

A Brief History of Steel

Advanced

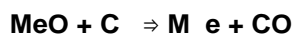
This is a much embellished translation of an earlier version written in German (it can be found in the Hyperscript "[Matwiss I](#)") and with some footnotes added later.

In order to make [steel](#) not accidentally, but conscientiously, you obviously first need to make **iron**. In contrast to the noble metals like gold, silver or platinum (and the occasional find of pure copper), iron is [never \(?\)](#) found as an element but practically always as an oxide.


- However, in contrast to other metals found as oxides (especially **Cu** and **Sn** oxides needed to make bronze), the temperature of a "normal" fire is not sufficient to reduce iron oxide *and* to make the elemental iron liquid - the melting point of iron is $T_m(\text{Fe}) = 1535 \text{ }^\circ\text{C}$; far above the **(1000 - 1100) $^\circ\text{C}$** that the ancients could produce [\(?\)](#).
- For **Copper (Cu)**, e.g., it is different - its melting point is $T_m(\text{Cu}) = 1083 \text{ }^\circ\text{C}$. Throw some copper minerals in a nice hot fire made with plenty of charcoal (producing **CO** which is great for reducing oxides), and liquid copper will result almost automatically.
- This happened *and* was noticed probably a good **6000** years ago, when early potters tried to adorn their pottery with nice green **malachite** - a copper mineral known in antiquity and used as a [gem stone](#). What a surprise, when one day in a particularly hot fire, instead of decorated pots they found an ingot of pure - and then extremely precious - copper in their oven. Copper was otherwise only found in small quantities (much less frequent than the (then) ubiquitous gold) in mountain ranges and river beds.

This was a decisive discovery for mankind: Precious and shiny metals could be made from dull stones. Things could be changed from one seemingly immutable form into a completely different one - [alchemy](#) has its roots right here, and the yearning for "[transmogrification](#)" has never stopped since.

- Early metal industry and the short-lived "**copper age**" began to be replaced rather soon by the **bronze age (Cu + (5 - 10)% Sn** and often some **As**); and the bronze age lasted more than **2000** years (it was not abruptly replaced by the iron age, but coexisted for about **1000** years).
- Here we first encounter the importance of impurities: A little bit of **As** as an impurity atom makes bronze "harder", it doesn't deform so easily any more. Of course, nobody knew this. All that was probably known was that some sources of copper and tin ore, together with all kinds of tricks (including some magic or prayers, of course) produced superior bronze.
- It is quite natural that tin and other metals were discovered shortly after the momentous discovery of copper **smelting**. Once you saw that precious copper could be made from some kind of rock, everybody not completely stupid would of course try what you could get with other rocks.
- We also have the beginnings of an environmental disaster, because for metal smelting you need tremendous quantities of **charcoal**. First in order to obtain high temperatures but, just as important, for reducing the metal oxide according to



- About **100 kg charcoal** are needed to smelt **5 kg** of copper.
- Besides shipbuilding, charcoal production is responsible for the disappearance of large parts of European forests (the disappearance of **yew** trees (which were ubiquitous in antiquity) from present day forests, by the way, is due to the middle age bow-and-arrow industry - nothing beats a yew bow!). Charcoal production was a major industry and the source of the many **charcoaler** ("Köhler") stories in fairy tales and folklore.
- Beside **Cu** and **Sn**, **Pb**, **Hg**, **Ag**, and of course **Au**, were known and produced on an industrial scale - especially by the Romans. But the Romans (and the Chinese, and the Indians, and the ...) had also **Fe** - but still no fire hot enough to melt it.



Auf Köhlers Spuren
Bis ins 16. Jahrhundert war Schleswig-Holstein ein Waldland. Dann wurde abgeholzt, um unter anderem Holzkohle herzustellen. Wie das geht, zeigt Stefan Brocke aus Sophienhamm bei Rendsburg jetzt im Loher Forst. Seite 6 Foto: W&A

From the "Kieler Nachrichten", front page, one day after after I wrote this paragraph. It says:
On the Track of Charcoalers
Up to the **16th** century, Schleswig-Holstein was woodland. Then the trees were felled to produce charcoal (among other things). How that is done will be demonstrated by Stefan Brocke in the Loher woods.

