10.1.3 Smelting Copper - The First

What is Smelting?

What exactly is smelting? I will let you know in *some detail* in the next sub-chapter.. Here, as a kind of foreplay, I look on smelting, melting and casting of copper in a more general way that can be extended to most metals.
I will start by looking into what smelting is *not*. I have done that long ago in an advanced module but now we need it right here in the mainstream part, so I'm going to repeat and enlarge a bit on what I have stated before.

First of all, let's do away with some common **misunderstandings concerning smelting**.

1. Smelting has nothing to do with melting!

Smelting is *not* the same thing, or almost the same thing, as *melting*. Smelting relates to melting like hitting to s...ting, to put it drastically, or shot to hot, shop to hop, spot to pot: not a all! Take romanic to romantic, or silicon to silicone for examples where misunderstandings are also quite common. Only one letter is different in all these pairs, but the meaning is very different in all cases. And for you Germans out there: yes indeed - smelting looks and sounds even more like "*schmelzen*", the German word for melting than melting itself, and that is the case because the English "smelting" does go back to the Old High German "smelzan"=schmelzen=melting. Fine. Those Old High (and Low) Germans just didn't know better. *You*, however, have no excuse. You could and should know better 2). Especially if you work for the science section of one of Germany's leading newspaper.

Smelting means to rip apart some molecule that contains a metal. It will be broken up into the elemental metal and something else. In chemical lingo you *reduce* the molecule in a **reduction** process. Most of the time you do that by reacting it with some *reducing agent* like **carbon monoxide** (CO).
If I apply the term for a moment to *all* molecules (something one normally doesn't), things get clear:

1. *Melting* ice produces water (H_2O); *smelting* ice produces hydrogen (H) and oxygen (O).
2. *Melting* wax (the hydrocarbons or alkanes of a candle, for example (C_nH_{2n+2}, e.g. $C_{31}H_{64}$) produces liquid wax; *smelting* would produce carbon (C) and hydrogen (H).
3. *Melting* copper ore (compounds of copper and other stuff like oxygen, carbonates, sulfides, ..) produces a molten copper compound. Chalcocite, a copper sulfide (Cu_2S) or cuprite, a copper oxide (Cu_2O), for example, melts at 1130 °C (2066 °F) or 1232 °C (2250 °F), respectively. *Smelting* copper ore produces copper (Cu) and residues of whatever else was in there.
4. *Melting* galena (lead sulfide, PbS) at 1114 °C (2037 °F) produces molten galena, *smelting* it produces lead (Pb) and some sulfur (S) compound.
5. *Melting* lead (Pb) at New Years Eve at 327 °C (621 °F) produces molten lead, *smelting* lead can't be done because lead is already the elemental metal.

Confusing smelting and melting comes from the naive perception that an ore is some rock that contains the elemental metal inside; in some fine pores or whatever. If you heat the ore beyond the melting point of the metal, it liquefies and oozes out - like water from a soaked frozen sponge upon thawing / melting.
That is a naive perception - except for noble metals like gold or platinum. These noble metals are indeed contained inside "rocks" as tiny particles in most cases. On occasion there might also be large "nuggets". Compound of these noble metals (proper ore) do exist but are very rare.
Relatively noble metals like silver or copper might also occasionally be found as "native" metals, sometimes even in large lumps and large quantities (e.g. in the Old Copper Complex in the USA). But the bulk of these metals is contained in compounds called ores.
This leads directly to the second basic misunderstanding concerning smelting:

