Tin from the Bronze Age smelting viewpoint Bryan Earl

Abstract

The problems associated with the discovery of tin ore, its separation and smelting to metal are discussed. Probable Anatolian Bronze Age techniques are examined with reference to later, AD period, British practice.

Introduction

Tin has had a bad media coverage: something cheap is 'tinny' – a reputation derived from the use of tin plated mild steel used to make 'cheap' objects and toys, many of which however are now appreciated as valuable and so far from cheap. True to tin's paradoxical nature, it is nearer to gold than other metals in many of its properties. Indeed, in the way in which it is mined and dressed, the techniques required are close to those used for gold. On the one hand it is a wonderfully benevolent metal, safe to use with food and also a key component of a whole cornucopia of useful alloys – the tin bronzes, solders, pewters and type metals – but it is also, true to its nature, a key component of some very nasty fungicides and bullet metal.

When fresh, tin is a brilliant, white, lustrously twinkling metal that feels 'heavy' with a low melting point of 231°C. It soon tarnishes, producing a thin layer of oxides which give it a dull, slightly brown-tinged grey surface appearance, very much like lead with which it can be easily confused. This may lead the unwary into considering that tin metallurgy is close to that of lead – this is far from the case in many of its aspects. Also, its nature seems to encourage the belief that it is easy to mine and smelt. It is not until one actually, really, tries to become involved in tin mining and smelting that agonizing reappraisals of many widely accepted ideas have to be made (Earl 1994).

Tin ores and their exploitation

By far the most important ore of tin is cassiterite, tin oxide (SnO_2) . From the point of view of bronze age metallurgy it was probably the *only* ore. Usually cassiterite is an unremarkable brown material, only giving away its presence by its high density and, if crystals can be seen, a brilliant sparkle from its high refractive index. Alas for the miner, nearly all sources

of cassiterite are notable for their drabness. Also it is rare to find any form of deposit with more than an average of 5% tin metal: 3% is considered rich ore, and down to 0.2% material has been mined from stream deposits. Cassiterite may be found in virtually any rock type, but there is always an association with acid igneous rock, either directly associated or nearby; examples are high silica rock types such as granite. The ore may be concentrated in a lode structure or in the form of enrichment within the country rock. When the host rock is weathered and eroded the cassiterite is released and is then deposited in sedimentary form, either eluvial on the moors or as an alluvial deposit carried into stream beds, some of which would since have dried up. Cassiterite is very resistant to weathering, so associated contaminating elements such as arsenic, which occur in the accompanying mineral arsenopyrite, are often removed when weathering has been extensive. However, within detrital cassiterite deposits pebbles of unweathered gangue material are often found which contain entrapped cassiterite, only the surface of each pebble having had the contaminants weathered out. Such contaminated 'grain' stream deposit tin ore is far more common than most writers would have us believe.

The unimpressive nature of most tin ore begs the question as to how tin metal first came to be won at the start of the tin-bronze age; throwing some heavy pebbles onto a camp fire has only a low probability of being the revealing process. A few experiments with rich tin ore as found in pebble form soon demonstrates this assessment. It is more probable that the cassiterite was revealed during some metallurgical operation that required the gravity concentration of an ore being won for another metal - such as gold - since the processes required to win gold are very similar to those needed for tin. The West of England tinstreamers regularly picked out the small amount of gold which was present in their ore, keeping it as their 'perk'. It would need the early miners to be quite sensitive to the potential value of the unusually dense cassiterite in order to attempt to subject it to a smelting process. A suitable smelting could in fact be achieved with reasonably concentrated cassiterite if the methods used for the direct carbon reduction, as used for copper ores, had been tried. Alternatively, but rather less probable at such an early stage, would have been the addition of the cassiterite concentrate to a copper smelting run; the tin would be co-reduced with the copper to form tin bronze. Iron minerals, often present with tin, would not be

particularly harmful under these conditions as the iron would be largely rejected by the copper, such that the resulting tin bronze would have only a low iron content.

If, however, the early miners were not sensitive to high density as an indicator of a potentially valuable material, some other property of the ore was likely to be equally important. This may be a reason why tin was worked in the Taurus mountains of Anatolia. Here a deposit containing both cassiterite and gold has been extensively mined, and associated with this has been intense, hand crushing activity (Earl and Yener 1993). Within this Anatolian deposit much of the cassiterite has an unusual, but notable, ruby-red colour which is readily revealed when the crushed ore is dressed by such operations as vanning. As radiocarbon and ceramic sherd evidence dates the mine to the early tin-bronze age, it seems possible that it was the skilled miners and metallurgists of the region, which had witnessed intense metallurgical activity for several millennia previously, who first worked the tin metal.