Early experience with the smelting and melting of other metals did not help in producing iron - it first came into use about **1000** years later than bronze. This must have been a kind of puzzle, because the ancients *did know* that iron existed. It was extremely rare and precious - because it fell from the sky in exceedingly small quantities.

- **King Tut**, matter of fact, had a little iron dagger made from meteorite iron right on his breast - obviously his most precious object. In old Sumeria, iron was called "*sky metal*" and the pharaohs in old Egypt knew it as "*black copper from the sky*".
- Of course, only pictures of his less precious and useless but more showy gold dagger are easy to find. The picture on the right shows both.
- The **Eskimos** in **Greenland**, matter of fact, made their iron tools for hundred of years from a large (**30 tons**) meteorite.
- Some American explorer (**Admiral R. Peary**) finally stole it (he wouldn't have expressed it that way, though) in the **1890s** and had a hard time to transport it to the Natural History Museum in New York. Here it is:



We may safely assume that the old materials scientists tried everything to smelt iron from suitable stones. They did have tricks to raise the temperature of a fire - in a **4500** old mastaba in Egypt, I took a [picture of a relief](#) showing six gold smiths (probably rather their **Ph.D.** students) blowing into the fire with hollow reeds. But just blowing with lung power will not do the trick for iron - maybe you get **1200 °C**, but that's it.

- So in a typical fire with temperatures well below **1500 °C** you do not get *liquid* iron - but you do get *solid* iron because reduction does take place - in a solid state reaction. What you get is an **iron bloom** ("Eisenblüte" in German), a mixture of fine iron particles, unreacted iron oxide, slag and charcoal residue. Here is an actual picture of some ancient bloom (from around **600 AD**; I actually "found" this myself (in some museum).



- The iron in the bloom was rather pure (and thus comparatively soft) because a solid state reaction produces *only* iron - carbon or other impurities have to diffuse in from the outside (if the iron would be liquid, it would just dissolve the dirt up to the solubility limit).

The early iron smiths (probably being **Hethites** of some form) could "wring" the iron from this bloom by separating the iron from the rest mechanically and repeatedly hammering together what was left at high temperatures (about **800 °C**; some of the slag then is liquid and gets squeezed out) with, no doubt, proper prayers to the respective gods and many (magical) tricks.

- What they finally obtained was "**wrought iron**" ("Schmiedeeisen"), i.e. a lump of rather pure iron consisting of small pieces welded together, with plenty of small inclusions (small, because of the hammering that breaks up large pieces of slag).
- Extreme care was necessary - from the selection of the iron ore, the reduction process and the hammering business. If you were careless, the iron oxidized again (it really "burns" at temperatures in excess of about **800 °C**), and if you kept your reduction process going too long, carbon diffuses in and you may end up with **cast iron** (C content about **3% - 4%**; melting point as low as **1130 °C**). Then you actually got it liquid - "casting" was possible - but cast iron is brittle and useless (for weapons, that is).