2. The temperature needed for the reduction has very little to do with the melting point of the metal!

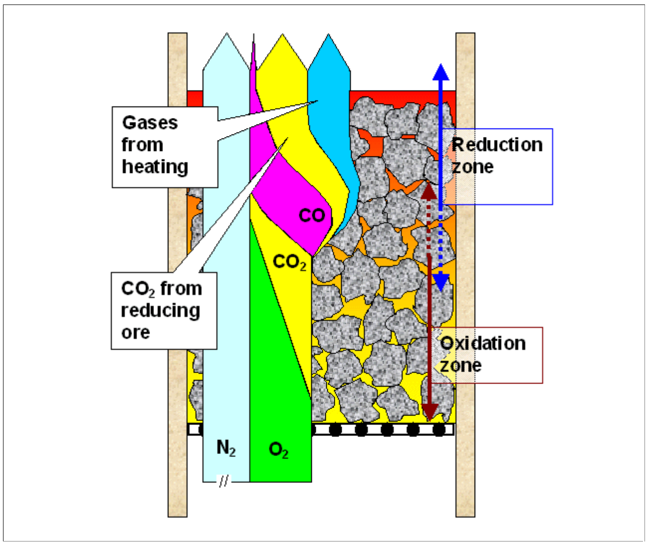
The temperature needed for reducing some *ore* has nothing or only very little to do with the melting point of the metal. It is of some importance on how you run the smelting *process* but does not determine *at all* the temperature you need for reducing the ore. True, making the metal liquid in a smelter is advantageous for the whole process because the liquid metal can easily trickle down - but you can only liquefy a metal *after* you made it!

To make a long story short, pretty much all smelting requires high temperatures for *several* reasons:

- The original source of heat comes from energy liberated by burning fuel, typically charcoal in old times. You need a lot of energy and the temperature in the burning charcoal bed should be around 1 200 ^{o}C for efficient smelting; 1 300 ^{o}C is better. What we call "burning" is the reaction of the carbon (C) in charcoal or wood with the oxygen (O_2) of the air, producing **carbon dioxide**, CO_2, and a *lot of energy* in the **oxidation zone** of a smelter. The energy liberated increases the average energy of the atoms and molecules involved, and thus the temperature. Moreover, air streaming through a bed of burning charcoal gets completely depleted in oxygen since that is used up after a few layers of burning charcoal lumps.

- Whatever sits above the burning charcoals - in smelting this would be your mixture of charcoals, ore and possibly a "flux". This mixture, called the charge or **burden** of your smelter, gets hot but can't burn because of the lack of oxygen. Instead other chemical reactions take place.
- At high temperatures (at least 1 000 ^{o}C for efficient smelting) hot charcoals react with the carbon dioxide (CO_2) produced lower down to **carbon monoxide** (CO). This reaction consumes energy, i.e. cools the smelter. Two molecules of CO are produced for one molecule of CO_2 and that is quite important for rather tricky thermodynamic reasons given here. The CO produced, streaming up through the burden, reduces the ore particles it meets as long as it is hot enough for that process to happen. It gets consumed in a process that typically produces fresh CO_2 and the elemental metal.
- All the hot stuff in your furnace (including the flux) may produce more gases, for example the stuff produced in a typical pyrolysis process, that also come out of the flue. If you use sulfitic ores, chances are that sulfur fumes, typically sulfur dioxide, (SO_2) are produced. And so on.
  It is a good idea to stay upwind of a running early smelter!
- All the hot stuff in your furnace (especially the flux), including the ore and the furnace wall, may react to produce liquid slag. While that seems wasteful, it is absolutely essential for iron smelting for reasons we shall see.

The drawing below shows all that schematically. It is not to scale; the **reduction zone** is typically far longer than the **oxidation zone**. The charcoals also rest on a kind of grate just to make the drawing easier. Moreover, for simplicity only the charcoals in the burden are symbolically shown.
Most of the gas flowing through is nitrogen (N_2) from the air, doing nothing but funneling of energy from the oxidation zone, helping in heating the burden above. Air, by the way, consists of 78 % nitrogen, 21 % oxygen, 1% argon, 0.04% carbon dioxide; forget the rest. In the reduction zone, CO is produced *and* consumed for reducing the ore, producing CO_2 once more



Schematic flow of gases through a smelter.
There is far more nitrogen then shown.

We aren't done yet in the listing of major points about smelting:

- Any halfway efficient smelting reaction needs to produce liquid *slag*, and slag is only liquid if it's hot - at least 1100 ^{o}C; 1200 ^{o}C is better.
- If you want to obtain your metal in the *liquid* state, you obviously have to exceed its melting temperature, at least in the lower part of your smelter, where it collects. However, it is usually advantageous to melt the metal already in the reduction zone; we shall see why presently. That is the only part where the melting temperature comes in!

