Cu, Zn, As or Ag, which shows that the antimony goes off with the lead. In the EBA, the silver content of the smelted lead would have had to exceed 600g/ton (ppm) to make cupellation profitable, Lead isotope work shows that over half of the Cycladic silver derives from Siphnos ores. Much of the Archaic silver went to the Aegina mint.

Iron ore mining dominated the scene in the 19th-20th centuries but there is a chimney at Kamares which suggests that some reprocessing of lead slags was carried out on the Island at this period.

The geological and mining section comprise the main part of this book and the extractive side only takes a few pages, due to the paucity of evidence. Unfortunately this shortcoming also extends to the mineral dressing side and we are not given any indication of the grade of ore smelted. It would appear from the variability of the slags that no standard fluxing system was used.

The production of this report is of the usual high standard which we now expect from Bochum with good maps and colour prints. The authors cannot be blamed for failing to provide the archaeometallurgist with all the information he would like. The back-filling of the early workings and the 19th-20th centuries workings in search of iron ore have not made the mining historian's job any easier and one looks forward to further work on the Island to solve the remaining problems.

R F Tylecote

Gerhard Sperl: Die Steirische EisenstraBe (with English supplement), *Montanhistorischer Verein fur Osterreich, 1984: 96pp (61pp English supplement).*

The 'Styrian Iron Trail' is a route that takes one through the heartland of ancient and modern Austrian metal production, and through some of the spectacular scenery which that country has to offer. Gerhard Sperl, a scholar well-known to all interested in the study of prehistoric and early iron-working, has been deeply involved in the study of the development of metallurgy in the region. In 1978, he began the promotion and publicising of the route running roughly north-south from Altenmarkt and St Gallen to Leoben as almost a living museum of archaeometallurgy. This attractive guide charts the 'Iron Trail' with well-illustrated descriptions of each of the sites to be seen along the way. It includes also essential 'tourist' information on how to reach the starting points from the main centres in Austria.

The guide begins with a brief overview of the history and archaeology of the region, followed by a concise and informative description of thegeological formations on which its metallurgy was based. We are then taken through each of the main towns starting (not surprisingly) with the author's home town of Leoben. In each case, attention is paid not only to iron production, but also to the social and economic framework of the industry. The architecture of the works and that of dwelling houses and public buildings is afforded equal attention, giving the traveller a wealth of nicely presented information. In addition, folklore, place-names and historical data are blended into the text. The German edition contains a most useful (German) glossary of the main technical terms (unfortunately not translated in the English supplement). Both the German edition and English supplement include a list of the main museums to be found along the route.

Throughout the guide, Dr Sperl's enthusiasm for his subject is evident, and the text, maps and illustrations together make this both a handsome guide and sourcebook. Perhaps the point should be made that the author is a trifle optimistic in his estimates of travel time between the various centres, since the reviewer doubts that, with Dr Sperl's guide to hand, it would be possible to do other than dawdle along the 'Styrian Iron Trail'.

B G Scott

News and notes

Conferences

Several conferences of interest to members have recently been announced. The Metals Technology Committee of the Institute of Metals are sponsoring an international conference on **Aluminium Technology '86**, to mark the centenary of the invention of the molten salt electrolysis method, in London on the 11th-13th March 1986.

The Classics Department of the University College of North Wales is having a conference on Ancient Mining and Metallurgy on the 10th-12th April at Bangor. Those interested should get in touch with John Ellis Jones in the Classics Dept, LL57 2DG.

The next 'Archaeometry' Conference will be held at the Democritos Institute north of Athens between the 19th and the 24th May. Those interested should get in touch with the Oxford Laboratory for the History of Art and Archaeology at 6 Keble Road, Oxford.

International News

The International Secretariat for Research on the History of Agricultural Implements is a new organisation which reports on the studies being undertaken by the Danish National Museum and the Metallurgy Department of the Technical School of Denmark concerning ancient forging techniques. The Department has already worked on Viking period knives, prehistoric horseshoes, and 19th c stern frames, and metallurgical analysis of an assymetrical 17th c plowshare is currently underway. The results of the investigations will be published in the Secretariat's journal **Tools and Tillage**. For information, write Grith Lerche, International Secretariat for Research on the History of Agricultural Implements, National Museum, Brede, DK-2800 Lyngby, Denmark.