Ore preparation and smelting

Up until the early 1700s AD tin was smelted by mixing the cassiterite concentrate with charcoal which was heated to about 1150-1200°C, the charcoal acting partly as a reducing agent and partly as fuel. The fire was driven by some form of air blast. The earliest smelting was probably effected by holding the charge in a ceramic container or 'crucible' and blowing with the mouth down a blowpipe tube. The tin metal which formed collected in the bottom of the crucible and was then removed, either as prills-in-slag to be recovered by crushing and gravity separation, or as liquid metal that could be ladled out. More cassiterite concentrate and charcoal were added and smelting continued until the crucible ashed up. The cassiterite used in this work was won either from primary lodestuff, or from material resulting from the weathering of the primary lodes. It was virtually never found in a highly concentrated form, except at a few isolated sites. Moreover, in nearly all the mining operations the tinstuff had to be crushed to free it from entrapping gangue (waste) minerals, and this was done at first by hand, using stone pestles working onto stone mortars. Such crushing stones can be found on at least two sites in Cornwall and, when these are put side by side with the stones from Anatolian Turkey, it is nearly impossible to tell them apart.

Later, during the medieval period, crushing stamps were developed for this work – first in Cornwall, not Germany. These were one of the first technological improvements to this process. Stamps consisted of vertical wood logs shod at the business end with iron, which were picked up and let fall onto the tinstuff by tappets fixed into a barrel, usually turned by a waterwheel. The fine dressed material, be it stamped from stream or lodestuff, was then concentrated by various means to yield a cassiterite feed sufficiently rich to enable the tin to be smelted out of it. Although it is still popularly supposed that the old tin smelting was done on high grade stuff – 65% or better metal content – it is now being revealed that much lower grades were often used, sometimes down to 10% or even less. The manuscript by Thomas Beare (c 1550 AD) in particular should be consulted on this matter (Buckley 1994).

While the slag from high grade concentrate smelting nearly always consisted of assimilated furnace lining and therefore could be skimmed off the metal, the low grade material smelt came out as metal prills in a slaggy mass, and this had to be crushed, separated as metal prills, and then re-melted with a flux, such as borax, so it could be cast into a block; usually the mould for this consisted of a hollowed out granite boulder.

Historical tin smelting

'Crucible smelting' in this manner thus evolved into a furnace, consisting of a pit in the ground which was lined with a clay/stone grog lute. The blast was produced by hand worked bellows, the nozzle (tuyere) of clay being directed into the charge. Tin smelting by this technique was still in operation in Japan at the start of this century. A better refinement, which was much used in the West of England and later elsewhere, consisted of a small (up to 6 feet high) blast furnace made of stone and lined with a clay/grog (stone chippings) lute. The base was made of a stone trough, partly in and partly outside the furnace, into which the molten tin could flow out: the 'tynn hole'. The blast, which was provided by bellows that were either hand or waterwheel powered, was brought in through the furnace 'eye' that was above the tynn hole. The charge of alternate lots of charcoal and concentrated tinstuff (usually wetted to cut down losses from the blast) was charged in at the top. In many cases a flue led to a chamber where the furnace dust could be collected and recycled as it often held a recoverable amount of fine tin, either as mixed oxides or unreduced cassiterite. The tin metal flowed out, bright red hot, into the external section of the trough (in the West of England this was termed the 'float') and was ladled into the granite mouldstone to solidify. The tin was then usually remelted and 'tossed' - poured in streams from some height to oxidise some of the impurities - and finally cast into blocks. In the West of England the whole process was called 'melting' or 'blowing' tin.

In some cases furnaces using natural draught were used, particularly in the Far East but not in Britain. The actual reaction(s) involved in the reduction of cassiterite to metal do not seem to have been studied in any great

detail. The simple

 $SnO_2 + C \rightarrow Sn + CO_2$

does not appear to satisfy those of academic rigour. Several alternative routes have been suggested, such as the production of CO which then reduces the oxide, or the synthesis of CN⁻ leading to the formation of a cyanide which then reduces the cassiterite. One problem to note is that under laboratory conditions cassiterite can be reduced in a crucible at 600°C, whereas in practice the much higher temperature of 1100°C or above appears to be required to make the process work satisfactorily. It can be taken as 99% certain that if the low temperature was sufficient, the West of England blowers would have found how to achieve success using it. In practice they went to great lengths to provide large bellows to produce the blast required for a high temperature, higher than that required to produce iron by the bloomery technique. Whatever occurs, when one looks into a 'melting' furnace at work the cassiterite is seen to 'fizz' on the bright red hot charcoal and then produce a brilliant shining drop of metal. It is more than likely that several processes are involved in cassiterite reduction, from straightforward solid/solid reaction, formation of intermediates, and some form of ionic diffusion. The melting point of cassiterite is 1625°C.

