Steels

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Chapter 3

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1. Introduction

Steel has a long history. Until the 19th century, it was a rare, sophisticated material, whose combination of strength and flexibility had been recognized and valued since Antiquity [1]. Steel has fascinated philosophers, alchemists, scholars, merchants and ironmasters because it is both indispensable, and a rather delicate undertaking. Vanoccio Biringuccio (16th century) termed it *subtile*, in homage to its refined qualities.

Today, steel is a common, mass-produced commodity whose production has increased steadily since the 1950s. Output rose from approximately 211 million tons in 1951 [2], of which 95 M were produced by the United States (45%) and 0.9 by China (<1%), to 1.7 billion tons in 2000[3], including 81 million tons by the United States (5%), 168 million by the European Union (10%), 100 million by the former Soviet Republics (6%), 104 million by Japan (6%), 831 million by China (49%) and 101 million by India (6%). This material is of geostrategic importance because it is vital to industrial development, as evidenced by the increasing role of Asian countries, especially China, in global production over the last 20 years.

Yet, the importance of steel is not new, even though production capacity has exploded in modern times. As early as the 14th century, the Duke of Milan's stranglehold on steel from Brescia, whose production was still irregular, was a key part of this prince's expansionist agenda. Much later, the Cold War magnified the bitter competition between the two blocks that were also fighting via steel. Europe's economic unification began with the creation of the European Coal and Steel Community. Today, the steel giants are China Baowu Steel Group and ArcelorMittal. The collective influence that these groups bring to bear on world politics is quite evident

But when, how and why did steel, which was for so long a rare mate-rial, attain this dominance? Is it even the same material? The ways of defining steel have clearly evolved over the centuries; in fact, the modern definition only came into use in the 19th century. Today, steel refers to an alloy of iron and carbon. Compared to iron, the presence of very small quantities of carbon (as little as 0.2%) in steel increases its yield strength and its hardness. Quenching further increases the hardness of steel. However, steel existed long before contemporary science assigned it a calibrated definition based on measuring the amount of one of its components. Since Antiquity, steel has been associated with iron. Until the end For of the 18th century, scientists and consumers characterized steel on the basis of its particular qualities. So the question to be examined here is whether the variations in definitions over time are a result of the evolution of theoretical tools, processes, uses and/or markets.

2. Definitions and Designations of Steel

For a long time the Aristotelian definition of steel prevailed: an iron that has undergone various treatments. According to Aristotle, steel is produced by separating the earthy slag from iron by means of successive smelting. Thus, Albert the Great, in his volume *De Mineralibus,* was in full agreement with Aristotle when he described steel as an iron that is refined, pure, hard and very dry; harder and more compact than iron, and which can become brittle with further treatment. This designation of steel as "pure" "refined" iron was fundamental. During the Middle Ages, it was considered common knowledge among the elite, be they aristocrats or merchants. Noticeably the purity of steel resonates with the purification techniques applied to it, constituting the common thread among steel production techniques from the Middle Ages to the present. This idea continued to dominate scholarly circles from the 16th through the 18th centuries, in conjunction with the alchemical tradition. The latter only turned its attention to steel in the 17th century, and then not with the *Acier des Philosophes*, which corresponds to antimony and its derivatives, but with the concept of the *état moyen*. This concept then paved the way for the definition of steel based on its carbon content. It was echoed in the books of secrets appreciated in learned circles during the 18th century, which certainly influenced Benjamin Huntsman (1704–1776), inventor of English crucible steel. For Enlightenment natural philosophers, steel was composed of a metallic base and phlogiston (like all metals) with the addition of carbon. By the end of the 18th century it was clear that iron, steel and cast iron differed by the proportion of their carbon content. It is important to emphasize, in close relation with the scholarly world, the importance of the practical knowledge of craftsmen such as Grignon or Jars in France, and Blakey in England who supported, completed and even critiqued the scientists' theories and experiments related to the question of steel and its definition, especially in dictionaries (E. Chambers' *Cyclopedia,* London 1728; *Encyclopédie* by Diderot and D'Alembert) and technical treatises.

