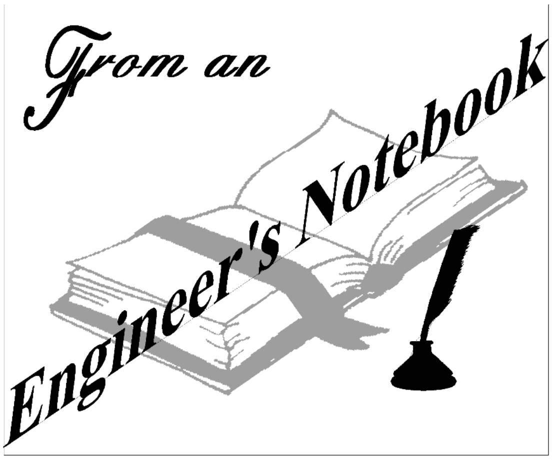


HISTORICAL AVAILABILITY OF STEEL

STEEL IN ANTIQUITY

Steel

Fundamentally, steel is a mixture of two substances. About 85% or more of the mixture is commercially pure iron, and the remainder is the chemical compound iron carbide (Fe_3C). On a crystal or granular scale, the two substances are uniformly dispersed in the mixture.

Commercially pure iron is a soft, ductile metal. Its Brinell Hardness Number (BHN) is 80, its Ultimate Tensile Strength (UTS) is 19 tons per square inch (speak to me not in kPa) and a two inch length will stretch to three inches before it breaks. Cold working pure iron will increase its strength. Not a lot different from copper or simple bronze you will note, however, its melting point is comparatively high at about 1500°C.

Iron carbide is eight times as hard as commercially pure iron and is very brittle. Its UTS is thought to be as low as 2 tons per square inch. The properties of steel, its hardness, toughness, strength and ductility, are in the first instance determined by the quantity of iron carbide present in the mixture and the way in which it is dispersed.

So, the properties of the steel available to our ancestors will have depended upon how well they could produce and control iron carbide.

Historical Production Methods

Scholars who are supposed to know about these things say that civilisation had moved into an Iron Age by 1000 BC. No less a person than the eminent civil engineer and President of the United States of America Herbert Hoover researched such matters at length and tells us that people were smelting iron ore before 3500BC. Others agree. Hoover, incidentally, puts a cogent argument that the Iron Age in fact preceded the Bronze Age [1].

Now that is a fair while ago, and the long and the short of it is that, while the ancient iron founders and blacksmiths provided the tools of civilisation, their work began so long ago, and became so accepted as commonplace, that we have only the most meager record of their methods. In Hoover's view it is not possible to assemble more than forty pages of pre-Renaissance text on metallurgical processes.

We are bound to assume firstly that the ancients treated iron ore by the general methods they used for other metallic ores, and secondly, that they used early versions of the methods recorded as being used by iron-masters in the 1500s.

Smelting

Thus we assume that the first process was "benefication" of the ore. This involves breaking and crushing the ore, concentrating it by removing trash, and then "calcining" ie roasting the ore to remove deleterious sulphides and volatiles. The useful part of the ore at that point consisted of fairly finely divided metallic oxide mixed with minerals from the rock - predominantly silica.

The second process was to use charcoal to take up the oxygen, to "reduce" the metallic oxide to metal. This smelting was done by mixing the ore with charcoal and a flux in a furnace and setting the lot on fire. The common flux was limestone and it helped with separation of the trash as a slag and with coagulation of the metal.

Charcoal was the fuel of choice for smelting. (Interestingly, charcoal was called *anthrax* in Greek and *carbo* in Latin.) Unlike wood, charcoal does not contain cellulose or water, either of which would retard the reduction of the ore and would also limit the rate of heat production. Charcoal has a calorific value of about 12,000 BThU per pound and modern reproductions of Roman furnaces have produced temperatures as high as 1300C.