M Goodway

News from Washington

The National Association of Corrosion Engineers (NACE) has formed a Public Affairs Subcommittee on Conservation of Historic and Artistic Works. The new committee is chaired by Dr Robert Baboian of Texas Instruments Inc and includes Arthur Beale, Herbert Bump of the Florida

Department of State, A Elena Charola of the Metropolitan Museum, W Thomas Chase III of the Freer Gallery of Art, E Blaine Cliver of the National Park Service, Martha Goodway of the Smithsonian Institution, Jerome Kruger of The Johns Hopkins University, Norman A Nielsen of Wilmington, Michael Richman of the National Trust for Historic Preservation, Phoebe Weil of St Louis, Gilbertt M Ugiansky of the National Bureau of Standards, and Dale Miller of NACE as secretary. A purpose of this committee is to facilitate the exchange of information on corrosion between corrosion engineers and others having a professional interest in corrosion phenomena. Liaison is being established with the American Institute for Conservation (AIC), the Association for Preservation Technology (APT), and the International Sculpture Center. Plans are being discussed for republishing NBS Special Publication 479, **Corrosion and Metal Artifacts**, which has been out of print for many years. For further information write Dale Miller, Deputy Executive Director for Public Affairs, National Association of Corrosion Engineers, P O Box 218340, Houston TX77218, or telephone 713-492-0535.

A symposium on the restoration of the Statue of Liberty was held in February at The Metallurgical Society (TMS-AIME) 114th Annual Meeting in New York City. This symposium was organised by E Blaine Cliver of the National Park Service and sponsored by the American Society for Metals Committee on the History and Archaeology of Materials. This committee is also sponsoring a one-day symposium on Canadian Archaeometallurgy at the Fall Meeting of TMS-AIME to be held on Toronto October 13-17. The program is being organized by Dr Michael Wayman. For information write Dr Wayman at the Department of Metallurgy and Material Sciences, University of Toronto, Toronto, Ontario M5S 1A4, Canada or telephone him at 416-978-3012.

An Historic Iron Studies Workshop sponsored by the Society for Industrial Archaeology (STA) was held last November in Greenwood Lake, New York. Another meeting was planned for early March in Virginia. For information write Edward S Rutsch, Box 111, RD 3, Newton NJ 07860 or call 201-383-6355.

A workshop to provide practical guidance on the choice of analytical techniques, Analytical Tools in Archaeometry I: A Workshop on the Study of Ancient Metals and Ceramics, has been scheduled for October 7-9, 1985 at the University of Delaware in Newark, Delaware. Papers and posters are solicited and a proceedings volume is planned. For details write the convenors: Dr Charles Swann, Bartol Foundation, University of Delaware, Newark DE 19716, and Dr Stuart Fleming, MASCA, University Museum, 33rd and Spruce Streets, Philadelphia PA 19104.

Srinivasan Raman of Madras, India, has come to Philadelphia to study the history of science under Professor Nathan Sivan at the University of Pennsylvania. Srinivasan has his undergraduate degree in metallurgy from the Indian Institute of Technology in Madras, where R K S Koomaraswamy was his professor. Srinivasan brought samples from the almost unknown iron pillar at Kodachadri and other research materials with him for technical study. His telephone at UPenn is 215-387-3443.

If you have news you would like to contribute, please call me at 202-287-3733 or write me at CAL MSC, Smithsonian Institution, Washington DC 20560.

Martha Goodway, Smithsonian Institution

Obituary

Leonard Salkield, who died at Rugby on 24 February, was employed by the Rio Tinto Company at the Spanish Mines from 1928 to 1937 and again from 1946 to 1967.

The following tribute was written by Joe Jowers OBE who worked at the Mines during the post-war period.

I first met Leonard Salkield when I arrived at Rio Tinto in June 1948 when Leonard was on the metallurgical staff at the smelter, then, of course, located at the Mines; I found him to be an extremely equable and helpful 'senior officer'.

At that time he and his wife, Nancie, were recovering from the terrible shock of the loss of her brother-in-law, Arthur Lawrence, killed in the Alnwick railway accident around the end of the war while in the UK on duty. Both he and Leonard were brilliant and precise scientists who were recruited by the Mines to carry out research work. In fact, I believe Leonard was never in charge of a department but he gave constant help to those who were and helped them fight for technical improvements.

