INTRODUCTION

By the name "process of cementation" is meant any process which permits of partially or totally carburizing an iron or steel object without subjecting it to fusion, and in such a way that the carburized metal shall possess or preserve the structure and the properties of a true steel. This result is attained by heating the object to a high temperature—but below its melting point—keeping its surface in intimate contact with carbon or with substances which decompose at the temperature worked with, liberating carbon. In the majority of cases the carburizing substances—or "cements"—used in the manufacture of cement steel are solid; such, for example, are wood charcoal, lamp-black, various organic substances, etc. Solid cements are usually employed in the form of powders in which are immersed the pieces to be cemented; in such a case it is necessary to secure intimate contact of the cement over the whole surface of the metallic piece.

Besides the solid cements, liquid cements (for example, fused potassium cyanide) and, still more, gaseous cements (such as the volatile hydrocarbons, carbon monoxide, etc.) have found wide application, especially in recent times. Both offer in many cases very marked advantages as compared with solid cements; not least among such advantages is that the uniform contact of the carburizing substance with the whole surface of the metal guarantees complete uniformity of carburization at every point of the said surface. There are also often cases where the simultaneous use of solid cements and gaseous cements is advantageous.

In all cases the process of cementation consists in the gradual penetration of the carbon yielded by the cement into the mass of the iron or steel. We shall see that this penetration, or *diffusion* of the carbon—always quite slow—is due to two different, usually concomitant causes. At any rate the product obtained—or *cement steel*—is always characterized by the fact that the concentration of carbon in it diminishes from the surface toward the interior until it reaches usually, at a greater or lesser depth, the value which it originally had in the iron or soft steel worked with, so that, in general, the carburization obtained by means of the process of cementation is limited to a more or less thick zone adjacent to the exterior surface of the object. In the exceptional case of the so-called *core cementation*, the treatment is prolonged as long as is necessary to obtain carburization of the whole mass of the metal. We shall study in detail, further on, the various cases which may come up in practice.

The first indications of a process for the transformation of soft iron into steel which presents the characteristics of a true process of cementation, are found in the work of the Sienese metallurgist Vannuccio Biringuccio, published in 1540 under the title of *Pirotechnia*, and in the treatise *De re metallica*, by George Agricola, published in 1556.

The process minutely described by Biringuccio and by Agricola consists in heating for a long time the billets of soft iron in molten cast iron, which latter yields up carbon to the soft iron, behaving exactly like a liquid "cement."

Beck, in his classical *Geschichte des Eisens*,[1] after referring to the description of this process which is given by Agricola, adds that it can not be established with certainty whether in the Middle Ages or in earlier times a process of cementation was known analogous to that which has had the widest application in recent centuries and is even to-day the most frequently applied, that is, the partial transformation into steel of iron objects already worked, obtained by heating these objects in contact with a carburizing *powder*, protected from contact with the air. Beck considers it probable that manufacturers of daggers, arms, needles, etc., knew such processes from very ancient times but kept them secret, transmitting them verbally from father to son. Such a hypothesis seems confirmed by some legendary passages which are found at the beginning of the Middle Ages.

In the sixteenth century there were certainly known processes of cementation proper, based on the use of carburizing powders, consisting essentially of carbon mixed with organic substances. Such processes were then used exclusively with the object of obtaining a superficial zone of steel—capable of being hardened by quenching—in the iron objects which were subjected, after being finished, to the process of cementation. We shall see later that to-day also the process of cementation is widely employed for entirely analogous purposes; in this case the process is frequently designated by the name of "case hardening" (Italian *tempra a pacchetto*, German *Einsatzhärtung*, French *trempe à paquet*).

Only in the following century (the seventeenth) did the manufacture of cement steel develop rapidly, when the process of cementation began to be applied no longer solely for the superficial hardening of finished articles of soft iron (an application which, owing to the limited development and imperfection of the industry of mechanical construction, was then by far less important than it is at present), but also for the transformation into steel of bars of iron intended to be subsequently hammered or forged. A clear indication of this process we already find in the *Bericht von den Bergwerken*, published in 1617 by G. J. Löhweiss. The manufacture of bars of cement steel—put on the market under the name of *artificial steel*—already flourished

[1] Ludwig Beck, *Die Geschichte des Eisens in technischer und kulturgeschichtlicher Beziehung* (Braunschweig, 5 vol., 1884–1903). See Vol. I, pp. 834–836.

at the beginning of the seventeenth century in Piedmont and in England, and during the same century it spread into the other European states, especially to Belgium and Germany.

