ARCHAEOLOGY DATASHEET 203
Tin: smelting and production of alloys

Summary

Tin (Sn) is a soft, silvery-white metal which has been used for the production of a wide range of artefacts. Tin has occasionally been used on its own but most tin has been used in alloys with other metals. Tin is obtained by smelting suitable ores which are found in only a few parts of Europe. Until the end of the 19th century Cornwall was one of the most important sources of tin in the world.

The uses of tin

In England, tin was used as an alloying element in copper alloys from the 2nd millennium BC. The addition of tin to copper produces an alloy (bronze) which is harder, has a lower melting temperature, and is a different colour. Most bronzes contained 5-10wt% tin but high-tin bronzes (up to 25wt% tin) have had some specialised uses (HMS Datasheet 202).

A second important use of tin from the Roman period onwards has been in pewter. Early pewter was a lead-tin alloy but from the 18th century a range of elements (such as antimony and bismuth) were also used. Pewter has most commonly been used for the manufacture of domestic ware (plates, tankards and spoons). Tin-lead alloys have also been widely used as soft solder, for bearings and printing type.

Tin was used extensively in the 19th and 20th centuries for the manufacture of tinplate (sheets of iron with a thin surface coating of tin).

Tin and its ores

There are very few economically significant tin sources, and one of the most historically important was in Cornwall and Devon. It is most unlikely that any evidence for tin mining will be found in England outside of these two counties. The tin ores occur as cassiterite (SnO_2) in veins surrounding the massive igneous intrusion, and are sometimes accompanied by fluorides such as topaz and tourmaline or by sulphides of iron, zinc, copper and arsenic. These deposits are found in hard-rock, deep mines with a run of mine ore containing typically 0.5wt% Sn. In some deposits the cassiterite can be liberated relatively easily by crushing and gravity concentration. Concentrating cassiterite in this way is very effective as it is considerably more dense than most of the gangue minerals it is associated with. There is no direct archaeological evidence for hard rock mining of tin ores before the post-medieval period.

The other main type of ores are alluvial placers formed by the weathering of the hard rock deposits. Here tin is found as cassiterite, which may be further concentrated by gravity techniques. River bed deposits are worked by dredges or by hydraulic pressure jets and contain typically 0.01wt% Sn or less. The working of such alluvial tin deposits in Devon and Cornwall has also recovered a range of prehistoric artefacts, suggesting that these deposits have been exploited from perhaps the Bronze Age.

Tin ingots

A number of tin ingots have been recorded from the British Isles (especially Cornwall) but few from an archaeologically secure context. Some ingots are plano-convex in shape while others are rectangular; however, none have stamps or markings which would indicate when they were produced.

The chemistry of tin smelting

The reduction of cassiterite to metallic tin is simple and can be brought about by heating to red heat in the presence of charcoal. The reactions are:

$2C + O_2 = 2CO$

$SnO_2 + 2CO = Sn + 2CO_2$

The main difficulties arise from the gangue minerals present in the ore and fuel ash. Much tin can be lost by combination with silicates and can only be released by smelting at high temperatures and under highly reducing conditions. Unfortunately, these conditions also lead to the reduction of metallic iron, present in the ores or fuel ash. Even small proportions of iron in tin are undesirable as it will form iron-tin compounds (hardhead) which will make the metal brittle. Refining conditions which will remove this iron will tend to lead to the loss of some tin.

Early tin smelting

There are historical references to tin mining and smelting in Cornwall and Devon which extend back to the 14th century. Before the 18th century, however, direct archaeological evidence is extremely limited. Occasional evidence has been found from prehistoric (e.g. Caerloggas), Roman (e.g. St Just) and medieval contexts (e.g. Crift Farm). This has usually been limited to fragments of slag and no furnace structures. It is assumed that the tin ores were smelted with charcoal in relatively simple clay furnaces (or perhaps even crucibles) blown by hand-operated bellows.

Early tin smelting slags are usually fairly small lumps with an 'irregular rod-shaped tap-slag' morphology. Such slags are black, dark grey or dark brown and glassy. Microscopic examination usually shows that they are glassy with some metallic tin droplets trapped within the slag. Overall the tin content of these early slags is often fairly high but they contain relatively modest levels of iron. It is possible that the smelting conditions, in particular a low-iron charge with a moderately reducing atmosphere, and the inevitable loss of tin to the slag, were tolerated in order to obtain metallic tin with a low iron content. There are no obvious differences between early tin smelting slags of different date; indeed they share many of the same characteristics as blowing house slags (see below).

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Blowing house smelting

From mediaeval times, blast furnaces known as 'blowing furnaces' or 'blowing houses' were used in Cornwall and Devon for smelting tin ores. While earlier furnaces were probably blown using hand-operated bellows, the blowing furnaces made use of water to power bellows. Blowing furnaces were constructed from granite blocks and blown by a single tuyère at the rear with a taphole at the front. Tin and slag was run into a forehearth at the front known as a 'float'. Slag would have been removed as a solidified cake from the surface and tin ladled out into moulds. Analogous single tuyère blast furnaces were used throughout the world up to the start of the 20th century. Most were blown by single or double bellows powered by hand or foot.

An account of 1586 tells that tin prills ('pillion tin') were recovered from slags after crushing and that tin was also recovered from slags ('sinder tin'). The implication of this is that the slag was re-smelted after removal of the prills. Both types were sold as separate grades. In addition a lower grade known as 'hard tin' was sometimes produced, either by further slag smelting or perhaps as a result of contamination by arsenic or copper. Blowing furnaces were used up to the mid-19th century in Cornwall and appear to have been able to obtain supplies of charcoal despite the scarcity of woodland in the county.

Reverberatory furnace smelting

In 1699, John Lydall, a smelting expert from the Neath copper works was granted a patent for the use of a reverberatory furnace for smelting tin. This was a coal-fired oven having a fire at one end and a chimney stack at the other; the fuel did not come into direct contact with the ore. Slags were removed by scraping from the surface of the metal as 'drawn slags', or by tapping as 'run slags'. The use of the reverberatory furnace (also referred to as a 'cupola' or 'flowing furnace') for smelting tin appears to be a natural extension of its application to copper and lead at Neath and Flint respectively. The reasons for the acceptance of the reverberatory furnace in Cornwall was partly that it could use coal as a fuel. More importantly, the reverberatory furnace could be used as a roaster to remove arsenic before smelting for tin and metallic iron could be added to the charge to remove arsenic and antimony as a separate phase known as 'speiss'.

The reverberatory furnace was adopted as the furnace of choice throughout the world for the smelting of medium- and high-grade tin ores. It generally replaced primitive blast furnaces with one or two tuyères. Smaller reverberatory furnaces with more substantial reinforcement and thicker refractories were built for the second stage smelt. Even smaller reverberatory furnaces were built with sloping hearths for sweating iron drosses.

Reverberatory furnace slags (like early tin smelting slags) are mainly black and glassy. They usually have a lower tin content and higher iron content compared to earlier tin smelting slags.

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