During so many post-war years, he had a particularly happy relationship with the head of the smelter, the dedicated and immensely capable Eduardo Figueroa and with his counterpart, principally in research, the late Felipe Luzon.

His steady hand and serene temperament were invaluable during the changeover to Spanish management in the latter 'fifties, and he became the last Englishman to achieve managerial status, when his appointment was SDEP (sub-director de Estudios y Proyectos). He was awarded the OBE in the 'sixties.

He had broken service because he insisted on returning to the UK during the war for work in a vital war industry. This took him to a chemicals factory in South Wales where he abandoned his preference for research and worked in an operational managerial capacity, chiefly with that dangerous element Phosphorus, which caused at least one serious explosion. Leonard was fortunately one of those who survived.

During his last few years in Spain, he gave unstinting help to David Avery* in the compilation of *Not on Queen Victoria's Birthday* and also to the many industrial archaeologists from Spain itself, Israel, Germany, and in particular, to Professor Tylecote of Newcastle University in his studies of early smelting processes. Leonard had recently completed his 'Technical History of Rio Tinto'.

On retirement in the early 'seventies the Salkields went to live in their charming book-lined bungalow near Estepona where they were renowned for their kindness to their neighbours, Leonard being mainly responsible, on one

* Dr Avery describes an incident during the Civil War in which Mr Salkield was accidentally injured during an encounter with local militia while returning to the Mines from Punto Umbria with a party of Rio Tinto people.

occasion, for nursing a Scottish neighbour back to health, almost without a break for seven days.

My wife, Dolly, and our children had a happy association with Leonard and Nancie and their family over many years and we grieve with them at the loss to us of our erudite companion and a good, kind friend and colleague.

Joe Jowers, Seville, March 1985.

Ivor Herbert writes:

One of Leonard Salkield's greatest interests, outside his work, was the history of the Rio Tinto Mines. From his early days in Spain, he was fascinated by the antiquity of the operations and he spent many hours discussing their origins with interested listeners. (The operations date back several thousand years and research into the earlier periods of mining is continuing.)

One problem which Leonard studied in depth concerned the huge slag dumps accumulated during 500-600 years of operation by the Romans. Closely related was the question of which metal the Romans were trying to extract. Extensive studies of slag at the Mines, by Leonard Salkield and others, together with other evidence, indicated that the Romans' chief interest was silver.

Leonard kept many notes of his researches and his historical knowledge of the Mines was made freely available to others. He was encouraged by the late Sir Val Duncan to assemble his notes – along with old photographs, drawings and other historical data – into a detailed chronological record of technical development at the Mines. He spent many of his retirement years on this project and the work now in (unpublished) manuscript form, covers the early, pre-Roman history, as interpreted from the many archaeological finds, as well as Leonard's own researches. This is a valuable reference source for future historical research and a copy is kept in the RTZ archives in London.

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Early UK Blast Furnaces

A volunteer is needed urgently to complete the work that has been started by Charles Blick and has been running for many years in Early Blast Furnace Notes in this Journal. It is hoped with his aid to compile a loose-leaf reference manual on Visible Remains of Early UK Blast Furnaces. Data on nearly 90 units has been collected and is ready for printing. All that is now needed is the disciplined transfer of material to individual record pages.

A similar work is envisaged for Early Overseas Blast Furnaces on data collated by D W Crossley.

Erratum

Dr Doyle has drawn our attention to an error on page 47 of the last issue (Vol 19 Part 1, 1985). His qualifications should have been:- M.Eng., Ph.D. (Liverpool), C.Eng., FIM.