There are various ways of classifying steels. Until the 19th century, steel was often associated with its place of manufacture. Taxonomies also provided buyers with information about the technical conditions during production which, in the eyes of experts and informed consumers alike, were associated with specific areas. In reality, there was not one steel but many steels. In the West during medieval times, the generic term was commonly derived from the term *chalybs*/*calibs* (which designates both steel and iron). It gradually evolved into *aciare, aciarum* and its derivatives *acer, azero, azale, accai* in vernacular languages. Other terms were often substituted when steel appeared as a particular iron in the case of a heterogeneous product that brings together irons and steels. This was the case for the bloomery reduction in Europe from the Middle Ages until the 19th century (that of the "*molinae/moulines*" and then the *forges à la catalane*) where steel was designated as *fer fort* and *fer cédat*, with differentiated and graduated proportions of carbon, indicating a standardized use of products that were nevertheless heterogeneous.

The names of steels also referred to the trademarks inlaid in the metal indicating the workshop where it was made (for instance, medieval steels from Brescia in Lombardy: *gamba* and *campana* style steels). Buyers immediately recognized these brands and associated the product with the reputation and renowned technical mastery of a given workshop. Most commonly, however, it was the location of production that prevailed, even in the 19th century. An outlier is the emblematic case of "German steel",of which only part was actually imported from Westphalia, Styria and Carinthia. The appellation was, indeed, hijacked on occasion, victim to commercial strategies attempting to take over the market by appropriating the name. But it also made reference to certain assembly techniques of German origin (ex: “English German steel” for English re-carburized steels forge welded into faggots). The modern era was also characterized by practical taxonomies that referred to utilization (razor blade steel, steel for clocks) in order to distinguish specific steels in a market where the competition was escalating, and to ensure appropriate quality for the intended use. Clearly, these designations often combine and restore threads of practical information that can lead to an individual and to his steel. This was the case with Ambrose Crowley’s “Crowley steel” near Newcastle (19th century). A final method of designation prevailed in mod-ern times, which led to the identification of processes. This was the case for *acier naturel*, which denoted steel produced by the process of direct reduction and which appeared in the *Encyclopédie*. Yet, the categories can be much more complex. English re-carburized steels provide a good example. These steels benefit from designations that inform the buyer about the repeated operations of cementation and forge welding (successive hammering): shear, double shear, triple shear, among others.... Visual recognition can lead to designations by appearance: cut steel or diamond steel, blister steel, and also identify technical processes.

With the advent of the Bessemer process in the 1850s, the steel industry, which had previously produced predominately heterogeneous mixtures of iron and steel, could finally deliver homogeneous materials. This marked a transition from a world where the location and production techniques made it possible to identify and describe a material and its quality, to a world where the quality itself could be produced at the customer’s request. The carbon content of the material and its chemical composition thus became the primary factors in classifying steel. The role of chemical and metallurgical tests became preponderant. With the development of microscopy, metallography and systematic scientific studies at the end of the 19th century, the constituent phases of steel (α and γ iron, perlite, cementite) were identified (notably by Floris Osmond and Henry Le Chatelier in an 1897 article). The earliest versions of the iron-carbon diagram were also proposed (Auzne, 1896), and certain processes, such as quenching, began to be understood experimentally in the laboratory and described theoretically [4]. This was the beginning of a close relationship between laboratory research and industry, which would be strengthened with the production of special steels beginning in the 1880s.

Special steels consist of iron-carbon alloys to which certain quantities of other elements have been added (chrome, nickel, vanadium...) to finetune their properties, in particular for the manufacture of weapons. Stainless steels developed throughout the 20th century. The mass-production of special steels had been greatly encouraged by the introduction of electric furnaces in the 1920s. They are particularly well adapted for the production of finely measured grades. Presently, these steels continue to diversify and to address specific needs related to particular uses (corrosion, resistance, hardness, coefficients of expansion...).

3. Early Processes for Steel Making

According to the chronological and geographical contexts, a combination of different disciplines (history, archeology, physico-chemical analysis of the products and waste found onsite and of the objects themselves, situ-ated in their context) is necessary to understand the ways in which steel has been produced.

Steel can be produced directly from the reduction of iron ore and its transformation into metal under the reductive action of the carbon monoxide produced by the combustion of charcoal in a bloomery. Due to the high temperatures attained and the reducing