Early furnaces were shallow pits or holes in the side of a hill. Later they became above ground structures shaped like the traditional beehives and then increased in size and sophistication. These early iron furnaces are now called "bloomeries". Egyptian inscriptions show above ground furnaces by 2000 BC with forced draught from bellows by 1500 BC. Crucibles for secondary melting were known to the Egyptians by 2000 BC. By the time of the Biblical prophets and the first Greek literature, say 800 BC, there are frequent references to bellows and there are archeological remains of smelting furnaces which are still fairly primitive. The writings of the Greeks around 50 AD reveal considerable advances and we may conclude that their furnaces were fair sized structures of some sophistication - perhaps comparable to those of 1500 AD for which we have written descriptions. We know that the ancients were able to achieve temperatures between 900°C and 1100°C in these furnaces at an early date. Pottery furnaces dating from around 4000 BC were able to reach temperatures of 1000°C, and we can see the later evidence of smelted copper and cast silver and gold which also require such temperatures. Of course, the larger the furnace the very much greater the forced draught that was required to achieve the higher of these temperatures.

Smelting Iron in De ReMetallica

What then came out of these furnaces when used for iron? Well, it depended on the temperature at which they were actually run.

Many complicated reactions take place in the furnace and most of them are reversible depending on the concentration and temperature. The following simplified version is given by Mayze and Barrell [2]

If the operating temperature is about 500°C:

> The iron oxide is reduced by carbon monoxide from the burning charcoal, and at the same time the iron reduces the carbon monoxide. The limestone is decomposed. The iron coagulates into a spongy mass.
>
> $Fe_2O_3 + 3CO \leftrightarrow 2Fe + 3CO_2$
>
> $2Fe + 3CO \rightarrow Fe2O_3 + 3C$
>
> $CaCO_3 \rightarrow CaO + CO_2$
>
> At this temperature the reduction process is very slow.

If the operating temperature is about 900°C:

> Carbon monoxide is decomposed to carbon dioxide and carbon. Any remaining iron oxide is reduced by the carbon. The iron, however, is still well below its melting point and

remains a spongy coagulate. The silicate trash is picked up as a calcium silicate slag is formed and this slag is molten.

$2CO \leftrightarrow CO_2 + C$ this is a reversible reaction but as temperature increases it goes mainly to the left so that

$CO_2 + C \rightarrow 2CO$

$Fe_2O_3 + 3C \leftrightarrow 2Fe + 3CO$

$CaCO_3 + SiO_2 \rightarrow CaSiO_3$

So note now the surplus of carbon monoxide. This has an important consequence.

Now here we must digress a moment. Most readers will be familiar with the concept of case hardening steel and the method in which the first step is called "carburising". An intriguing thing about that process is that it is not carbon so much as carbon monoxide which does the trick.

Experiments have shown that no carbon is absorbed by the steel if all the air or oxygen is removed. That is why commercial casehardening compounds contain oxygen-carriers such as sodium carbonate. According to metallurgists,[3] it is probable that the carbon absorption at the surface occurs by a reaction between iron and carbon monoxide.

$$2CO + 3Fe \leftrightarrow Fe_3C + CO_2$$

The carbon dioxide produced by this reaction breaks down to form more carbon monoxide and the process continues at the expense of the charcoal in the hardening compound.[4]

Thus in the furnace at 900°C the ancients were able to get iron carbide into their mixture. The higher the temperature the more carbon monoxide and the faster the carbon was absorbed and this had a further interesting effect.

As the proportion of carbon dissolved in the mixture increased, the melting point went down. At about 2% dissolved carbon and 1100°C the mixture was a slush, and carbon diffused much more rapidly and evenly through it. On reaching 4% and 1200°C the mixture was a pourable fluid.

Now we can see what these furnace would produce.

If as soon as the slag was molten it was run off and the furnace was opened, the product would be a lump of spongy iron that could be wrought into solid metal bars - "wrought iron". It would contain less than 1% of dissolved iron carbide and would be intermixed with about the same amount of slag.

If the furnace charge was allowed to soak at 900°C before the slag was run off, the yield would be greater and there would be less included slag, but the iron sponge would not be particularly malleable and would, at first, have been difficult to use. Parts of it would have up to 15% or more iron carbide.