Abstracts

GENERAL

E Mello and F Garbassi: Surface Spectroscopy Studies on Patinas of Ancient Metal Objects. *Stud Conserv, 1984,* **29,** *172-80, pls, figs, refs.* *CBA*

W Minchinton: Lead Shot Towers Around the World. *Hist Today, Aug 1984,* **34,** *48-50, pls.* *CBA*

D T Moore and W A Oddy: Touchstones: Some Aspects of their Nomenclature, Petrography and Provenance. *J Arch Science, 1985,* **12,** *59-80.*

Touchstones are pieces of fine-grained black stone which are used for assaying gold by comparing the colour of streaks made on the surface by alloys of known composition, with the colour of the streak from an object of unknown composition. The technique has been in use since at least the 6th century BC. The petrographic aspects of the identification of touchstones are reviewed and 42 historical touchstones or museum specimens of similar looking stone are described, most of them including the results of petrographic examination. The results show that the touchstones usually consist of sedimentary rock types, of which the most frequently occurring ones are tuffs, cherts and siltstones. *Authors*

J D Muhly: Sources of Tin and the Beginnings of Bronze Metallurgy. *American Journal of Archaeology, 1985,* **89,** *275-91.*

Comprehensive survey based mainly on the Mediterranean-Middle East area. *PTC*

W S Nelmes: The Secondary Copper Blast Furnace. *Trans Inst Min and Met, 1984,* **93C,** *180-6.*

The paper has a considerable amount of relevance to the early smelting of oxidized copper ores and deals particularly with the role of iron. *RFT*

N North: The Role of Galvanic Couples in the Corrosion of Shipwreck Metals. *Int J Naut Archaeol Underwater Explor, 1984,* **13,** *133-6.* *CBA*

E Pernicka: Instrumentelle Multi-Elementanalyse Archaeologischer Kupfer-und Bronzeartefakte : Ein Methodenvergleich. *Jarbuch Römisch-Germ Zentralmuseum, 1984,* **31,** *517-31. (In German).*

Comparison of the analytical techniques used on copper-base alloys and trace element determination. *ECJT*

J Piaskowski: Kazimierz Gierdziejewski – The Historian of Technique. *Stud I Mat Dziej Nauki Polski, D Z, 1984,* **10,** *165-179. (In Polish).*

The main trends in his researches on the history of technique are discussed. *ECJT*

D A Scott: Periodic Corrosion Phenomena in Bronze Antiquities. *Studies in Conservation, 1985,* **30,** *49-57.*

Investigations into the structure of some ancient bronze artifacts revealed periodic corrosion product formation. Examination by reflected polarized light microscopy suggested that information concerning the banding observable in these objects could be used to support the hypothesis that Liesegang phenomena were responsible for the periodicity of corrosion product formation. Some analytical data for the bronze fragments were obtained by electron probe microanalysis, using both spot analyses and elemental line scan traverse across the polished sections of the fragments under study.

Author

M S Tite, I C Freestone, N D Meeks and P T Craddock: The Examination of Refractory Ceramics from Metal Production and Metalworking Sites. *In The Archaeologist in the Laboratory (ed P Philips), CBA Research Report 58, 1985, 50-55.*

Describes the techniques used and the information to be recovered from furnace fragments, crucibles, tuyeres etc. Study by SEM with electron microprobe analyser, XRD especially useful in determining smelting temperature, duration of operation and reducing conditions.

PTC

BRITAIN

Anon: Iron Nails of the Roman Age. *Nippon Steel News, February 1985, 1.*

Gives the inclusion analysis of one of the Inchtuthil Scottish nails and a Japanese halberd of the 1st century AD for comparison. In both cases the slag inclusions were high in lime (Roman nail had 7.6% and the halberd 14.3 to 17.2%). Both were low in iron and in view of their high alkali content would seem to stem from the fuel ash used in smithing.

RFT

R Brownsword and E E H Pitt: A Technical Study of Some Medieval Steelyard Weights (reclassification of Drury). *Proc Dorset Archaeol Natur Hist Soc, 1983,* **105,** *83-8, pl, figs, table, refs.* *CBA*

T Bryce and J Tate (eds): The Laboratories of the National Museum of Antiquities of Scotland, Volume 2. *Edinburgh, Nat Mus Antiq Scot, 2nd, 125pp, pls, figs, refs.*

Includes : C Mortimer (62-7), Bronze Age gold analyses (Easter Ross hoard and 12 other pieces; XRF results mostly concordant with earlier OES-Stuttgart work); J Tate, I Barnes and A MacSween (89-94), Analyses of massive bronze armlets (XRF and ASS; no support to style/chronology relationship); Marjory Findlay (95-102), Report on the conservation of the Orkney hood (Viking?); N White and J Tate (104-10). Non-dispersive XRF analyses of Viking silver from Orkney (Burray and Skaill hoards, largest Scottish Viking collection). Also includes conservation of iron, dye identification XRF of silver. *CBA*

P Gadsden and B Trinder: The Old Furnace, Coalbrookdale. *Trans Instn Mining and Metallurgy, 1984,* **93C,** *118-22. Illustrated.*

The development of the furnace is outlined and the benefits and difficulties of substituting coal or coke for charcoal as fuel for the blast furnace are fully discussed. Since 1950 much archaeological work has been done on the site but much remains to be done.