atmosphere, part of the car-bon contained in charcoal diffuses into the metal during this operation. So, to a certain extent, this is really a cementation (see what follows) in the reduction furnace, which results in more or less carburizing the bloom. However, the metallic product of the direct reduction remains heterogeneous, with a carbon distribution that can be highly variable depending on the thermodynamic and kinetic conditions inside the bloomery used for the operation. This reduction process was used until the early 20th century in Southern Europe (Iberian Peninsula and the Pyrenees) and even later in Africa. In Japan, after nearly disappearing in the 1920s following the modernization of the country, the process was rediscovered about ten years later (*Tatara*) for making traditional weapons (*Katana*) [5]. In the bloomery, the melting temperature of the metal is never reached, so it is a formless mass (bloom) when removed from the furnace. A certain number of forging and compacting operations (hammering, folding, welding) either by hand or with a hydraulic hammer are required to obtain a semifinished product (bars, etc.) or a final product. This process is called direct reduction, in contrast to the process for producing pig iron, known as indirect reduction (see what follows). During these post-reduction treatments, the bloom can be treated as a whole. The material keeps the initial heterogeneous distribution of the carbon content (as with the bars from the Roman era found in Mediterranean shipwrecks, or those still in place in medieval cathedrals). The different parts of the bloom (more or less carburized) can also be identified and sorted out by mechanical operations to obtain relatively homogeneous steels from heterogeneous blooms. This delicate operation has been documented in Toulouse (France) in the 14th century by razor manufacturers. Over a very long period of time this technique developed in a wide range of cultures. Comparable practices were attested during the same period in a key steel production area: Styria (Austria). Steel production by fragmentation and sorting was also observed in Africa in the 20th century. Today it is still used in Japan to make *katana* swords (*Tamahagane*).
Another direct method to produce steel consists of deliberately carburizing the bloom, either to make the previously mentioned separation operation highly profitable, or to produce blooms almost entirely made of steel, particularly with the aid of hydraulic bellows. This more systematic process yields larger quantities and may also be linked to the use of manganese ore. In fact, certain regions renowned for their steel production, especially in the Middle Ages (Bergamo Alps, Pyrenees, Carinthia...) are located on iron ores highly charged with manganese. In Europe and specifically in Rhineland at the end of the 13th century, a new process emerged with the generalized use of hydraulic power: the indirect reduction process presenting several technical variants. The Walloon process, named for its origins in 15th century Wallonia, spread widely in northern France and Great Britain from the end of the Middle Ages and produced pig iron and iron. However, the production of steel with this method remained secondary, at least until the 19th century. Indirect reduction differs from direct reduction in that a higher temperature is obtained in the furnaces (blast furnaces) due to the systematic use of hydraulic power to operate the bellows that introduce air into the furnace. The elevated temperature accelerates the diffusion of carbon from the charcoal (or from coke in recent periods) into the metal, so that its content in the reduction product exceeds 2%, ushering it into the domain of pig iron as defined by contemporary metallurgists (see what follows).As a result of the high carbon content of the metal, its melting point is significantly lower than that of iron; thus cast iron comes out of the reduction furnace in a liquid state. It can then be molded into the form of cannonballs, firebacks, cauldrons, etc. Its high carbon content gives it another property that differentiates it from iron and steel: it becomes brittle under the hammer of the forge. It is indeed another material. Remarkably

the production of cast iron appeared in China between the 7th and 5th centuries BC, and the processes of decarburization of this cast iron to transform it into iron or steel were known in the 1st century BC [6]. During this period, China was taking a quite different technological pathway than the rest of the world, especially compared with Europe where cast iron only appeared by the end of the Middle Ages. Considering the indirect process, the transformation into iron or steel occurs during the refining stage, which consists of decarburizing the pig iron in a second hearth. This decarburization results from the introduction of air into the hearth and the interaction of the molten metal with the slag. The product of the refining operation is a paste-like mass of metal, very similar to a bloom. Thus, itis clear that if the operation of decarburizing the pig iron is interrupted before the carbon is completely removed from the metal, the product of the refining process will be a steel, more or less carburized depending on the progress of the operation. It seems that steel produced by decarburization in Europe during the Middle Ages was quite rare. It has been documented in France (Dauphiné then Nivernais, Perche, Champagne) in the 16th century. However, a notable increase in French production did not occur until the beginning of the 19th century, going from 1,000 to 3,500 tons per year between 1800 and 1850. However, this progression seems fairly limited when compared with the production of cementation steel (6,500 tons in 1850, see what follows).

4. Methods and Markets

A new milestone was reached in England in 1784 when Henry Cort patented a process for decarburizing pig iron, puddling. Here, the metal is treated in a reverberatory furnace that heats coal in a fireplace separate from the hearth containing the metal, thereby eliminating all sulfur pollution (remembering that the use of coke in blast furnaces for ore reduction appeared in England in the early 18th century and became widespread in the 1750s). All decarburization processes produce mostly heterogeneous metals containing more or less carbon depending upon the refining conditions. However, the part devoted to the production of steel remained minor (the Eiffel Tower is made of puddled wrought iron, it is not made of steel!).