When a concentrate containing an iron mineral such as limonite is 'blown', the tin which is produced is virtually always contaminated to some extent (largely controlled by the temperature of smelting) by a series of hard, tin-like tin-iron compounds collectively known as 'hardhead'. Such metal, however, is still quite useable for the production of tin-bronze by alloying with copper, provided trace quantities of iron in the alloy is acceptable. In the West of England - notwithstanding many reports to the contrary - nearly all of the tin concentrate 'melted' initially contained some hardhead. However, by careful liquation techniques, originally performed in the 'float', the metal was purified up to a very high grade: well over 99.9% was not uncommon, and such tin was exported worldwide, for example being specified for organ pipes of particularly fine tone.

Finding early tin-working sites

There is one problem that has to be confronted by an archaeologist looking for tin working sites. Virtually all of the slag produced would have been reworked in an attempt to extract as much tin as possible. Provided the conditions are correct, slag-tin compounds can be reduced to the metal to some extent. Those accustomed to the enormous slag piles associated with the smelting of many other metals, such as copper, have to readjust their philosophy. The largest of the slag dumps remaining in the West of England, where many thousands of tons of tin have been produced from the blowing process, could easily be scooped up and put in

the boot of a car!

It can be readily appreciated that the 'blowing' process was only a slight elaboration of the earliest Bronze Age methods. The problem confronting us today is what to look for if we are searching for Bronze Age smelting sites. Once one has seen an 'unusual' early artifact, it is surprising how they suddenly appear all over the place. Thus, once an early crushing stone with its little 'dimple' had been found at Crift Farm, near St Austell, it was no surprise to find that all of a sudden pebble paths to cottages in West Penwith were, in some cases, made of such stones. Their date however is a problem. Tin-smelting furnace remains dating to Iron Age or earlier times have yet to be found in the UK but if the Anatolian material gives up some more of its secrets, it may be only a matter or time before early UK sites can be identified. If the crushing stones are any guide, they may be very closely related.

Assaying ores

A particular problem of tin working is the detection, while prospecting, of the ore. The `classical' West of England method was by vanning. For this, the orestuff was crushed to a fine powder and a handful put on a shovel. Water was scooped on, and by a series of swirls and upward flicking motions the heavy cassiterite, if the miner was fortunate to have found it, was thrown up and formed a 'head' on the shovel. By this means a reasonably skilled vanner could easily judge if a deposit held either a half or one per cent of values (ie of a valuable constituent, tinstuff) and a skilled vanner could estimate several times more accurately. With vanning in its fully developed form, both the charge for the shovel and the 'produce' of cassiterite thrown up were weighed which made the assay less dependant on the skill of the assayer or 'tryer'. The method closely imitated the conditions that a potential orestuff would undergo if it were dressed in the full scale, by being crushed and then subjected to a flow of water that would carry the lighter waste gangue material further than the denser tin ore. Also, if the cassiterite was particularly fine, the trial on the shovel would report less available cassiterite than was actually present, thus closely reproducing the losses that would occur in full scale working. The assay only fell down when very advanced tin-dressing methods, particularly flotation, were introduced in the 1970s.

The vanning assay was not so satisfactory for concentrated material so a 'fire' assay was developed. This involved mixing the stuff with fine anthracite in a crucible which was then heated bright red hot by being buried in a bed of coals urged to a high temperature; the 'lump' of tin metal produced was weighed to give the assay. In the mid 19th century a better fire assay was developed where the stuff was heated to a mid-red heat with either potassium or sodium cyanide, which rapidly reduced the ore to give a remarkably accurate result. This was extensively used by Cornish smelters into the 1930s, and the quantity of unchanged cyanide that was washed down the streams would probably cause a present day ecologist considerable distress.

Wet, titration based, assay methods also came into use in the 19th century and are still used for checking overall results. Routine assaying is now carried out by measuring the fluorescent X-rays excited when the sample is bombarded by a suitable radioactive source; for tin the man-made element americium is the radiation source.

Modern developments

Two methods of tin smelting which differed radically from the Bronze Age process must be recorded. The first, developed in Cornwall by 1704 AD was the reverberatory furnace: the charge was kept separate from the heat source, to some extent imitating the crucible fire assay. Coal fuel was used initially, but in the 1920s the main Cornish smelter used oil fired furnaces. Fine anthracite and fluxes were added to the cassiterite charge. This method did produce some fairly large slag dumps; such slag is usually quite distinct in appearance. The last technique, used on a tonnage scale, was by the glow discharge from carbons in an electric furnace. Three phase electricity at 2500 amps was used, so one can appreciate it was rather more than a laboratory trial! This was well under way at St Ives Consolidated Mines by 1913, but then the First World War put a stop to its more general use. The technique is

just now being re-introduced.

United Kingdom tin is not finished yet. In March 1994, during her visit to Truro, Her Majesty the Queen was presented with an ingot of tin which had been mined and smelted in Cornwall during the past year. It came from South Crofty mine, part of which was already an 'ancient werke' in the 16th century AD.

References

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The author

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