- Somewhat later, with larger furnaces and increased experience, the bloom obtained may have contained some high-carbon melted parts on its top layer. It then consisted of a whole range of iron-carbon alloys - from rather pure wrought iron to cast iron with *good steel* - say **0,5 % - 1,5%** carbon - in between. The art of the smith then included to pick the right pieces. This was a highly developed skill, we know about it especially from [Japan](#); but that does not mean that the Kelts or others did not do it just as well.
- ▶ But beware. The art of making iron and steel, developed over **2000** years in many civilizations, cannot be contained in a few lines, not to mention that very little is known about that story - iron, after all, rusts (see the link showing an [old sword](#)), and not much has been found that gives detailed knowledge about how the old romans, Indian, Chinese, etc. made their steel and iron products.
- Nevertheless - the early smiths, starting with the Greek god [Hephaistos](#) (the roman Volcanos) and containing many fabulous figures like the Nordic "[Wieland the smith](#)" or "Mime" in Wagners "Ring des Nibelungen", could produce articles, especially swords, from the iron bloom that were much better than the customary bronze stuff (and than of course "[Magical](#)" swords). In other words, they sometimes succeeded in making good steel.
- ▶ What was their secret? It is rather simple - looking at it retrospectively: You need the proper concentration of **C** in the **Fe bcc** lattice at room temperature (some other impurities are helpful, too; while others - especially **S** and **P** - were harmful). Raising the about **0,1% C** in wrought iron to an optimal **0,7 - 0,9%**, raised the [hardness](#) (or better the yield point) threefold! But if you got too much - say **2%** - you were on the road to brittle cast iron not useful for swords.
- Not being able too melt iron (and thus not being able to throw some magical stuff into the brew) the only way to get carbon (or on occasion **N** which also "works") into the **Fe** lattice was diffusion via the surface. What you needed to do was to "roast" you iron (possibly the whole sword) for the right time at the right temperature in a charcoal fire. Magic and praying helped - it did indeed: How do you keep track of the time without a watch? You utter a long prayer that you learned from your master - the right ones "worked"! The rest of the magical ritual was helpful in providing reproducible conditions.
- Of course the old practitioners had no idea of what they really were doing; if they thought about it, they felt that were purifying the iron in the (more or less holy) fire. This erroneous believe (like so many others) goes back to the (from a materials science point of view somewhat questionable) philosopher **Aristoteles** who certainly asked the right questions about life the universe and so on, and is righteously famous for that. His answers, however, were invariably wrong - even in the few instances where he could have known better.
- Well, we have made but the first step to steel. We now must make a few more steps for good homogeneous steel - or we delve into a fascinating world of its own, the various [damascene techniques](#), one of which is blending different kinds of steel into a compound material. More to that in the link.
- ▶ Here we look first a bit on what happens in heating up and cooling down your material. *We* know, after all, that going up in temperature, iron changes at **910 °C** from the **bcc ferrite** phase to the **fcc austenite** phase.
- Carbon feels much more at home in austenite - its [solubility](#) is higher than in ferrite. If the smith kept his iron in a good fire very long, he now might have had a rather carbon rich austenite in the outer layers of his sword. So what happens upon cooling down?
- Well, it depends. If the iron cools down *s l o w l y*, the carbon rich austenite will change to carbon rich ferrite. If there is more carbon in the austenite than the ferrite can dissolve, carbon will precipitate, forming a new **Fe - C** phase called **cementite** (with a quite complicated lattice). We now have cementite particles in **fcc** ferrite; usually in a very typical structure - both phases appear like a stack of plates. This kind of structure is called **perlite** because, looking at it under a microscope, it has a luster like pearls..
- Pearlite, the mixture of ferrite and cementite, however, is not much better than bronze as far as its mechanical properties are concerned. So you must prevent the phase change from austenite to perlite if you want to keep your sword "magic"! In other word, you must not allow enough time for the carbon atoms to diffuse around during cooling as would be necessary for forming precipitates. In other words: *You must cool down rapidly* (hopefully you did the proper [exercise](#) for calculating how fast you must cool down).
- ▶ Here we have the next *big trick* - after making bloom, extracting wrought iron, and carburization: **Quenching** - often the big secret of master smiths (there is a whole Japanese mythology to this subject). The hot sword is stuck in a liquid for some time and thus quenched - and only very unimaginative smiths would have taken common water at room temperature for that.
- If the cooling time was too short to allow **Fe-C** precipitate formation, we now have a supersaturation of **C** in the ferrite phase which then will have a strongly disturbed lattice structure. A kind of mixture between **fcc** and **bcc** phases will prevail which has its own name: "**Martensite**".
- *Now you did it*: Martensite has the fivefold "strength" of wrought iron!
- Unfortunately - if you got martensite at all, it tends to be brittle! Now the *next bag of tricks* is needed: Heat up your sword again - but keep the temperature moderate.
- Some of the *defects* that make martensite brittle anneal out and its ductility goes up. Bang it (i.e. deform it plastically), and you produce *dislocations* (hey, that's were we started from some time back!). Now you are manipulating a second kind of defect for optimizing mechanical properties!
- But now we stop (so does the smith). If you *really* want to know much more about this, use [this link](#).