Since the origins of metallurgy in protohistoric times, another way of obtaining steel consisted of forcing carbon into iron brought to a high temperature through diffusion by exposing it to a hardening agent or cement, a highly carburized material or gas. This process known as cementation takes place over several hours depending on the thickness to be carburized. Thus, there is a distinction between surface cementation intended to harden a limited part of an object and the cementation process giving rise to a material that is entirely steel. The first method makes it possible to treat already-formed objects (blades, arrowheads and files as mentioned by the monk Theophilus in his text *Schedula* around 1120). A simple, easily carried out process, this type of cementation is a practice for perfectioning material. Still widespread in modern times, the technique remains in use today. It is often accompanied by quenching, which hardens the steel after it has been heated to a high temperature then rap-idly cooled. For earlier time periods, there is little data about the exact nature of the cements used and their efficacity (roots, bones, leather, guano, etc....). Today, these agents are usually gaseous because this state promotes the exchange of matter.

In contrast, the cementation process has been introduced in 17th century Europe, with steel production in a cementation furnace. In the 18th century, this technical innovation of English origin spread in northeastern England and especially in Sheffield, a steel-manufacturing city since the Middle Ages. The production of English cementation steel from small iron bars was 1,440 tons/year in 1730 and 2,600 tons/year in 1750.The temperatures in the cementation furnaces exceeded 1100°C. Here, the cement was a charcoal powder. However, the use of bituminous coal is documented as early as the 17th century in Coalbrookdale. The carbon content of the material obtained after one week of cementation could exceed 1%. The heterogeneity of the distribution of the carbon inherent to the diffusion process required subsequent forging, accompanied by mate-rial separation or even re-cementation to homogenize the material. These different types of treatments made it possible to produce steels of varying quality (blister, shear — see above) for markets ranging from hardware to surgical instruments and musical instrument strings. Certain metals (Swedish irons) were better suited than others for this operation. In contrast, irons containing phosphorus yielded brittle steel. Cementation steels really opened up the markets from the 18th century onwards, and were incorporated into a wide variety of objects. Cementation steel was polished (English-style polishing) and then combined with other metals, cop-per for example, to produce all sorts of household goods, toys and jewelry.

It is worth focusing a moment on a specific process for manufacturing steel that enables to reach the liquid state, in small quantities, and thereby control the homogeneity of the products obtained: the so-called “crucible” process. The origin of crucible steel has been widely debated, but it surely dates back to the 3rd century AD, or even to the beginning of the Christian era [8]. The term crucible steel encompasses several technical conditions. Vanoccio Biringuccio in *La Pirotechnia* (16th century), which was revisited by Agricola and other authors in the 17th century, described its production in Europe during the Renaissance. Presumably, in a bath ofpig iron and other fluxes, small pieces of barely-worked iron, resulting from
the decarburization of pig iron, were plunged into a crucible. The extracted product, after undergoing quenching, was thus appraised as steel. Crucible steel was also made in Central Asia, where *pulad* steel was produced, especially in Iran as early as the medieval period. Archeological sites have also been excavated in Uzbekistan and in Turkmenistan, the oldest of which date from the 8th century AD, where crucibles used for steel production have been found. Two techniques for obtaining crucible steel have been developed in this context. One consists of carburizing iron with an organic cement, sometimes by adding a mineral compound. The other technique is co-fusion, which consists of mixing pig iron and iron in the same crucible to obtain steel at the end of the operation. In India at the beginning of the 19th century, the cementation process (known as the Mysore process) was observed by European travelers [7] particularly at the production sites of Chinnarayanadurga and Devarayanadurga, while co-fusion (called the Hyderabad process) was more widely practiced in the district of Nizamabad,in the former state of Hyderabad (now Telangana). Note that the co-fusion process has also been documented in China in the 17th century but may be even older. In Sri Lanka, only the first technique was used, but it spanned from at least the 6th century to the 19th century. In the 17th century, it was the use of a highly carburized crucible steel of Indian origin, called *wootz,* that after forging made it possible to produce blades with the characteristic appearance and “superplastic” properties known as recrystallization Damascus (not to be confused with the pattern-welded Damascus resulting from welding sheets of iron and steel, as with Merovingian swords). Finally, crucible steel also spread throughout the Islamic world. The production of crucible steel has been confirmed in 12th century Seville, the capital of the Almohad Caliphate. Written sources also

