Early Metal Technology

3. Tin and Zinc

Tin

- Copper (Cu) plus some Tin (Sn) equals tin **bronze**; copper (Cu) plus some Zinc (Zn) equals **brass**. Copper plus something else like arsenic (As) equals ????. Some (like the British Museum) call all copper alloys "bronze" but here I reserve the name for Cu-Sn alloys. Copper plus arsenic and so on will be "**arsenic copper**" and so on.
  The name "bronze" was bestowed on copper alloys at a relatively recent christening that occurred during the renaissance in Italy ("bronzo"). In the 1611 King James Bible, all copper alloys are called “brass”, irrespective of composition. Interestingly, the origin of the word "brass" is obscure; it is also germane to English. We have "Messing", "Laiton", "Ottone" in German, French and Italian, respectively - and the origin of those words seems to be obscure, too.
  The making of bronze started around 3000 BC in Europe and the Mid-East; possibly earlier in Thailand, and about 1000 years later in ancient Egypt. The Cu-Sn alloy containing around 10 % tin that we call bronze became the leading metal for two millennia and more. We know how to make copper, now we also need to make *tin* by smelting some good tin ores. That's were the trouble starts.
  - Tin ores are hard to find. They are far rarer than copper ores. What Mother Nature formed deep down was mostly "tin pyrite" a sulfide like Cu_2FeSnS_4. Closer to the surface, in the oxidation zone of a deposit, the sulfides were transformed to oxides, and in the case of tin pretty much only tin oxide (SnO_2) called **cassiterite** remains. Heavy dark cassiterite or "tinstone" is often embedded in ultra-hard granite, which makes direct mining very difficult or rather impossible in old times. This is similar to the case of gold where "mining" in antiquity was restricted to placer gold, the stuff that was freed from the quartz / granite by erosion and washed downstream, ending up in river beds or "alluvial fans". That's the name for those fan- shaped deposits of sediment built up by water eroding rock and washing the broken-up stuff downhill. As in the case of gold, cassiterite mining was often done by digging up suitable alluvial deposits.
- After 2500 BC or so, bronze became the dominant metal in the Mediterranean and Europe (and elsewhere) and before 1985 or so, nobody knew where all the tin needed for alloying came from. The Phoenicians, trading far and wide, were the main suppliers but it wasn't so clear where they got it from. True, Cornwall in England (very close to the edge of the world in those times) was a known source, and a few more had been discovered, but that simply wasn't enough to make all that bronze.
  Meanwhile, more than 40 ancient sites of tin mining have been discovered in southern Turkey that were unknown before 1985. Anatolia has rich deposits of many metal ores and, as we also learned in more recent times, some of the very oldest towns and civilizations that used copper rather early.
  A rather large tin-mining activity took place in the Kestel mine, near **Göltepe** (not to be confused with Kültepe), a large bronze-age town thriving from about 3300 BC to 1800 BC. The tin ore in the **Kestel mines** was mainly contained in hematite (an iron oxide) easily distinguished from other stuff by color and texture. This also allowed mining; typically by making a fire that cracks up the rocks in its vicinity.
  - Cassiterite is not a very distinctive and easily recognized ore like the colorful copper ores, for example. You won't notice it easily. In alluvial deposits you just see darkish stones; on occasion nice crystals. Here is an example of cassiterite ore already separated from most of the other stuff, the gangue.

Cassiterite ore

Source: "Dragon Minerals"; Internet at large

  - Cassiterite deposits thus are never rich; it's like gold in this respect. In fact, cassiterite is often found together with a bit of gold. The crucial process after finding some deposit is to separate the cassiterite-rich "stones" from the rest.

This is helped by the fact that cassiterite is rather dense ("heavy"), weighing in around 7 g/cm^3 (for comparison, gold (Au): 19.3 g/cm^3; lead (Pb): 11,34 g/cm^3; silver (Ag): 10,49 g/cm^3; iron (Fe): 7,87 g/cm^3; quartz (SiO_2): 2.648 g/cm^3; limestone ($CaCO_3$): 2.73 g/cm^3).
That's why experienced prospectors could judge the quality of some ore by "**vanning**". A powdered sample of raw ore is swirled with water on the blade of a shovel and then flicked upwards. The heavy cassiterite is tossed up through the water and settles at the top of the charge with the lighter waste below. The process is still used and a skilled vanner can detect as little as 0.1% cassiterite in the lodestuff - and that is good enough for mining!
A lot of "washing" and "sluicing" with running water concentrates the heavier stuff at the bottom. Ore processing can be seen as the decisive step in tin production since smelting of concentrated cassiterite is comparatively easy.
There are even indications that the old Turks employed (unknowingly) magnetism in the process! [1)]

In Göltepe the remains of crucibles used for tin smelting have been found. In a more primitive early process, smelting produced some slag containing "prills" or globules of pure tin. This necessitates crushing and separation of the stuff, so altogether tin making was done on a small scale per run and was rather labor intensive. Nevertheless, enormous deposits of slag in Göltepe are reported: 600 000 tons in just one pile! Göltepe must have been a major industrial site for much of the Early and Middle Bronze Age.