The temperature where the actual *reduction* of the ore takes place can be rather low, however. Reducing iron or copper or with carbon monoxide can start at temperatures as low as 400 ^{o}C (752 ^{o}F). That has some serious consequences:

- Reduction of ore, provided there is carbon monoxide around, starts already way "up" in your smelter, in regions where it is not all that hot. The reduction process therefore is practically always a *solid state process*, producing small and porous *solid* metal particles already high up in your smelter.
- The problem is to get those particles down *without oxidizing them again!*. They need to by safely transported

through the very hot oxidation zone down into the "dump", where you collect them either as a liquid, or as a solid lump of welded together particles - a "**bloom**" - if no melting takes place as in the case of iron.

This is not easy. You need liquid slag for doing this efficiently.

- The confusion often encountered about the "temperature" of smelting comes from neglecting that there are several "critical " temperatures. The condition that the metal produced by the smelting should be *liquid*, is just one of many. It is true, however, that producing a *liquid* metal by smelting often makes things easier and thus is preferred in many cases. If you want to do that, you must go beyond the melting point of the metal, of course.
    - It is not that easy, however. Even if you could get the temperature in your *iron* smelter up to the melting point of iron, you wouldn't be happy. You would *not* get liquid iron! You would get a liquid mix or alloy of iron and carbon that we (unfortunatey) call call "**cast iron**". The reason for this deplorable fact is that very hot solid or liquid *pure* iron simply laps up so much carbon from its surroundings that it quickly and unavoidably turns into the "useless" stuff mentioned above. When I stated that the old smiths' couldn't get it up (the temperature) I told you only half the truth. The other half is: They didn't want to, either. They could have done it but they didn't want to produce cast iron.

Link Hub

Science Smelting

- Smelting is a rather complex thing to do. If I now have whetted your appetite and you can't wait for a deeper look into smelting, go right ahead and click your way through the science module right now.
Otherwise, let's go on:

3. Slag found on a dig does indicate smelting. The absence of slag does *not* indicate the absence of smelting.

- It is generally assumed that smelting always produces liquid **slag**, and you can tell that smelting took place when you dig up a lot of slag. You know slag when you see it. I'll get to slag in more detail later. If you can't wait, here is the link.

Slag from iron smelting

Slag from copper smelting

Source: Internet at large

The second part of the first sentence above is almost correct. If you do find substantial amounts of slag, there must have been some smelting going on. The first part is not. The basic copper smelting reaction $\mathbf{Cu_2O + CO \rightarrow 2Cu + CO_2}$ produces copper and volatile carbon dioxide *and nothing else*. The same is true for many possible reactions where an ore is reduced to the metal and gases like $\mathbf{CO_2}$.
In other words: it is perfectly possible to smelt an ore *without* producing slag or anything else that is discarded and left behind.

- It is just not very common. First of all, ancient (or modern) smelting does never have just the right amount of pure ingredients in the smelting furnace. There is always some "**gangue**", as we call the "rocks" that the ore is embedded in. Some gangue is pretty much always mixed up with the pure ore. The charcoal contains some "dirt" and the inside of your furnace might get dissolved to some extent, helping in producing slag. Even some of your ore, possibly all of it, might participate in producing slag.
And this is good! Slag production, if done right, is good for you. That's why *in serious smelting* slag-producing stuff (called "**flux**") is always intentionally added to the mix that goes into a smelting furnace.
To make matters a bit more complicated: Slag can also be produced *after* smelting, when a "bloom" of iron or

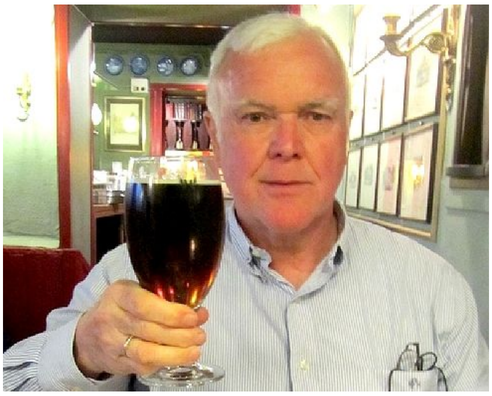
whatever product was taken out of the smelting furnace was refined or cleaned in a hearth. Slag then still indicates that some smelting must have taken place - just not necessarily where you found the slag.
So, yes, smelting does produce slag - whenever it is done on a *large scale*, i.e. most of the time. "Large scale" smelting starts essentially as soon as bellows are used to supply the air. A shaft furnace with an inner diameter of 30 cm or so, is already "large-scale"!