If the iron-master allowed the furnace to soak at around 1100°C, or forced the temperature above 1250°C to achieve faster reduction of the ore, the iron would run to the bottom as a slushy liquid and freeze into a hard brittle useless mass. It would contain about 50% iron carbide uniformly distributed.

Steeling

The desirability of the harder, higher strength material coming from the furnace soaked at 900°C must eventually have been recognised, and we can well imagine that serious attempts were made to find ways of working it. We know that can be done by working it hot with iron hammers. Once that was discovered there would have been more call to produce this steeled iron. The obvious approaches would have been:

trying to control the furnace output to produce it directly,

putting wrought iron back into a charcoal furnace and heating it up again,

or mixing soft wrought iron with the hard brittle waste product of the overheated furnace by melting them together.

Steel in Antiquity

There seems to be little doubt that steel was being made and used as early as 1000 BC.

Iron articles dating from about 1200 BC show higher carbon content on the outside surfaces than the interior. Hardened tools made around 800 BC have been found in both Assyria and Egypt. The Hittites, living in what is now Turkey, were said to have the secret of hard iron. Homer's Odyssey of around 800 BC contains, as translated, the lines:

> "And as when armourers temper in the ford
> The keen-edg'd pole-axe, or the shining sword,
> The red hot metal hisses in the lake"
>
> (This was on the occasion of Ulysses bunging the Cyclops in the eye with a stake.)

Quench hardening, a characteristic of steel, was well known in classical Greece and was subsequently taken up by the Romans who it seems also knew about tempering. The Romans had a word, in Latin, for a hard form of iron "chalybs". Scholars translate this as "steel" but we must not rely too literally on that translation.

When the Roman legion was pulled out of Inchtuthill near Perth in Scotland in 76 BC it was instructed to leave nothing that could help the enemy. Timber was taken away, pottery smashed and wattle was burned. They buried 875,320 nails and spikes ranging from 2" to 16" long. Sir Ian Richmond dug them up in 1961. Metallurgists reported that the composition of the nails varied from pure iron to high carbon steel.

The place where one would use the best iron product available would be in swords and there is a variety of legends about very special swords.

The sword that was so sharp that if held in a stream it would slice in two a lock of wool or a lily floating on the current against its edge. The Saracen's magic Damascus sword that would cut through a silken veil which fell through the air against its edge. Excalibur and Durandel, the swords of Arthur and Roland, and those of Siegfried, Godfried, and Charlemaigne.

Our records of these legends come from medieval times or later and it is very hard to establish when the owners of these swords were actually in business. The legendary swords may have existed as the very special, perhaps fortuitous, products of the iron-masters. They may have been an attempt to medievalize ancient mythological concepts, or they may simply represent another unattainable ideal of the romantics - like perfect chivalry and chastity, and no more real than fire breathing dragons.

The story of King Arthur and his sword was first written as a history text in Norman England of 1135 AD. (We use Sir Thomas Mallory's romanticised version of 1485.) Arthur's sword was called Caliburn in 1135 and this may be a derivative from the Latin word for hard iron "chalybs". Though my Welsh friend doesn’t think it sounds right, Phillips and Keatman [5] suggest it may be a derivative of the earlier Celtic name for Arthur's sword "caledfwlch" meaning flashing sword..

Their modern scholarship suggests that the legend has some basis in Celtic history, that Arthur probably existed as a tribal military leader, that he had a good sword, and that the sword was probably a Roman sword made for the Roman garrison of Caernarvon England. The death of Arthur is placed at 519 AD. The Romans pulled out of Britain in about 400 AD so this would mean that Arthur's sword was 50 or 100 years old when he acquired it. (Incidentally, it was a Celtic practice to throw swords into ponds at funerals as an offering to the goddess of water.)

Thus there is ample evidence of the early existence and use of steeled iron, but there is no record of the means of manufacture. It is very hard to assign dates or even an era to the first use of a steeling process. We do not know how Roman swords were made. The fact that there are legends about especial swords suggest ordinary swords were probably not made by methods giving invariably high quality. The quality varied as it did in the nails. Thus the swords were probably made by hammer-welding strips of soft wrought iron and steeled iron. Harder steel strip may then have been scarf welded to the edges under the hammer.