document the practice in the 13th century in the Middle East and Egypt [9]. The complexity of this process using small crucibles vastly limited production.
The scale was different for crucible steels produced in Europe from the 18th century onward. Emerging in England, processes intended to produce "molten steel" or cast steel, crucible steel, were invented in Sheffield by Benjamin Huntsman and experienced rapid production growth from 1820 onward. They made it possible to homogenize cementation iron, without re-carburizing or forge welding, by incorporating a smelting step in a refractory crucible. In this manner, fragments of blister steel placed in the crucible with wrought iron and a flux are converted in a few hours into molten steel, cast into ingots. The temperatures in the crucible, placed in a furnace fueled by coking coal, enable the complete melting of the metal. In the 19th century, the emergence of large production units made up for the limited capacity of the crucibles. The ingot molds for casting molten steel were gradually perfected as well as the material of the crucibles themselves in the second half of the 19th century. This process persisted until the Second World War (with special steels — see what follows).

5. Industrial Processes

Patented in 1855 and industrialized in the 1860s, the Bessemer process significantly changed pig iron refining. By blowing air directly into molten pig iron inside a converter, the subsequent elimination of silicon and carbon causes an exothermic reaction to occur elevating the temperature to reach the melting point of iron. Through this process, metals with very different carbon contents are obtained and thus, very easily, steel in large quantities. Nevertheless, phosphorus, an element present in significant quantities in some pig irons, is not eliminated in this process. This important limitation is circumvented by the use of a basic lining inside the converter. By forming a calcium phosphate, this lining permits treatment of phosphorus pig irons and thus significantly increases the range of processes for obtaining metal in the liquid state. This new process, known as Thomas-Gilchrist, appeared around 1880. In parallel (1864), the Martin-Siemens process, another innovation, used additions of scrap metal (enabling their recycling) for refining pig iron and similarly reached the melting temperature of the refined metal. For all of these processes, obtaining the final metal in its liquid state made it possible to eliminate a large number of non-metallic impurities by flotation, thereby producing a homogeneous metal and better controlling its mechanical properties. At this stage, the possibility of rapidly producing large quantities of steel with these processes increased production capacities tenfold. This evolution was also driven by growing demand (railway tracks, weapons, machinery, metal constructions...). Steel became a common commodity. Gradually, this material took the place of iron produced by the old processes (puddling especially). Thus, the production of steel definitively exceeded that of iron in England beginning in 1885, and in France by 1895.
In the 1950s, the Martin-Siemens process dominated the global scene even though, in Northern Europe the Thomas-Gilchrist process accounted for two-thirds of the steel production. The use of pure oxygen for refining (known as "basic oxygen steelmaking") emerged in the 1960s and rapidly spread worldwide. Highly flexible, it can be used to treat all types of pig iron. Simultaneously, the abundance worldwide of scrap iron accompanied the intensified development of the electric furnace, which dates from the beginning of the 20th century and enabled recycling by smelting. It accounted for 20% of global steel production in 1990. The development of continuous casting, which increases the forming efficiency of long semi-finished products, is also progressing. Lastly, in the 1960s, specific techniques during metallurgical operations increased control over the composition of the

steel in the ladle. The analysis of steels during the manufacturing phases and the instrumentation of these measurements increases control over the composition and the reproducibility of the different grades sought. Since the 1980s, only two coexisting sectors have remained: plants combining the production of pig iron and oxygen refining and those using electric furnaces and processing scrap metal.

6. Conclusion

From this brief survey of the history of steel it is clear that the steel used around the world, from protohistory to the present, is a multifaceted mate-rial. Its identity is closely linked to that of iron and pig iron. As outlined here, the diversity of steels depends as much on technical processes as on the uses for which they are intended. Regardless of the fabrication method, the operating chain of steel manufacturing is complex and nuanced according to market demand.

Another striking feature of this long history is that the production processes come from all over the world. Steel has no homeland, it has been produced and improved in many countries, often in relation to weaponry. From the Middle Ages to the present day, steels have responded to requests and commissions: steels for Damascus or *katana* blades, steels for medieval and Renaissance European armor, scythes from Styria from the Middle Ages to modern times, special steels for aeronautics. Since the 19th century, steel has been produced in large quantities (railway equipment and weapons, among other examples). Yet, regardless of the period and area considered, steel is a refined product whose production remains a geostrategic challenge.

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