History of Metallurgy

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Preface

This paper was written in order to examine the order of discoveries made in the history of metallurgy. It is part of my efforts to put the study of social and cultural history and social change on a scientific basis capable of rational analysis and understanding. This has resulted in a hard copy book *How Change Happens: A Theory of Philosophy of History, Social Change and Cultural Evolution* and a number of websites such as http://homepages.paradise.net.nz/rochelle.f/, Sense Perception and Reality and How Change Happens and How Change Happens Rochelle Forrester's Social Change, Cultural Evolution and Philosophy of History website. There are also papers on Academia.edu, Figshare, Mendeley, Vixra and Social Science Research Network websites and other papers on Google docs such as Sense Perception and Reality, How Change Happens, The History of Medicine, The Discovery of the Atomic World and the Constituents of Matter and on Guttman Scale Analysis and its use to explain Cultural Evolution and Social Change and on Issuu and Scribd.

Abstract

The ultimate cause of much historical, social and cultural change is the gradual accumulation of human knowledge of the environment. Human beings use the materials in their environment, including fire and metals, to meet their needs and increased human knowledge of fire and metals enables human needs to be met in a more efficient manner. Fire and metals have particular properties and human knowledge of those properties increases over time in a particular order. Increasing human knowledge of how to create higher and higher temperatures enables the smelting and melting of a wider range of ores and metals. Those ores and metals that could be smelted and melted at lower temperatures were used before the ores and metals which had higher smelting and melting points. This meant that copper, and its alloy bronze, were used before iron and its alloy steel. Pure metals, like copper and iron, were used before alloys such as, bronze and steel, as the manufacture of alloys is more complicated than the manufacture of pure metals. The simplest knowledge is acquired first and more complex knowledge is acquired later. The order of discovery determines the course of human social and cultural history, as knowledge of new and more efficient means of smelting ores and melting metals, results in new technology, which contributes to the development of new social and

ideological systems. This means human social and cultural history, had to follow a particular course, a course that was determined by the properties of the materials in the human environment.

The history of metallurgy developed in an order related to the properties of the metals available to human beings, and to the ever increasing human knowledge of those properties, and of how to create environments of greater and greater temperature, enabling metals to be smelted, melted and alloyed with other metals. Metallurgical history began with the use of native metals, which are metals not attached to an ore. Such native metals are fairly rare so the widespread use of metals really began when humans learnt how to extract metals from their ores, a process known as smelting.

In, *Before Civilization: The Radiocarbon Revolution and Prehistoric Europe*, Colin Renfrew described the development of copper and bronze metallurgy in the Near East.

"This development in general tends to follow a series of steps. These have been well documented in the Near East by Theodore Wertime, and can be listed as follows:

1. Simple use of native copper. Native copper - almost pure copper as found in nature - occurs fairly widely in many regions where there are copper ores. In most areas copper may first have been valued simply as another attractive mineral or stone - just as meteoric iron was used in the Near East to make cylinder seals, along with a whole range of attractive stones long before its metallic properties were exploited.
2. Cold hammering of native copper. It would soon be realized that this new mineral did not fracture on hammering so easily as other stones. Shaping by hammering was an obvious way of working.
3. Annealing of native copper. Repeated cold hammering makes the copper brittle so that the object fractures. By heating it in an open fire, and hammering while hot, this brittleness can be avoided. Cold hammering can then be used to finish the object, and to give harder cutting edges if desired.
4. Smelting of copper from its ores. This represents a notable advance. The ores themselves are often brightly colored, like azurite (blue) and malachite (green). The oxide and carbonate ores are more easily reduced than the sulphide ones, and a temperature of about 700°C is needed, which can be attained without the construction of a complicated oven. Only fairly small and irregular pieces can be obtained in this way, however, unless the copper is allowed to run off at a higher temperature.
5. Casting the copper in an open mould. Casting requires heating to the melting point of copper, 1,083°C, and allows the production of good thick blanks in roughly the required shape. These can then be further worked by annealing and cold hammering.
6. Casting-in, and the use of the two-piece mould. More complicated shapes can be obtained by these methods. Shaft-holes, for instance, can be produced during casting by inserting a charcoal core in the mould. A two-piece mould allows a more elaborate shape than in a one-piece mould where the upper surface of the casting is always flat.
7. *Alloying with arsenic or tin.* Arsenic bronze and tin bronze are much stronger than pure copper, so that the objects are less likely to snap in use. Alloying can also improve the hardness, and also the process of casting, avoiding the formation of blow-holes made by gases dissolved in the melt as they come out of solution on cooling.
8. Lost wax casting. A wax model is made in the shape of the desired bronze casting, and coated with clay which forms the mould. The wax melts as the molten bronze is poured in to replace it in the mould. The mould itself is broken and removed when the bronze cools. In this way, castings of much more elaborate shapes can be produced.