Alternatively, they may have been made from what is now called natural steel. That is, steel produced directly from the smelting furnace. Iron ore from several locations in Europe contains manganese and when smelted, even by early methods, can result directly in a steel having say 0.2% to 0.8% carbon - a very desireable product. The Romans had a product called Noricum iron which may have been a natural steel.

Now Professor Emeritus C.S. Smith of Massachusetts Institute of Technology tells us that the famed swords of Damascus were made entirely from hammer-welded strips of what we now call Wootz steel. This was a very uniform product but does never the less have a sort of lamellar structure.[6] We associate Wootz steel with India and we know that the Romans traded with India and particularly that they imported "Seric iron", lustrous silky iron, from India between 0 and 400 AD.

But it is my guess that Wootz steel originated at the eastern end of the Mediterranean, which was a generally technologically advanced area in ancient times. Successive waves of conquerors and émigrés probably took the process to India. It seems probable that Romans, Macedonians and Greeks also knew of or obtained Wootz steel from Turkey or Syria well before the Roman trade with India. It is no coincidence that the Roman word for hard iron is "chalybs" and that the name of the Hittite tribe in Turkey who knew how to make hard iron was the Chalybes . St John V. Day uses an obscure expression of Aristole to suggest that the Wootz process was known to the Greeks in 350 BC. Any such knowledge would have spread through Europe with the Romans before the decline of their Empire around 400AD. So perhaps Arthur got lucky and found a Roman sword made from Wootz steel or natural steel.

Wootz steel

Wootz steel was made by mixing soft wrought iron with the hard brittle waste product of the overheated furnace. The hard brittle material, which today we would call pig-iron, was re-melted in a crucible and a faggot of thin wrought iron strips or plates was immersed in the liquid. Capilliary action drew the liquid between the plates and fused them together. It is not clear whether there was any significant carburisation of the wrought iron. On cooling, the ingot had a fine lamellar structure that was further refined by hammering at red heat as it was forged into the final article. It did not need tempering after quenching. It was the remnants of the initial lamellar structure that gave the characteristic surface patterns on Damascus swords. [7]

Blister steel

Perhaps the earliest method of steeling iron was to take the iron as it first came from the furnace and run it through again. It seems the iron mass was broken into small pieces and again mixed with limestone. This was re heated with charcoal in a forced draught furnace and when the iron coagulated it was quenched. The resulting lump was broken into pieces on the anvil and each piece checked for hardness. The soft pieces were returned to the furnace and the steeled pieces were hot forged into bars[8]

A—Forge. B—Bellows. C—Tongs. D—Hammer. E—Cold stream.

Steeling Iron in De ReMetallica

In a later refinement of the process, wrought iron bars were packed with charcoal in a crucible and reheated. At first the crucible was fired internally. Later the crucible was made air tight and heated externally. Bealer says cast iron boxes were also used - presumably at a much later date. [9] The wrought iron could not be melted but it was made hot enough to react with carbon monoxide, as previously described, to give an iron and iron carbide mixture. The carbon diffused about 1/8th inch into the steel per day. Steel produced by this method contained from 5%% to 30% iron carbide and could be hardened and tempered - though the properties of each piece were different. The process was called "cementation" and iron carbide became known as cementite. We do not know when this process began, but Hoover says it was a method used in primitive Japan and India.

This type of steel, as we would expect, appeared burnt on the outside and was called "blister steel". It was invaluable for making tools and weapons. It was easily welded to iron so that axes, plane irons, draw knives, scissors and shears were made of the cheaper wrought iron with steel edges welded on. For this reason it was also called "shear steel". Blister steel quality was uneven and unreliable. Each piece had to be tested.

Forge case hardening

The technique of pack hardening a nearly finished article seems to have been known in medieval times at least. The item would be heated in charcoal in the forge and the edge hammered up before quenching and tempering.