- Anyway, if everything worked, you now have a very good (and of course magical) sword which was far superior to the bronze stuff of your opponents. In particular, you could make it *longer* without having to worry that it might break in battle (which was about the worst health hazard imaginable then).
- ▶ And don't think that an increase in strength by a factor of **4 - 5** is not all that much. The old Gauls, **Asterix** and **Obelix** notwithstanding, were conquered by the Romans not least because their swords bent and needed straightening (over your knee) after a forceful blow - something the Roman swords did not need. [Haha](#) - don't you believe all this Roman propaganda!
- ▶ Well, making a good steel sword was lots of work, lots of knowledge, and lots of luck. Considering what could go wrong, it is quite remarkable that the old smiths actually did produce superior steel swords now and then. Of course, probably more often than not, only the outer layer was steel, while the inside was still soft wrought iron - the sword was made from compound materials, in fact.
 - This gives us (and possibly also the old smithies) the idea of doing that from the start: Weld together soft and hard layers, carefully picked from the bloom or made by carburization, and hope that the result will combine the positive properties of both materials. We are talking *damascene techniques* here.
 - However, the word "**damascene techniques**" is a collective identifier of several very different technologies. Most people associate it with a kind of compound technology where two different kinds of steel were put together in layers and then forged into a sword or whatever. While this is something that was done - especially by the **Kelts** and other North Europeans - it was *not* what the guys in Damascus did, the purported source of the famous damascene blades.
 - As far as we know today, the "true" damascene technique actually worked with a famous kind of steel, so called "**wootz**" which was produced in **India** for maybe a **1000** years in a kind of closely guarded monopoly. Wootz was rich in carbon (about **2%**; there was a secret carburization technique) and the trick was to precipitate the surplus carbon in a pattern of fine **FeC₃** precipitates.
- ▶ A fascinating world unfolds behind the catch word "damascene technique", if you like you can browse the following links
 - [Damascene Technique in Metal Working](#)
 - [Literature to Damascene \(and Other\) Techniques in the Production of Iron and Steel From the Internet](#)
 - [A Cross-Linked Glossary of Some Terms from the History of Metal Working](#)
- ▶ Steel technology was not confined to the Mediterranean and the European North West. India may well have been at the apex of steel technology and **China** had its own technology centered around **cast iron**, used not so much for warfare but for civil objects like pots and pans.
 - And lets not forget the **Haya**, a people who lived in what is now **Tanzania**. They had a highly developed **Fe** technology and used it for beautiful sculptures, too. Their myths and fairy tales contain many stories relating to the making of iron, using a vocabulary that was heartily enriched with expressions relating to the making of humans.
 - There is even [some evidence](#) - collected recently (and, of course, [being discussed controversially](#)), that the old Africans had the highest temperatures of all, even reaching the melting point of iron some **2000** years ago (long before everybody else did)
- ▶ Whatever happened whenever and wherever, during the millennia, and despite the many difficulties, iron and steel became common materials. At some time in the middle ages or Renaissance, the melting temperature could be reached, but the mass production of good steel still had to wait for the **19th** century. Before, only "thin" objects - the paradigmatic "sword" or katana, scimitar, saif, shamshir, tachi, tulwar, yatagan,.. - could be made by in-diffusion of carbon.
- ▶ Charcoal was replaced in the **17th** century with coal, but not without unpleasant surprises. Iron that was smelted with coal instead of charcoal was very brittle and completely useless. We now know, of course, that minute amounts of sulfur in the **Fe** lattice - it segregates in grain boundaries - are sufficient to make **Fe** brittle, and **S**, like other harmful impurities, is contained in regular coal in rather large concentrations.
 - The solution to this problem, surprisingly, did not come from the military related strata of society, but from the second most important enterprise dear to the hearts of men: **beer** brewing. Brewers had tried to use coal instead of charcoal for roasting the barley - and produced a stinking abominable brew. Thusly coke was invented: Roast coal in an environment deprived of oxygen - the stinky stuff will evaporate and what remains is clean carbon - called **coke** - which could not only be used to brew beer, but was also usable for the iron smelting industry.
- ▶ The beginning of the industrial revolution was severely hampered by the lack of a large-scale process for the production of good steel. (Just imagine how the **Si** revolution would have fared without large dislocation free and rather perfect **Si** crystals). The (at least in German and French) paradigmatic **Eisenbahn** (chemin de fer in French), the rail road, needs rails; with regular wrought iron or cast iron the rails had to be renewed every **6** month because they deformed under the load (or cracked). Accidents were frequent and often catastrophic.