Further developments are possible of course, and the story does not stop there. It is important to note that each step is to some extent dependent on the preceding one, and indeed the sequence can really be regarded as one of increasing competence in pyro technology, in the handling of materials at high temperatures. Increasingly specialized skills are involved at each stage, and efficient casting of bronze usually requires some sort of oven where the flow of air can be controlled.

In the Near East, stages 1 and 2, and probably 3 as well, were reached very early over a wide area. Many of the earliest Neolithic settlements known, including Ali Kosh in Iran, and Catal Huyuk and Cayonu in Turkey (the last perhaps not even a farming community), have yielded finds of native copper. Stage 4 is reportedly documented at Catal Huyuk around 6000 b.c. in radiocarbon years. Stages 5 and 6 come later - the earliest reported instance, not yet documented by metallurgical analysis, is a mace head from Can Hasan in Turkey dated around 5000 b.c. in radiocarbon years.

Alloying with tin, stage 7 in this sequence, was a much later development and is seen around 3000 BC. (c. 2400 b.c. in radiocarbon years) in the Near East, the Aegean and the Balkans. It is about this time also that lost wax casting, stage 8, is first seen.

A similar sequence of development can be demonstrated also in the Balkans. Stage 1 is documented by the find of beads at the cemetery of Cernica in Romania, described as of 'copper mineral', which in this case implies ore rather than pure native copper, worked in the same manner as beads of stone or shell. Cernica is a contemporary of the earlier Vinca culture, and must be dated back almost to 5000 B.C. in calendar years. A little after this time, but still before 4700 B.C., awls and small objects of native copper are found in the Vinca culture and its Balkan contemporaries.

The earliest scientifically documented indication of stage 3, hot working, comes from a site in the western U.S.S.R., dated before 4000 B.C. It is a copper fish-hook which had been heated to 300°C and worked to shape. Tools made from smelted copper, which can be recognized by their greater content of minor impurities, occur at about the same time.

The most striking advances, illustrating stages 5 and 6, are seen in the Gumelnitsa culture. There, certainly before 4000 B.C. in calendar years, impressive axes were cast, with the shaft-hole already in position. Examination by J. A. Charles shows that these were indeed cast in open moulds, with the shaft-hole cast-in rather than being drilled out subsequently. Several have been found stratified at sites in Bulgaria including Chotnitsa, and one was included in a hoard of flat axes or chisels at a Vinca culture tell in Jugoslavia.

From this form developed the axe-adze, with its working edge at each end (Plate 7). Some of these are magnificent objects, and their manufacture may have begun before 4000 B.C., and must have continued for a long period after this time. But alloying was apparently not practiced in the Balkans until the Bronze Age, from around 2500 B.C. in calendar years, at much the same time as it began in the Aegean and the Near East.

This gradual and logical development, which took at least a thousand years, from the first tentative use of copper and copper ore to the accomplished casting of the shaft-hole tools, clearly reflects considerable advances in pyro technology. But it is important to realize that, in the copper age at least, it was pottery rather than metallurgy which led the way in pyro technological innovation.