Up to this time (end of the seventeenth century) the process of cementation, like all other siderurgical processes, continued to be applied according to exclusively empirical data which alone had led first to its discovery and later to its improvement, and the first attempts to determine with exactness, by means of systematic investigations, the real course of the process of cementation date only from the beginning of the eighteenth century. The first—both in point of date and in importance—of the researches carried out with the above object we owe to the French scientist Réaumur, who undertook, with great success, the scientific study of the most important siderurgical problems.

The investigations of Réaumur on the cementation of steel are the subject of a series of Memoirs presented by the author before the Academy of Sciences of Paris during the years 1720–1722, forming the first part of a volume entitled: *L'art de convertir le fer forgé en acier et l'art d'adoucir le fer fondu, ou de faire des ouvrages de fer fondu aussi finis que de fer forgé.* As is seen from the title, the second part of this work—which has since become a classic—comprises a series of investigations on the manufacture of malleable cast iron.

As in the preceding centuries, so also at the beginning of the eighteenth century, the processes of cementation proper, widely employed, especially in Germany, in Italy and in England, for the production of fine steel to be subsequently worked, were jealously kept secret by the various manufacturers, each one of whom boasted the superiority of his own procedure. In France crude cement steel was not then manufactured, but various processes of *case hardening* for producing, as we have seen, on the surface of finished forged iron objects a thin layer of hard steel capable of being hardened were known and applied. Réaumur, starting from the correct assumption that these latter processes must be entirely analogous to the former, subjected to a systematic study the processes of *case hardening* then known in France, turning his attention especially to the effects obtained by varying the composition of the *cements*. These investigations led him to establish clear and precise rules for the effective technical application of the process of cementation, and since he was the first who was willing to make known to the public the results of his investigations, it is only since then that the manufacture of cement steel (at first limited to a few manufacturers who possessed the secret) became possible in all establishments, and it can well be said that it is to Réaumur that is due the scientific discovery of the cementation process.

After having excluded, by means of a long series of experiments, consisting in heating the iron in the presence of inert substances, such as chalk, clay, etc., the possibility that the simple action of prolonged heating was sufficient to transform iron into steel, Réaumur studied systematically the action of the various materials then used in France for *case hardening*, either using each one alone or making mixtures of them.

On the basis of results from a large number of experiments, in which he studied the action of a multitude of substances (such as the juices of various plants, many salts, fats, vegetable and animal carbons, ashes, etc.), he reached the conclusion that the best effects were obtained by working with mixtures with powdered wood charcoal as a base, to which are added salts and other substances. An example of the mixtures recommended by Réaumur for the manufacture of cement steel is the following:

Powdered wood charcoal	1	part
Ashes	1	"
Lamp-black	2	parts
Salt	0.75	part

Réaumur gives many examples of such mixtures, indicating the rules to be followed in varying their composition according to the quality of the iron which it is desired to transform into steel and according to the quality of the product which it is desired to obtain, qualities which he distinguishes and classifies with minute care (both for the raw materials and for the products) on the basis of the appearance of the surface of fracture.

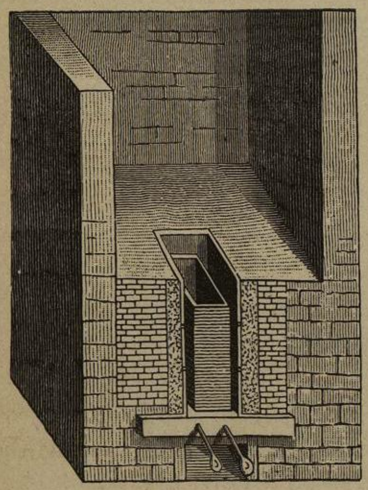

FIG. 1.

Réaumur then calls attention to the very great importance of the conditions of heating, and gives for this detailed and precise rules, adding the description and the plans of the furnaces devised by him, in order to best satisfy the conditions of the process, which he had determined with great exactitude (see Figs. 1–3). Figs. 1, 2 and 3, here reproduced, show the type of cementation furnace proposed by Réaumur.