- The production of large amounts of iron was common by then - the essential part was blowing large amounts of air into the fire with the aid of mechanical bellows powered by steam engines. The leading British production accounted for **2,5** million tons of iron in **1850**, but the production of steel was still a cumbersome and expensive business, accounting for a few percent of the total production.
 - It was also known for sure since **1786** that steel had something to do with carbon; the first person suspecting this was one **Tobern Bergmann** in **1774** (other sources, however, refer to **Vandemonte**, **Berthollet** and **Monge** from France).
 - Still, all efforts to produce iron with the proper carbon content (and the right structure) "from scratch", were in vain. Sometimes things worked, sometimes they didn't - there was no large-scale, reliable, and reproducible process. And thus no big bridges, sky scrapers, safe railroads, big ships, efficient engines, and so on - one rarely reflects how much cheap steel changed the world!
- This time, however, progress came from the military industrial complex. It became simply too embarrassing that the big canons (made from cast iron) had a tendency to explode. Something had to happen.
- It was Henry **Bessemer** who was especially interested in good steel for big canons, because he had just invented a new kind of projectile that received some spin even from smooth bore guns (and thus was harder to destabilize during flight). Unfortunately, the canons couldn't take the additional pressure building up while the projectile was building up spin as well as speed- they exploded more than ever. So Bessemer was looking for large amounts of cheap steel.
 - He was then the first person (so it was believed for a while) who had the genius idea of making steel by getting carbon *out* of cheap, carbon rich **cast iron**, instead of using the cumbersome way of getting carbon *into* low-carbon wrought iron. The way to "**drive out**" the surplus carbon was to blast large amount of oxygen through the cast iron melt (which, by the way, definitely needed the **steam engine**; quite hard to do this through a **reed**). **CO** will form in the melt which not only burns off to **CO₂** upon hitting the air, but by doing this supplies the heat to increase the temperature of the melt because the melting point will go up with decreasing carbon content. If you stop at the right time (looking at the color of the flame), you will be able to adjust the carbon content of a large amount of iron to just the right value and thus produce large amounts of good steel.
- Mr. Bessemer, who was not exactly unknown before (he already had some fame as the inventor of the "lead" pencil (which in reality contains graphite), after publishing his finding on Aug. **12th, 1856** became very famous - and very rich - quickly; everybody wanted his process. The London Times went as far as printing the whole paper two days later.
- But **point defects** were fighting back. The industrial realization of the **Bessemer process** with large quantities of ore and coke yielded a big and very unpleasant surprise: **Bessemer steel** from large size production, in contrast to the Bessemer steel from "laboratory" experiments, was brittle and not fit for anything. Bessemer felt like "being hit by a flash of lightning from the blue sky"; the descend from the Olympic heights of top inventors to desperation was quick and brutal.
 - But Bessemer was a good materials scientist and engineer; if it worked once, it must work again. There must be reasons for what happened, and with diligence, one can find out what is going wrong. What had happened?
- Well, Bessemer's work, and the work of many others, supplied the (here much simplified) answer. Bessemer used **Swedish iron ore** for his experiments (you always use the best in lab experiments), while his industrial country fellows used **English ore** - and this stuff contained some phosphorous. The Bessemer process (possibly in contrast to the old-fashioned steel making process) did not remove the phosphorous, and small amounts of **P** are sufficient to render steel brittle. As we know now, **P** segregates in the grain boundaries and changes the local properties in a detrimental way.
- Phosphorous had to be removed (if you lived in merry old England, out on a conquest to assemble an empire, you did not want to have your steel production depend on the supply of Swedish iron ore). Two cousins, Sydney Gilchrist **Thomas** and Percy Carlyle **Gilchrist**, found the way in **1875**: Take (among other things) chalk stone for the lining of the **Bessemer converter** and even add some to the melt. The phosphorus would react with the **CaO** of the burnt chalk and end up in the slag which could be skinned from the liquid steel, or stuck to the lining.
 - There were plenty of other problems - on occasion, e.g., some oxygen remained in the steel and rendered it useless. Mr. **Mushet**, another Englishman coming to the aid of his country, found the solution: Add some "Spiegeleisen" (an iron - manganese alloy found somewhere in Germany) and your problems are gone. The **Mn** reacts with the surplus **O** and forms slag. It also neutralizes any sulfur in the mix, which would otherwise create real trouble.
- So besides Bessemer, many people were involved in bringing large scale steel production to fruition. And, as it practically always will turn out with great inventions, somebody else **did it before**. In this case it was one Mr. **Kelly** from the **USA**, who had the "Bessemer" idea **10** years before Bessemer himself. While he made a mint over patent hassles, the name Bessemer remains attached to steel, and Kelly is quite forgotten as a materials scientist.