D Hall: The Excavation of an Iron-Smelting Site at Easton Maudit, Northamptonshire. *Bedfordshire Archaeol, 1983,* **16,** *91-5, figs.* *CBA*

H Härke and C J Salter: A Technical and Metallurgical Study of Three Anglo-Saxon Shield Bosses. *Anglo-Saxon Stud Archaeol Hist, 1984,* **3,** *35-66.* *CBA*

C F C Hawkes: Ictis Disentangled, and the British Tin Trade. *Oxford J Archaeology, 1984,* **3,** *211-33, pl, figs, refs.* *CBA*

J C and R B Inglis: An Early Metalworkers' Mould from Corsegight, New Deer, Grampian (for flat axes). *Proc Soc Antiq Scot, 1983,* **113,** *634-6, fig.* *CBA*

J M Lewis, (with a contribution by R Brownsword and E E H Pitt): A Medieval Brass Mortar from South Wales and its Affinities. *Antiquaries Journal, 1984,* **64,** *(2), 326-335.*

Ten medieval ribbed mortars from British collections, only three with known provenances are described and their relationship with the Hispano-Moresque and Islamic series of such vessels discussed. Most of the vessels were of leaded bronze or leaded gunmetal. The Deptford mortar, however, was made of an impure copper and the Coity vessel from a leaded brass.

Author (abridged)

J G McDonnell: The Metallurgical Study of Iron Artefacts from Coppergate (York). *Interim 1984,* **9** *(4), 35-8, fig.* *CBA*

C R Musson: Metalsmiths of the Welsh Borderland (Llwyn Bryn-Dinas Workshop, Hillfort at SJ 172247, Clwd.). *Illus London News, Aug 1984* **(272),** *44-5, pls.* *CBA*

D Pratt: Speculative and Exploratory Lead Mining in Llandegla. *Denbighshire Hist Soc Trans, 1982,* **31,** *29-46.* *CBA*

D Pratt: Minera, Township of the Mines (14th Century Leadmines Worked Part-Time by Farmers). *Denbighshire Hist Soc Trans, 1976,* **25,** *114-54, figs, refs.* *CBA*

R McNeil Sale: Excavations at Bersham Ironworks, 1976 (19th-20th century Traces Only). *Denbighshire Hist Soc Trans, 1978,* **27,** *150-77, figs, tables, refs.* *CBA*

W I Stanton and A G Clarke: Cornish Miners at Charterhouse-on-Mendip (19th century Shafts and Reworking of Old Lead Mining Refuse). *Proc Univ Bristol Spelaeol Soc, 1984,* **17** *(1), 29-54, figs, pls, refs.* *CBA*

C Tabraham: Life after the Blast – Bonawe Iron Furnace, Argyll. *Country Life, 1984,* **(176),** *1222-4, pls.* *CBA*

R F Tylecote: Scottish Antimony (from Westerkirk in Eskdale). *Proc Soc Antiq Scot, 1983,* **113,** *645-6, table.* *CBA*

EUROPE

A I Kubyshev and I T Chernyakov: Towards the Problem of the Weight System Among the Bronze Age Tribes in the East European Steppes. (Materials found in a metalworker's burial of the Catacomb culture). *Sov Ark, 1985 (1), 39-54. (In Russian).*

Soviet studies of the East European Bronze Age metallurgy centers showed that there existed, stable ties between them and the Caucasus, Hither Asia, Eastern Mediterranean and the Balkan and Danube regions. They also revealed a high technological level of metallurgical production and the fact that the weights of the bronze components were strictly measured before melting. In 1981, a burial of a 17th century BC metalworker was discovered at Malaya Ternovka village (to the north-west along the Azov Sea coast). The burial contained 6 crucibles, 9 moulds, 2 tuyeres, 2 clay patterns for bronze castings. The crucibles and moulds were of different sizes, making up a set. The weight of metal for each crucible and that of the bronze ingots made in the moulds was established with the help of dry substances (salt) put into them and the computation of their specific weight in terms of the specific weight of arsenic bronze. It made it possible to determine their weights: 42, 48 etc in grammes. They can also be expressed in ancient Babylonian measures (5, 8, 12, 18, 29 shekels, 3 minae) and ancient Egyptian weight measures (5,8 qedets, 1.5,2.6 debens). The connection between the open weight system is indirectly supported by ancient oriental imported objects found in the East European steppes. Moulds for making metallic weights were found in other steppe sites dated to the Middle Bronze Age.