- The very first smelters, however, did *not* work on a large scale. It is quite possible or even likely that only little slag was produced in very early copper smelting. Indications are that this was done on a small scale "at home", possibly by a few specialists, who had the ore brought in from wherever it was found.
  So the absence of slag does not necessarily signal the absence of *small-scale* smelting.

A first Go at Smelting Copper

Now that we understand each other, let's smelt some copper. Let's do it in such a way that it will be liquid, meaning that we must exceed the melting point of copper at 1130 °C (2066 °F) in our smelting apparatus.

- *You* do it - with only the implements you had some 6 000 years ago. After all, you know by now a lot more about smelting than whoever did it first. Should be easy.
  I'm waiting with bated breath!



Waiting

Aha! It didn't work! That's what I expected. So you took a ceramic tube, filled it with charcoal and copper ore, set it on fire and waited. And waited. And no copper was produced! Well - I couldn't produce any either. Lots of people recently tried - just for fun or with science in mind. Typically, it doesn't work the first time. Or the second time.
So let' see how the ancients did it and ask the old (and slightly stupid, as we know now) question:

Who smelted (and cast) copper for the first time?
When and Where?
And how, exactly?

Note that I deliberately put smelting and casting together. While it is possible that somebody melted *native* copper and then cast it into a mold, there is no evidence for that. This might look a bit strange on first sight - why shouldn't Frodue's grandson **Frodoe**, who was a nice chap showing great promise despite his furry feet, not get the idea of putting some native copper in a pot, melt it, and pour it into some mold?

- Because melting and casting copper is actually *more difficult* in a way than just smelting it from ores. All you need for "inefficient and messy" smelting is a regular-size ceramic bowl or crucible, some malachite or azurite, some charcoal and a **blow pipe**. Any hollow reed with a clay re-enforced end will do. The rest is just "know-how".
  For melting and casting you need *in addition* to all of the above:
  - A *crucible* for the molten copper that can take the heat *and* the liquid copper. That need not to be much different from the smelting crucible but you must be able to handle it.
  - A *mold* with the right shape that won't fracture on impact with hot liquid copper.
  - A way to *manipulate* very hot things. Your kitchen gloves will not be good enough for handling a pot hotter than 1130 °C (2066 °F)!

Basic Link

Hardware

The link gives an overview about the hardware needed to smelt, melt and cast. It also defines terms (e.g. the difference between heart, oven, stove, kiln and furnace). Seen in this way (and there is no other way) it is small wonder that melting and castings came quite likely together with smelting. As far as the archeological evidence goes, both techniques appear around the same time.

There are innumerable books and articles (including my own ones) that assume that smelting was discovered more or less accidentally by a potter doing high-fired pottery. I'm not considering low-fired pottery, spanning the range from sun-dried mud bricks to some simple stuff made from local goo and put into a regular camp fire (typically not exceeding 600 ^{o}C; 1 112 ^{o}F). That is fine for making the Venus of Dolni Vestonice but not good enough for making a crucible Read the very good essays on Geology, History, and People of Richard Cowen and you get an idea of how this might have happened. Or read on.

Link Hub

Pyro-technolgy

Anyway, high-fired pottery needs **pyrotechnology**, the processing of things at high temperatures, and pyrotechnology in a non-trivial sense is actually older than pottery. Çrockü, Nölüdyæ, Frodü and their contemporaries already knew how to burn lime in quantity (not an easy thing to do) and even to make concrete (rather tricky) long before they hit on pottery and smelting! Check the link for details.
When people finally started to go into serious pottery, it stands to reason that some of them tried to adore their pots with those well-known green or blue stones - malachite or azurite - but after firing they found dull pots and a bit of copper. That's how the usual story goes. It is not wrong. Something like that could happen in principle. It's just not very likely.