- There is no copper at Göltepe and the tin must have been exported to other centers for making bronze, for example to near-by Kültepe or Acemhüyük where bronze was used and traded in quantity.
  Once more, history needs to be rewritten. The view that everything good came from Mesopotamia cannot be maintained anymore. In a way, this view was biased on religious ground - Christianity came from there - and religion is almost as unreliable as Aristotle when it comes to science.

Zinc

Zinc is presently one of our more important metals. It comes in as No 4, right after iron, aluminium and copper; closely followed by lead. On the surface it looks like a metal that is easy to smelt. Its melting point is a comfortably low 428 ^oC (786 ^oF), not much higher than that of tin (232 ^oC) or lead (327 ^oC). One of its major ores is zinc sulfide, ZnS, known as **sphalerite** or "Zinkblende"; it is often found together with galena, the lead sulfide and on occasion forms nice crystals.

Cut sphalerite cystals

Source: Photographed in the Natural History Museum in NYC.

The German suffix "blende" is also used for some other minerals; it means "blind" or "deceiving". "Blenden" got their unflattering names because these minerals deceive you. They look like something useful but do not give the desired metal upon smelting. Zinkblende looks like galena but it doesn't yield lead upon smelting. *It doesn't even yield zinc!* We will see why in a minute. *Sphalerite*, by the way, is just Greek for "treacherous".
Sphalerite is the cubic version of zinc sulfide. There is also a hexagonal version, then it is called "**wurtzite**". I only mention that because the terms "sphalerite" and "wurtzite" are now used to describe the structure of *all* AB type crystals with a corresponding cubic or hexagonal lattice - and that includes all important modern semiconductors! Their lattice is either of the sphalerite type like GaAs, or wurtzite type like GaN.

- All things considered, one could righteously expect that zinc production should be as easy as tin or lead production. Funny enough, it ain't. Nobody has produced metallic zinc before about 1500 AD. The name "zinc" was coined by Paracelsus (1493-1541); it goes back to the German "zink" = jag, spike, tooth, beak because the metal then crystallized in a kind of "spiky" way.
  This is a bit strange - considering that **brass**, a copper - zinc alloy was by then more than 2000 years old.

Etruscan brass sculpture; around 500 BC
The museum actually describes this as: *Bronze* statuette of a reclining banqueter -but I'm rather sure this is brass.

Source: British Museum in London

- So we have a little puzzle here. The solution to that puzzle becomes evident when we do not just look at melting points of the metals (that are not decisive for smelting anyway), but also at **boiling points**. There we have Zn: 907 ^{o}C; Sn: 2 620 ^{o}C; Pb: 1 744^{o}C; Cu: 2 595 ^{o}C. in other words; the boiling point of zinc is abnormally low!
  - What that means is that zinc vaporizes completely and quickly at 907 ^{o}C (1665 ^{o}F), and somewhat more slowly but still rapidly at all temperatures above the melting point. In air the vapor will quickly oxidize to Zn oxide or ZnO.
    Take a glass of water and a glass of oil at room temperature, i.e. somewhat above the melting point of water and well above the melting point of oil. After a little while all your water is gone - evaporated - and all your oil, having a much higher boiling point, is still there. Zinc is like water in this analogy; all the other metals like oil.
    Smelting treacherous "zincblende" thus will not produce a nice silvery stream of shining metal coming off the hearth or furnace. All you get is perhaps a white or bluish powder caught in furnace cracks - but no recognizable metal.
    If you want to make zinc you have to do it from zinc *vapor* - and that takes retorts, distillations techniques and all such. The old Indians were probably the first ones to go into that.
- So how about ancient brass? This golden metal was known (as a kind of especially pure copper) since the first millennium BC and found particularly desirable by the Romans. In the times of Augustus and later they had brass coins, for example. Not that they worried much about what it was - just another flavor of copper, bronze, and so on, just as tin was some flavor of lead.
  Obviously Roman and other early brass was *not* made by alloying metallic zinc with copper. How was it done?