The role of Carbon

It must be emphasised that in all of this the iron-masters and blacksmiths knew nothing of the role that carbon was playing in their products. The charcoal was there to provide heat. Indeed it was not until late in the nineteenth century that the role of carbon was discovered.

Medieval metallurgy

If the ancient Europeans had a technique for making fine steel consistently then it was lost during the Dark Ages 450 to 1000 AD. Because for the next seven hundred years they persisted with the method described by Agricola and its derivative blister steel.

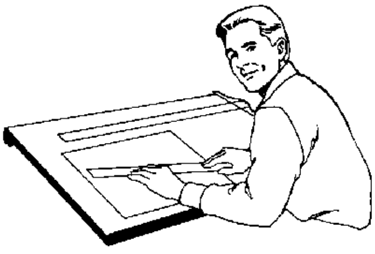
Neverthless, iron and steel were engineering materials in the fourteenth century. In the Archives of Aragon in Barcelona there are the financial records of the construction of a tower clock for the palace of King Pere IV of Aragon at Perpignon.[10] The work, which began in 1356, was administered and recorded by Ramon Sans. The total project cost was some $A8million in today's values. The clock was fairly large. The cost of the 970 kg of forged wrought iron components was about $A40/kg The steel used for some parts of the clock, and especially for files to finish and adjust the parts, was very much more expensive at about $A160/kg[11]

The best metallurgical practices were used by the armourers. Charlemaigne and his famous sword Joyeuse were quite real. He was King of the Franks and Lombards in 742 AD. In the thirteenth century the Germans devised a machine for drawing wrought iron through hardened steel dies to make wire. The wire was then used for making chain mail. Techniques for forging armour plate were refined and both chain mail and plate armour were probably casehardened. The characteristics of Wootz steel in the Damacsus swords of the Saracens must have been evident to the Crusaders, and European cutlers attempted to emulate the product by twisting and hammer-welding strips of blister steel and wrought iron - often enough with good results.

The popularised methods of Japanese sword manufacturers involving repetitive hammer-welding of strips of wrought iron and steeled iron seem to date from the fourteenth century.

Following the Renaissance, those Europeans who could afford the cost had their sword blades made entirely of steel - either blister steel, natural steel, or the Wootz steel imported from India. In the next 300 years a trade in Wootz steel developed between Europe and India, but the methods of producing it were not publicised until the nineteenth century.

We must next follow three different but not entirely separate threads - the wrought iron thread, the cast iron thread, and the steel thread.



To be Continued

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[1] Georg Bauer, nom de plume Georgius **Agricola** (Hoover H.C. and Hoover L.H. translators) **De Re Metallica** 1556, The Mining Magazine London 1912, reprinted Dover Publications New York 1950

[2] **Mayze** H.H and **Barrell** F.T **Senior Chemistry**, William Brooks and Company Brisbane, c 1955

[3] For example, **Clark** D.S. and **Varney** W.R. **Physical Metallurgy For Engineers,** van Nostrand Princeton New Jersey 1962

[4] Actually at these temperatures the carbon goes into a solid solution of carbon in austenite at the metal surface and then migrates towards the centre of the metal by diffusion. It forms iron carbide on cooling.

[5] **Phillips** G. and **Keatman** M. **King Arthur the True Story**, Century Random House, London 1992

[6] **Smith** C.S. **A History of Metallography**, University of Chicago Press, Chicago 1960

[7] This description is due to Bealer who in turn cites C.S. Smith

[8] **Agricola** op cit

[9] **Bealer** A.W. **The Art of Blacksmithing**, Funk and Wagnalls, New York 1969

[10] vide **Beeson** C.F.C**.** Perpignan 1356 and the Earliest Clocks, Antiquarian Horology 7, June 1970 pp 408-414

and **Beeson** C.F.C. Perpignan 1356: The making of a Tower Clock and Bell for the King’s Castle, Antiquarian Horological Society London 1983

[11] **Landes** D.S. Revolution in Time, Clocks and the Making of the Modern World. 2nd ed, Penguin Books Ltd London 2000