- It is not enough to have some copper ore and high temperatures for smelting copper. You need to produce carbon monoxide (CO) to reduce the ore, and that does not only need high temperatures but also lack of oxygen. You won't easily get the necessary high temperatures in a fire as shown below, nor a lot of carbon monoxide.
  Producing the required temperature *and* a reducing atmosphere in a good pottery *kiln* can be done - the red / black Greek vases from around around 500 BC bear witness to that. But that kind of technology did not exist when the first smeltings occurred.

Direct firing of pots

Source. Wiki Common; Tatoli Ba Kultura

What I'm saying is that the pyrotechnology people used around 7000 BC - 6000 BC wasn't likely to produce copper or any other metal accidentally because some smelting occurred. You aren't likely to win the check pot in the lottery next week either - but somebody will. Very unlikely things do happen if you try often enough. If you bring copper ores collected for their beauty and some pyrotechnology together often enough, somebody somewhere will have accidentally produced some copper at some time. And that somebody will very likely not have noticed that. How often do you rummage around in the ashes of your stove or chimney, looking for unexpected treasures?

- So let's face it: somebody somewhere and sometime got everything right *and* recognized that something special had happened. Maybe the lucky discoverer had some knowledge about working native copper. Maybe he noticed that something special was contained in the pile of garbage left over from making pottery because his wife forced him to get the garbage out, and in picking it up those reddish prills became visible. And wasn't the big chief, the guy who had forcefully united all the warring clans into his "kingdom", crazy about those useless things that one found every now and then?
  It could also have been quite different. Maybe some early potter was really bend on getting away from the standard pot decoration techniques of using **ochre** powder that was rubbed on the "green" pot to be fired. Ochre is a mix of earthy stuff but always contains haematite (Fe_2O_3) - an iron ore. What you got was a reddish-brown color in the typical oxidizing atmosphere encountered in primitive firing. This guy was bent on getting the bright blue or green of azurite or malachite and started to experiment. He didn't succeed in getting colorful pots, and he didn't get any copper either. But this guy was tenacious an kept going. Maybe he put some malachite *inside* a pot with some charcoal, just to see what would happen. Maybe some copper ore fell inside a pot by accident, together with some charcoal. With luck, some smelting in a crucible could then have happened in a really hot fire.
  Then again, maybe what happened was ...(Insert you scenario of choice)

The only thing we know for sure is that smelting copper was discovered about seven thousand years ago!

Who Dunnit?

Noticing that something special has happened was probably the decisive step. It must have lead to some experiments along the "let's forget pottery and make copper" line. A break-through had occurred, and it:

- either spread from the unique place of discovery by "diffusion", or
- was discovered independently in other places at some other time.

There you have the "diffusion" or "independent discovery" hypothesis once more.

Of course, both hypotheses might be right if you look a the very big picture. The Meso and South Americans certainly discovered copper smelting and follow-up technologies like making bronze completely *on their own* - and millennia later than the Old World guys. They never discovered iron smelting, though. On the other hand, there is little doubt that copper and iron metallurgy *diffused* into China from the West. But how about the "hot" very early regions stretching from the Middle East via Turkey to the Balkan? Let's see what the experts have to say:

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On the origins of extractive metallurgy: new evidence from Europe

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ABSTRACT

The beginnings of extractive metallurgy in Eurasia are contentious. The first cast copper objects in this region emerge c. 7000 years ago, and their production has been tentatively linked to centres in the Near East. This assumption, however, is not substantiated by evidence for copper smelting in those centres. Here, we present results from recent excavations from Belovode, a Vinča culture site in Eastern Serbia, which has provided the earliest direct evidence for copper smelting to date. The earliest copper smelting activities there took place c. 7000 years ago, contemporary with the emergence of the first cast copper objects. Through optical, chemical and provenance analyses of copper slag, minerals, ores and artefacts, we demonstrate the presence of an established metallurgical technology during this period, exploiting multiple sources for raw materials. These results extend the known record of copper smelting by more than half a millennium, with substantial implications. Extractive metallurgy occurs at a location far away from the Near East, challenging the traditional model of a single origin of metallurgy and reviving the possibility of multiple, independent inventions.