Already the very first Neolithic farmers in Europe had ovens for parching grain and baking bread; examples of these were excavated at the very early Neolithic site of Nea Nikomedeia in north Greece. And from the very beginning the Balkan farmers were accomplished potters. In the earlier Vinca culture temperatures as high as 700°C or 800°C may have been reached for the firing of pottery. It is particularly significant that the attractive graphite-decorated pottery of the Gumelnitsa culture required even more exacting firing conditions. Graphite will burn off, if it is fired in oxidizing conditions where the supply of air is not limited, at a temperature above 700°C. It is clear that the pottery was in fact fired at around this temperature in conditions where the flow of air was carefully regulated. Whether or not this involved the use of some more elaborate potter's kiln is not yet clear, but it certainly does indicate an increasing mastery in the control of materials at high temperatures.

All this had come about in Bulgaria and south Romania, where graphite decorated pottery was being produced, already before 4500 B.C. And the development of ceramic technology seems a logical one, for which no outside influence need be invoked. The exciting thing is that these conditions were not so far from those needed for the smelting and casting of copper - a temperature of 1100°C and the control of air to provide a reducing atmosphere. Seen purely in technological terms, the development of copper metallurgy in the Balkans was already heralded by the skills of the potter.

Technically, then, it is entirely possible that metallurgy developed independently in the Balkans. The natural resources were available, and so was the pyro technological skill. But this alone does not demonstrate that metallurgy was something worked out locally, without essential ideas from the earliest metal workers of the Near East." (Renfrew, Colin (1973) *Before Civilization*, Penguin Books, Harmondsworth, England 188-192).

The Colin Renfrew quote only covers part of the history of metallurgy. Arsenic bronze was developed before tin bronze probably because copper and arsenic are sometimes found in the same ores while tin is a relatively rare metal in Europe, North Africa and South Asia, although it is found in present day Iran. However tin bronze soon became the preferred form of bronze as arsenic bronze had a tendency to slowly poison those working with the metals.

The next major metallurgical development, after the use of bronze, was the use of iron. The earliest use of iron was iron obtained from meteorites. Iron trinkets were found in Ancient Egyptian tombs dating from 4,000-3,000 BCE. However such iron was rare and had little effect on human societies.

The first major impact of iron on human civilization was when the Hittites began smelting iron around 1500 BCE. Iron is smelted from its ores at around 1200°C and melts at 1528°C. The Hittites used furnaces lined with clay to produce the temperatures required to smelt the iron ore. The ore and wood was placed in the furnace to burn and the wood became charcoal. Carbon in the charcoal combined with oxygen in the iron ore to produce an oxide of carbon and the iron metal in the form of a spongy mass. The spongy mass contained earthy slag which could mostly be removed by considerable hammering to produce wrought iron. Additional hammering when heated would allow the metal to be shaped into tools and weapons. The furnaces available to ancient metallurgists did not produce enough heat to melt the iron to produce cast iron.

The situation was different in China where better furnaces and iron ore with a high phosphorus content which produced iron which melted at relatively low temperatures allowed the production of cast iron from around the 3rd century BCE. In Europe an improved furnace was invented about 700 CE in Catalonia. A bellows was used to force air through a nozzle called a tuyere into the charcoal to produce higher temperatures. The temperatures however were not sufficient to melt the iron and allow the production of cast iron.

It was not until the 14th century that iron smelting furnaces capable of melting iron were built in Europe. These furnaces were known as blast furnaces and were substantially larger than earlier furnaces. The blast furnaces had water powered bellows which produced much higher furnace temperatures as the bellows produced a continuous and strong flow of air through the tuyeres into the furnace. The higher temperatures allowed the iron to absorb a small quantity of carbon, which lowered the melting point of the iron to a temperature which the blast furnace could obtain. The melted iron, known as pig iron, could be poured into moulds or could be remelted and cast into any shape. The carbon in the pig iron could be removed to produce wrought iron which was more malleable than pig iron.

Substantial improvements were made to blast furnaces between 1500 and 1700. Reverberatory furnaces, with no chimneys and using underground pipes to bring in air achieved higher temperatures with domed shaped roofs lined with clay reflecting the heat back into the furnace. Continuous smelting processes, which involved ore and fuel being continuously feed into the furnace to provide a continuous supply of iron greatly increased efficiency and production.