Brass sestertius of Titus showing the colosseum on one side

Source: British Museum in London

  - Brass was made by "cementation". Put small copper pieces in an almost closed crucible. Add some charcoal and this and that, and finally some "**calamine**", the name given to either zinc carbonate *or* zinc silicates since it wasn't clear that those two were different minerals for a long time. If you have ever heard of calamine lotion or even used it to stop the itching from mosquito stings - it's zinc oxide or carbonate with a little this and that.
    Arrange the stuff in several layers in a crucible and heat it. It might also help to do some ritual dance, scant an invocation, or sacrifice a lawyer. If you do some of those things right, you will find some brass in your crucible when you're finished.
    Why? Because you reduced the calamine and the resulting zinc vapor permeated your copper and thus made gold-colored brass.
    Of course, you, the old Roman brass maker, wouldn't describe it like that. Since gold by then was seen as the most noble of all metals, it was obvious that calamine somehow *purified* the copper. Same basic idea as assuming that steel was especially pure iron. Nobody then was blessed with the dirty mind of material scientists.

It is not quite that easy, despite of the many articles that describe brass making by cementation just as I did above. If you did produce zinc by reducing the calamine (that's why you needed some charcoal), it would tend to just evaporate out of the crucible, oxidizing on the way. It might thus be a good idea to have a lid on your crucible (with a small hole to let the other gases like CO_2 out that are also produced) and to add some "flux", for example glass shards, to produce liquid slag that sits on top and keeps the zinc in. Not melting the copper at first, i.e. staying below 1085 ^oC (1985 ^oF), the melting point of copper, might be a good idea because crushed-up solid copper, intermingled with the calamine, offered more surface for absorbing the zinc. On the other hand you needed at least 950 ^oC (1742 ^oF) for the efficient reduction of the zinc ores, producing zinc vapor right away at this temperature. Only after coming to the end of the process you liked to melt the brass formed in order to homogenize the stuff. That meant either raising the temperature somewhat or, if your temperature was just right, waiting long enough. The melting point of the increasingly zinc-rich copper comes down. as (almost) always, and at some zinc concentration might be down to your furnace temperature. In other words: you needed pretty good temperature control. If you were really good you could even control the zinc concentration in the final brass to some extent.
So brass making by cementation is indeed not all that easy. We know quite a bit about how it was done because this technology was kept well into the middle age. There are written accounts and many archeological finds from this period in history. That doesn't tell us how exactly the Etruscans, Indians, and Romans did it much earlier but does give a good idea of what is needed. It also makes clear that brass was an expensive metal for good reasons.
Intentional brass making by cementation (with at least 10 % and up to 30 % zinc) started around the 1st century BC. the Etruscans and others left some artifacts before the Romans started to make brass in a big way. It is also claimed that brass technology evolved somewhat earlier in India - fine with me, so be it.

There are also copper or bronze artifacts from much earlier times around that do contain some zinc. That doesn't mean that people tried to make brass. Zinc ores are often mixed up with copper or tin ores and might get into your smelter. True, most of the time your processing would have driven out the zinc, but every now and then, or with some particular smelting recipes, some of the stuff might have been forced into the copper. You don't get concentrations above a few percent this way, however.

**Brass (called "bronze" by the museum) combat helmet
of the Roman cavalry in Britain**

Source: British Museum in London

The brass of that helmet was mostly for show. The real protection came from an inner iron lining that is now missing.

[1)] Gary J. Laughlina, Judith A. Todd, in the article: Evidence for Early Bronze Age tin ore processing", published in: Materials Characterization Volume 45, Issues 4–5, October–November 2000, Pages 269–273, make the following claim:

"*Recent discoveries related to ores from Kestel Mine in the Taurus Mountains of Turkey show how prehistoric miners used the magnetic properties of the black iron oxide* (magnetite; Fe_3O_4; density 5.18 g/cm^3) *to accomplish the difficult separation of cassiterite from low-grade cassiterite ores. Excavations at the site of Göltepe, dating to the third millenium BC, have yielded hematite ore nodules containing a few percent, or less, of cassiterite and a sequence of processed, ground, and separated minerals. Laboratory experiments showed that reduction at temperatures as low as 700–850°C converted hematite* (Fe_2O_3; density 5.26 g/cm^3) *to the black magnetic oxide, which could be much more easily crushed than the hematite ore. On grinding and panning this material, the magnetic oxide clumped together effectively to yield almost complete separation*

of the cassiterite grains, a separation which, without automatic magnetic clumping, would be extremely difficult to accomplish due to the similar densities of cassiterite and magnetite minerals. The deliberate production of magnetic oxide may explain the shallow crucible bowl furnaces, the vast quantities of stone grinding tools, the large amount of residual magnetite at the site, and the fine particle sizes (which were necessary for the magnetic separation)."