Authors

K Levinsen: Jernets introduktion i Danmark. *Kuml, 1982-83, 153-168.*

An archaeological study of the first introduction of iron and its role in the processes leading from the Bronze to the Iron Age.

ECJT

H F Mussche, J Bingen, J Servais and P Spitaels: Thorikos VIII, 1972-76. *Comité des Fouilles Belges en Grece, Gent, 1984, 151-174.*

A preliminary report to provide evidence for the mining of lead and silver at Thorikos during the 3rd millennium BC. A detailed description of the mine workings.

ECJT

W A Oddy: Ancient Jewellery as a Source of Technological Information – a Study of Techniques for Making Wire (in early Medieval Europe, pre-Ad 1000). *In International Restorer Seminar, 4th, Vezprem, Hungary, 1983 (ed A T Balazsy), 1983,* **4** *(2), 241-52, illus.* *CBA*

J Piaskowski: Further Metallographic Examinations of Ancient Iron Objects from the Cremation Cemetery at Niedanowo, Province of Olsztyn. *Sprawozdania Archaeologiczne, 1984,* **36,** *65-81 (In Polish).*

The results of examinations of 24 ancient iron implements were presented (9 objects were previously examined). About 70% of objects were made of low phosphorus, irregularly carburized iron (55% presented features of 'Holy Cross Mountains' iron). Nitrides were frequently observed in the metal (62%), especially in high phosphorus iron.

Author

J Piaskowski: The Presence of Arsenic in Ancient and Medieval Implements Made of Bloomery Iron. *Zeitschrift für Archaeologie, 1984,* **18,** *213-226 (In German).*

Investigation of the ancient and medieval iron implements from Iatrus-Krivina, Bulgaria, revealed the presence of arsenic (.03 - .25%). This element, similarly to phosphorus, segregates in the bloomery iron and forms a 'banded structure'revealed by Oberhoffer's reagent. It increases the microhardness and hardness of the iron. There is an inverse correlation between the degree of carburisation of iron and the As content.

Author

J Piaskowski: Metallographic Examinations of Ancient and Medieval Iron Implements and Slags from South-East Territories of Poland. *Materialy i Sprawozdania Rzeszwskiego Osrodka Archeologicznego za lata 1976-79, 1984, 171-205. (In Polish).*

The results of examination of 52 ancient and early medieval iron implements and 17 fragments of slag were presented. In antiquity and in medieval times there were no differences in metal characteristics and technology between central territories and south-east parts of Poland. Only in south-east region was the phosphorus content of medieval iron slightly lower than in central Poland.

Author

J Piaskowski: Metallographic Examinations of Iron Objects from Nowa Mecinka, Legnica Province, Osiek, Wrocklaw Province and Piotrowice Slaskie, Walbrzych Province. *Silesia Antiqua, 1984,* **26,** *45-61. (In Polish).*

Five ancient implements from Nowa Mecinka were made of low or high phosphorus iron. Twelve medieval objects from Osiek and one from Piotrowice Slaskie present typical technology for this period. The objects were made of high phosphorus iron or steel, the knives were welded iron and steel and heat treated.

Author

J Piaskowski: Metallographic Examinations of the Arrow-Heads from Late Medieval Settlement in Sloswewy, near Brodnica. *Acta Universitatis Nicolai Copernici-Archaeologia, 1984,* **8,** *136, 67-81. (In Polish).*

Nine arrow-heads from a forge producing these objects for Holy Mary Knights (14th-15th c AD) were analysed. All objects were made of high phosphorus bloomery iron (.19-.63%P) without hardening.