The use of coke, purified bituminous coal, in blast furnaces began around 1709 and greatly increased after 1760 when a method was found to get rid of silicon from iron produced from blast furnaces using coke. The silicon made it costly to convert pig iron into wrought iron. In the late 18th century coke replaced charcoal in most British blast furnaces. Blast furnaces produce pig iron but for many products the more malleable wrought iron was more suitable. The conversion of pig iron into wrought iron involved eliminating the carbon from the pig iron. An improved method of getting the carbon out of the pig iron was invented by Henry Cort in 1784. Cort’s puddling process melted the pig iron in a reverberatory furnace which burnt the carbon and other impurities out of the iron and produced a mixture of iron and slag. The slag was removed by hammering to produce the wrought iron.

A further improvement to blast furnaces allowing still higher temperatures and reduced fuel use was invented by James Neilsen in 1829. Neilsen’s invention involved using the furnaces own gases to pre-heat air before it entered the furnace. The air entered the furnace through a red-hot tube heated by the furnaces own gases and the hot air allowed the furnace to reach temperatures not previously obtainable. The pre-heating of the air blast was further improved by Edward Cowper in 1860 when he invented the hot-blast stove. Waste gases from the furnace were feed into a brick lined stove and heated the stove. Air entering the furnace is passed through the stove so it is heated before it reached the furnace.

Wrought iron was the principal material of the Industrial Revolution. Steel was a better material but was too expensive for widespread use during the Industrial Revolution. Steel is chemically mid-way between wrought iron, which contains almost no carbon, and pig iron which contains about 4% carbon. Steel usually contains between 0.2% carbon and 1.5% carbon. It was not until the second half of the 19th century that a process for creating cheap steel was invented. The Bessemer process was patented in 1856 and used a vessel called a converter into which molten pig iron was poured. Air was blown through holes in the base of the converter. The oxygen from the air combines with some of the iron to produce iron oxide which reacts with the carbon in the pig iron to produce carbon monoxide which releases some of the carbon from the pig iron. The remaining carbon is removed when the oxygen in the air is combined with silicon and manganese which form a slag. The resulting metal was brittle so manganese is added to remove the brittleness and then carbon is added to bring the steel up to the desired carbon content. The same process was independently invented in America by William Kelly.

An alternative method of making steel, known as the open-hearth process was invented in 1864 by William and Frederick Siemens and then improved by Pierre and Emile Martin. The open–hearth process involved pre-heating the air going into the furnace in two chambers that operated alternatively. The chambers, known as regenerators, contained a fire brick checker work and were alternatively heated by the furnace gases so the air passing into the furnace through the regenerators was heated resulting in higher furnace temperatures. As with the Bessemer process, iron oxide was used to remove carbon and other impurities, and manganese was added to remove brittleness and if necessary carbon was added to obtain the desired carbon levels.

The invention of electrical generators led to the use of electricity for heating furnaces. The first electric arc furnace began operation in 1902 and, while more expensive than the Bessemer and the open-hearth processes, was able to produce better quality steel due to it having fewer impurities than steel which had been in contact with fuel. Electric furnaces were able to produce greater heat and the temperatures could be more easily controlled than with ordinary furnaces. The use of electric furnaces was to result in the large scale production of metals such as tungsten, chromium and manganese which when added to steel gave it useful properties such as improved hardness and resistance to wear. The electric furnace also allowed the mass production of aluminum. Aluminum is widespread on the Earth but it was difficult and expensive to extract from its ore, bauxite, before the invention of the electric furnace. The electric furnace produces aluminum by a process of high temperature electrolysis which produces molten aluminum in large quantities, although the process uses substantial quantities of electricity.

It had been long recognized that the use of oxygen, rather than air, in steel making would produce higher temperatures, faster production and reduce fuel costs. The high cost of producing oxygen stopped its use in steel making, until the price fell substantially and in 1948 the L-D process for using oxygen in steel making was developed. The L-D process involves blowing a jet of nearly pure oxygen at supersonic speed on to the surface of molten iron. The oxygen quickly burns out the carbon and other impurities resulting in faster production and reduced fuel costs.