"**Extractive Metallurgy**", by the way, is the polite term for "smelting technology".
Well-know experts authored that recent paper. They go for "*Belovode, a Vinca culture site in Eastern Serbia*" and date it to around *5000 BC*. The Vinca culture is part of what I called the "Danube culture"; the link tells the full story.
Now we know. Or do we? Here is a paper from another very well-know expert:

TÜBA-AR III (2000)

Frühchalkolitische Metallfunde
von Mersin - Yumuktepe:
Beginn der Extraktiven Metallurgie?

Ünsal YALÇIN*

Early Chalcolithic Metal Finds from Mersin - Yumuktepe: Begin of Extractive Metallurgy?

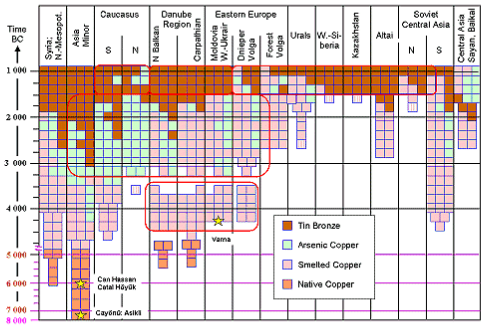
* Deutsches Bergbau - Museum, D-44801 Bochum /Deutschland

The Yumuktepe mound, now in the thriving town of Mersin, was first excavated 1937 - 48; digging resumed in 1993. **Ünsal Yalcin**, an author who already rectified the puzzle of the Can Hasan mace head, re-investigated some of the copper that had been found there and concluded that the copper was *melted* and came from "extractive metallurgy", i.e. *smelting* - around *5000 BC* once more.

I could show you more articles to "first smelting"; all of them sincere and convincing. Collecting "first smelting" articles could easily develop into a hobby, in fact. With more and more new finds or new analytical results of old finds coming in on a regular base, one could spend quite some time by acquiring, sighting and classifying new finds.
So let's give up. At least I do. Let's just recognize that smelting copper had been discovered around 5000 BC somewhere in southern Europe / Asia Minor.

Fine. Discovering something is a start. Where it gets you, however, often depends on many things. It was and is rather common that a lot of time might pass between a basic discovery and its being used for large scale applications. Some countries out there have not yet adopted democracy, something discovered 2 500 yeas ago and proven to be a good thing. Volta came up with the first battery and thus a source of electricity in 1800, and it was of no use to anybody but a handful of crank scientists. It took 100 more years before it started to change the life of people at large. Steel, our topic here, is a pretty old discovery but it took something like 3 000 year before it was really used on a large scale.

It's the same with the discovery of copper smelting. There is still a long way to go before smelting as an "industry" actually changed the life of people. The first copper tools must have been far inferior to good flintstone or obsidian tools, so why bother. In order to give you an idea of the complexity of early metallurgy development, I have redrawn a rather illuminating collection of data originally compile by **Chernykh**, 1992 1). It is best seen in the large version.



When and where copper and copper alloys (different colors) were used

Large Version

What you see is when and where copper and copper alloys (different colors) were used. I'm sure that many new data since 1992 should be included, and that some old data need to be corrected. I'm also sure that the over-all picture would not change drastically. What one recognizes without looking at details is:

- Regional differences are large.
- There is a "native copper pocket" in the "Middle East and Turkey and somewhat later in the Danube region. Here is a necklace with native copper beads from there.
- There is an "arsenic copper" pocket in the "South-east" before the coming of bronze
- Nothing much was going on before about 4 500 BC even in the "advanced" regions, where native copper was known for thousands of years by then.
- Copper smelting done by early cultures ("Varna") disappeared around 3 500 BC, leaving a gap of several 100 years before the technique reappeared again in the general area

Allright. Enough soft talk. Let's smelt some copper now

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1) E.N. Chernykh, (Inst. Archeology, Academy of Science, Moscow): "Ancient Metallurgy in the USSR; The early metal age" Cambridge University Press,1992

2) For example you, the guilty writers in the 1999 book "Kupfer für Europa" (Copper for Europe), ed. Ralf Busch- That's the book to the special exhibition of Cu and Cyprus in the former Helms museum in Hamburg, Germany (now it's the arcaeological museum).