Author

J Piaskowski and H Piaskowski: The Beginnings of the Cupola Process. Charcoal-based Melting Process and the Technical and Economic Characteristics. *Stud I Mat Dziej Nauki Polsk, Seria D Z, 1984, (10), 55-83. (In Polish).*

Types of furnaces for melting cast iron are discussed, dating to 18th-19th c AD. Dimensions and shaft diameter are given and rate of blast flow in regard to fuel savings. Chemical composition of the pig iron obtained and properties of different grades are compared.

Authors (abridged)

J Piaskowski: New Investigations into the Theory of the Ancient 'Holy-Cross-Mountains' Iron. *Stud I Mat Dziej Nauki Polsk, Seria D Z, 1984, (10), 3-54. (In Polish).* *JP*

V S Patrushev: Early Iron Age Pectorals from the Volga Kama Basin. *Sov Ark, 1985, (2), 173-96. (In Russian).*

The illustration shows that these so-called 'pectorals' are neckrings and have been classified for the first time. They were found in the Akhmylovo sites in the Volga basin and the Ananyino sites in the Kama basin (map, tables). 139 of these neckrings are known to date. They are divided into 3 groups: made of wire, round in section; made of wire, rectangular in section; and some in the form of a plate. The ends are divided into three types: a) with rounded or loop-shaped ends, b) with curved ends, c) with straight ends. The artifacts can be dated according to their type between the late 8th to the 6th century BC. The distribution pattern in the Volga and the Kama basins testifies to the isolated development of ethnic groups of the lower Volga and the Kama basin. All pectorals found in the region originated in the Caucasus. The majority are of bronze but three are of iron and two of silver.

Authors (abridged)

E Riha and W B Stern: Roman Spoons from Augst and Kaiseraugst; Archaeological and Metallurgical Research. *Augst, Amt Museen Archaol Kantons Basellandschaft (=Forschungen in Augst, 5), 1982, 80pp, pls, figs, refs. (In German).*

CBA

M de Ruette, M Dupas, G Genin, L Maes and I Vandevivere: Etude Technologique des Dinanderies Coulés; I Le Chandelier Pascal de Saint-Ghislain. *Bulletin des Musées Royaux d'Art et d'Histoire, 1984,* **55** *(1), 25-53. (In French).*

ECJT

M de Ruette: Les Resultats d'Analyse de Teneurs des Laitons, Coules dans les Anciens Pays-Bas Meredionaux et la Principaute de Liege (Moyen Age et Temps Moderns). *Rev des Archeologues et Historiens d'Art de Louvain, 1983,* **16,** *252-79. (In French).* *ECJT*

K Schafer: Late La Tène Currency Bar Hoard from Saffig (Sword-Shapes, Socket Handles). *Archaol Korrespondenzbl, 1984,* **14,** *163-8, figs, table, ref.*

CBA

M Schvoerer and C Forrieres: Etude Physique et Bilan de Sante d'Un Tresor Monetaire Medieval. *Les Cahiers de Physiques Appliquée a l'Archeologie du C R I A A, Oct 1983, (1), 5-28. (In French).*

Examination of a coin hoard dated to the 12th-13th century from St Laurent et Benon (Gironde), France. It was relatively homogeneous, the major elements being Au and Ag representing coins from mints in Aquitaine, Angoumois, Poitou and Touraine with Ag varying from 39-44%. The coins were silver 'plated' by blanching with thicknesses varying from some microns to 60 microns. The main corrosion product was cuprite. *RFT*

ASIA

Anon: The Inariyama Sword; Flakes of Rust tell the Story. *Nippon Steel News, Jan 1985, 2pp.*

A Chinese sword dating back some 1500 years contains CaO rich inclusions which it is claimed support the theory that the metal was produced by the fining of cast iron using a lime addition for the formation of a low melting point slag. (It is quite possible that the lime arose from the use of wood-ash in smelting-abstractor).