The social and cultural consequences of the discovery of metallurgy were initially quite minor. Copper was initially used mainly for ornaments and jewelry as it was too soft a material to replace the stone tools and weapons used in Neolithic times. It was only when bronze was invented that metal tools and weapons replaced stone tools and weapons to create a Bronze Age. Bronze however was a reasonably expensive metal and when iron smelting was discovered by the Hittites the new metal soon replaced bronze as the principal material for tools and weapons. Iron ores are reasonably widespread and iron is a harder material than bronze, making it better for both tools and weapons.

Iron was used for a wide variety of purposes such as nails and tools, cooking pots and kitchen utensils, axes for clearing land and for the tips of ploughs. The use of iron tools and weapons gave humankind greater control of their environment leading to increased population and larger settlements. Iron became the principal material for the Industrial Revolution being used in steam engines, industrial machinery, in railways for rails and locomotives, for bridges, buildings and in iron ships.

The Bessemer and open-hearth steel making processes led to a great reduction in the price and increase in production of steel. Cheap steel replaced iron in a great variety of applications. Steel was used in railways and for ships and in bridge building. Motor vehicles became one of the biggest users of steel in the 20th century and different types of steel began to be developed for different purposes. Cutting tools were made from steel containing chromium and tungsten as that steel remains hard even at high temperatures. Excavating machinery was made from wear resistant manganese steels and transformers, generators and motors were made from silicon steel due to its magnetic quality. Stainless steel containing chromium and nickel was widely used in kitchens and in industrial plants vulnerable to corrosion as it does not rust. Steel coated in zinc or tin also resists rust and is used for cans containing food and for equipment used around the home.

Metallurgy has had a great effect on human societies, certainly since the Bronze Age and increasingly since the Iron Age and particularly with the modern Steel Age where a vast range of products and structures contain metals. If metals did not exist at all then we would be restricted to stone, bone and wood tools. This would have had an enormous effect on human history. It is doubtful whether the Industrial Revolution and the industrial world that emerged from it, would have been possible without metals. It is hard to conceive of wooden or stone steam engines or internal combustion engines. Wooden engines would catch fire while it is doubtful that stone could be worked in a way that could create pistons and cylinders. Without metals it is doubtful that there would be usable electricity, as the transfer of electricity over significant distances would be difficult or impossible.

Even if there were metals, the properties of those metals would have had a major effect on human history. If the smelting and melting points of metals were different then human history would have been different. This can be seen by the use of counter-factuals. If for example there was a metal with all the properties of iron, except that it could be smelted at say 800°C and melted at 900°C, then the course of human history would be different. Given irons superior qualities to copper and bronze, iron would be used in preference to those two metals for most purposes, so there would have been no copper and bronze ages. Or alternatively if such a metal could be smelted at 400°C and melted at 500°C then such operations could take place on open fires without furnaces or other special equipment. In this case hunter-gatherers could or would have developed iron and steel weapons and tools so that there would have been no stone age. However, as the smelting point of iron was around 1200°C and its melting point was 1528°C, inevitably the human use of iron was limited until temperatures of 1200°C were possible and the Iron Age followed the earlier stone, copper and bronze ages.

The quote from Colin Renfrew illustrates a number of points. The first is that copper and bronze metallurgy in the Near East developed through a series of steps each to some extent dependent on the preceding step. The development of metallurgy took place in a particular order and the order of development was a necessary and inevitable order. The order involved a move from simpler metallurgy to more complex metallurgy involving increasing specialization and skills as the metallurgy developed. The reasons for this is that simpler forms occur to humans before more complex forms and the complex forms are often refinements or improvements of the simpler forms. In this sense the simpler forms will always come before the more complex forms.

The progress of metallurgy started with the use of native copper and iron from meteorites as the metals were obtainable without smelting the metals from ores. It was soon discovered that copper could be shaped by hammering a fairly easy discovery simply involving hitting the copper with a hard object. Annealing was soon discovered as it involved heating the copper in a fire and then hammering it, a relatively easy discovery as fire had been known to humans for hundreds of thousands of years.