- After the Bessemer process was sufficiently debugged, steel production took off and became supremely important strategically.
- **Siemens** in Germany and **Martin** in France developed the "Siemens-Martin process" and so on and so forth. The world production of steel grew exponentially (like Si or chips today): **22 kto** in **1867**, **500 kto** in **1870**, **1 Mto** in **1880** and **28 Mto** around the turn of the century. Today we are in excess of **500 Mto** a year.
 - In **1970** politicians generally still believed, that the wealth of a nation (and thus its power to subdue others) was directly coupled to its steel production (and thus to the degree of the nations prowess in manipulating point defects in **Fe**).
- You may feel now that we are talking chemistry here, and the typical urge of the chemist to produce pure substances. Nothing could be farther from the truth. We are exclusively discussing the dramatic influence of **point defects** on certain properties of a crystal lattice, like its resistance to the generation and movement of dislocations.
- If you would like to read more about this subject, refer to the splendid books of [S. Sass](#), [I. Amato](#) und [R. Hummel](#).
-

- Polybius was the guy who wrote about those bending swords of the Gauls. The Gauls as all other Celts, unfortunately, did not write anything. "[Publish or perish](#)" is not a new invention
- That the swords of the Gauls / Celts were inferior to those of the Romans is about as believable as the existence of weapons of mass destruction in Iraq **2000** years later: It was and is propaganda, stupid!
 - It probably was the other way around. The Celtic long sword made from Damascus steel was far superior to the Roman short sword, and eventually (around **300 AD**) was adopted as the Roman "spatha".
 - One is tempted to generalize: maybe the famous Roman technology was mostly adopted from other folks? Be that as it may, the way the Romans *used* technology - based on discipline, organization and large-scale production - was unprecedented and instrumental in conquering most everybody.
- Here are most modules dealing with the subject as a list:
- [Steel from a Materials Science and Engineering point of view](#)
 - [Details to Damascus Technologies](#) with many links to more sites.
 - [A "magical" Sword](#)
 - In German: [Magische Schwerter](#) (und japanische Schwerter)
 - In German: [Gruselige Schmiedegeschichten](#) (mit Magie).
 - In German: [Der Ring des Nibelungen](#) Zur Schmiedekunst und Siegfrieds Schwert