RFT

I L Kyzlasov: Tools of Tashtyk Jewellers. (On the History of Crafts in Southern Siberia). *Sov Ark, 1985 (1), 107-121. (In Russian).*

A new source for the study of craft and the socio-economic development of the Sayany-Altai society is represented by tools of Tashtyk jewellers of the Middle Yenisei (1st century BC - 5th century AD) found among random finds in the Minusinsk Museum and the State Hermitage. The fact that such complicated all-purpose tools were used testifies to the high skill of the jewellers of Tashtyk. Detailed descriptions of tools are given including double cut files dated from the 9th-12th centuries. The tools studied against the background of the contemporaneous production indicate that there was clear-cut differentiation and high level specialisation of crafts. *Author (abridged)*

J D Muhly: Timna and King Solomon. *Bibliotheca Orientalis, May-July 1984,* **41** *(3-4), 276-291.*

Review article based on the work of B Rothenberg in the Wadi Arabah, Israel. Critically assesses the published dating evidence and suggests there is no evidence for Chalcolithic or Early Bronze Age copper mining activity. *PTC*

D Davis, R Maddin, J D Muhly and T Stech: A Steel Pick from Mt Adir, Jordan. *JNES, 1985,* **44,** *(1), 41-51.*

The pick apparently from a level dated to 1200 BC was found to have a tempered martensite structure.

PTC

R H Smith, R Maddin, J D Muhly and T Stech: Bronze Age Steel from Pella, Jordan. *Current Anthropology, 1984,* **25** *(2), 234-5.*

An iron blade from a Middle Bronze Age tomb was found to be a eutectoid steel with about 0.8% C. Although only the center of the blade survived in metallic form it seemed to have been cooled quickly suggesting quenching. It is reported as the earliest true steel yet encountered.

PTC

N V Ryndina and L K Yakhontova: The Earliest Copper Artifact from Mesopotamia. *Sov Ark, 1984 (2), 155-65.*

Evidence of the use of metal in northern Mesopotamia was dated to the 5th-6th millennium. Excavation by Soviet archaeologist of the pre-ceramic neolithic site of Tell Magzallia in the foothills of Jebel Sinjar made Mesopotamian metallurgy older by a millennium. The earliest copper artifact, an awl of the 7th millennium BC was found there. It was cold forged from native copper with traces of silver, zinc, tin, lead, iron, bismuth and nickel. Its composition indicates that it came most probably from the

copper outcrops of the Anarak ore field in Iran (Talmessi and other places). This find is close to the earliest copper artifacts from the Middle East found in Ali Kosh, Tell Ramad, Çayonü Tepesi and Çatal Huyuk. Analyses show that metalworking in the Middle East originated and developed during the late 8th and 7th millennium BC with the forging of native copper; its main sources being at that time the deposits of Central Iran. *ECJT*

AFRICA

V E Chikwendu and A C Umezi: Local Sources of Raw Materials for the Nigerian Bronze/Brass Industry (with Emphasis on Igbo-Ukwu). *West Afr J Archaeol, 1979,* **9,** *151-165. (Published 1982).*

Detailed article on mineral sources in Nigeria and evidence for their early exploitation. Demonstrates that copper, tin and lead were all worked. *PTC*

P T Craddock: Medieval Copper Alloy Production and West African Bronze Analysis – Part I. *Archaeometry, 1985,* **27** *(1), 17-41.*

The uses made of analyses of copper alloys from West Africa are critically discussed in relation to the techniques by which metal was produced in contemporary Europe and Islamic lands. The conclusions of this study are that it is likely to be very difficult to provenance the metal source, or date the artifact by composition except in the rare case of high zinc brasses. Some analyses of European copper alloys, manillas and further samples from Igbu-Ukwu are given. *Author*

R Maddin, T Stech, J D Muhly and E Brovarski: Old Kingdom Models from the Tomb of Impy: Metallurgical Studies. *Journal of Egyptian Archaeology, 1984,* **70,** *33-41.*

Analysis and discussion of 11 'model' copper objects found in the tomb of Impy dated to the 4th-5th dynasty. All of high purity copper. *ECJT*

D A Welbourn: The Role of Blacksmiths in Tribal Society. *Archaeol Rev Cambridge, 1981,* **1** *(1), 30-40, refs.* *CBA*

AMERICA

D Nemeth: A Gypsy Wipe Tinner and his Work. *Journal of the Gypsy Lore Society, 1982,* **2,** *30-53.*

Describes the work of itinerant tinkers in present day United States. Butane blowtorch used to clean and heat surface. Tinning flux of zinc, hydrochloric acid and ammonium chloride is swabbed onto the object to be tinned using fibre glass pads. *PTC*

ABSTRACTS

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