A more complex discovery was how to extract copper from its ores. This requires temperatures of around 700°C so that some form of furnace or oven is required. As this involves an extra and reasonably complex element (the building of furnaces) it makes sense that metallurgy involving smelted copper took place sometime after the use of native copper. The casting of copper in open moulds requires a temperature of 1083°C which requires more complex furnaces and bellows to get the required temperature. This inevitably means that it occurred after the development of smelting and the use of native copper.

The use of casting in and two piece moulds inevitably followed the use of simpler casting with an open mould. More complex casting techniques could only be developed after simpler techniques had been mastered and had become well understood. The creation of bronze, an alloy of either copper and tin or copper and arsenic requires the ability to heat the metals to their melting points. This meant bronze could only be created after it was discovered how to produce heat of 1083°C, the melting point of copper which had the highest melting point of the three metals. Tins melting point is 232°C and arsenics is 818°C. To produce heat of 1083°C required sophisticated furnaces and bellows and then to acquire the knowledge that the alloy was stronger and harder than copper would have ensured that the development of bronze took place later than copper smelting and the more sophisticated copper casting techniques were developed.

The last step mentioned by Colin Renfrew was lost wax casting. This is a quite sophisticated form of casting far less obvious than casting in or the use of two piece moulds so that lost wax casting was developed later than the other two techniques.

The development of iron metallurgy proceeded in a similar manner to that of copper. The first use of iron involved the use of meteorite iron which is also the simplest use of iron as no smelting, involving the use of complex kilns with bellows, was needed. When furnaces were built that could achieve temperatures capable of smelting iron, the Iron Age began and iron replaced bronze as the principal material for tools and weapons. Temperatures capable of melting iron were eventually produced when furnaces were improved, the most important development being the introduction of the blast furnace. This required the prior invention of the water wheel. The water wheel was invented in Roman times and was steadily improved with cams and cranks to convert its circular motion into reciprocating motion so it could be used for a wide variety of purposes including powering bellows. Once the water wheel was used to drive bellows, the new blast furnaces were able to reach temperatures that could melt iron and produce cast iron. Further improvements were made to blast furnaces such as the use of reverberatory furnaces and the pre-heating of air before it entered the furnace, which led to still higher temperatures being obtained. Advances in the study of chemistry led to methods for the mass production of steel such as the Bessemer process and the open-heath process. Even higher temperatures were produced by electric furnaces and the use of oxygen rather than air for steel making and for the production of other metals.

The progress of metallurgy was partly based on the ability to produce higher and higher temperatures to smelt and melt metals. The use of open fires to allow the hammering of heated metals, then of furnaces and of furnaces with bellows, then of furnaces with bellows driven by water wheels, then of reverberatory furnaces, then of the pre-heating of air before it enters the furnace, then of electric furnaces and of furnaces using oxygen rather than air led to ever higher temperatures, which allowed a wider range of metals to be smelted and melted. These developments took place in a logical order in that the simplest ways of smelting and melting ores and metals were invented before the more complex ways. The gradual increase in temperatures available for metallurgy allowed metals to be smelted and melted in a particular order which was set by the particular properties of the ores and metals concerned. The particular properties were the smelting and melting points of those ores and metals so the order of development of Bronze Age to Iron Age was inevitable in human history. The Steel Age inevitable occurred later than the Iron Age, as to produce cheap pig iron or wrought iron is a much easier process than to produce cheap steel, with its requirements for relatively exact amounts of carbon to be mixed with the iron to produce steel.

Metallurgical processes that required prior inventions or discoveries were made after the prior inventions or discoveries. The discovery of how to melt iron (in Europe) was made only after the invention of the blast furnace, which was dependent upon the prior discovery of the water wheel and how to convert circular motion into reciprocal motion. The invention of the electric furnace was made only after the discovery of how to make, control and use electricity. The widespread use of aluminum occurred only after the invention of the electric furnace. The use of oxygen in metallurgy occurred only after the discovery of oxygen as a separate element and after it became possible to cheaply produce oxygen for industrial use. The whole development of metallurgy followed a logical process which was inevitable given the properties of the metals and ores available for human use.