He for the first time established clearly the fact that the transformation of iron into steel proceeds gradually from the surface toward the interior of the metallic mass. From this fact, which Réaumur deduced from the accurate examination of the surface of fracture of pieces of iron not yet totally transformed into steel, results at once the advantage of so choosing the *shape* of the pieces of iron which it is desired to cement that their surface shall, for a given weight, be as large as possible.

Réaumur observes, moreover, that as the result of the cementation the

steel *increases in weight*, so that (there being no valid reason for believing *a priori* that steel is a *purer* material than iron) the hypothesis then generally accepted that the transformation of iron into steel consists in a "purification,"

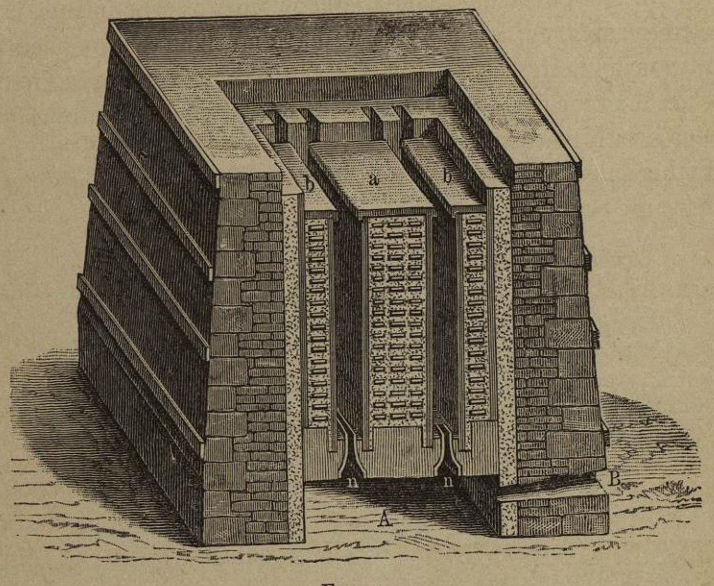

FIG. 2.

of the former can no longer be considered exact, and it is necessary to assume that the effects of cementation are due, not to the elimination from the iron of substances which rendered it impure, but to the penetration into it of foreign substances which evidently must be contained in the powders used as *cement*. Now, given the theory still prevalent at the beginning of the eighteenth century concerning the constitution of the substances which experience had shown to be most efficient in producing cementation (carbon and salts), Réaumur was led to assume that the substances which, during the operation of cementation, penetrate into the iron, transforming it into steel, are nothing but sulphur and volatile salts.

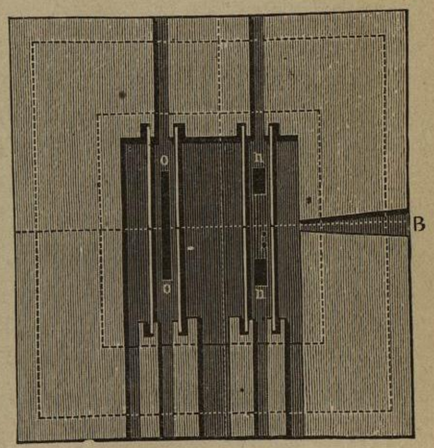

FIG. 3.

Finally, on the basis of the results of his investigations on the manufacture of cement steel proper, Réaumur carries out just as interesting researches on the process of *case hardening*, succeeding in establishing precise rules for the choice of the cementing mixtures, of the raw materials, and of the thermal treatment best adapted for obtaining good results. As for cementation proper, so for case hardening, the *cements* recommended by Réaumur are fantastical mixtures of organic substances, such as the hoofs, hides, dung and urine of certain animals. But we have no right to be too scandalized at this when we consider the fact that many of the cementation mixtures still largely used to-day and placed on the market under the strangest names and under curious contracts of secrecy, are no less fanciful than those of Réaumur; nor do they give better results.

The investigations of Réaumur gave a very strong impetus to the industry of the manufacture of cement steel, but, contrary to the hopes of the author, other nations profited more widely by them than France, which at that time did not produce iron of a quality adapted to furnishing good steels by means of cementation.

Within a few years after the publication of the investigations of Réaumur, many factories of cement steel sprang up in various European states, and while the French factories had very little success (for the reason I have just mentioned), those established in Sweden (for example, that of Barkinge, opened in 1725), in Germany and in England flourished.

In the latter country it appears that the manufacture of cement steel was imported in the year 1710 by a certain Bertram, a German operator, who had learned the secret in his native country. But, as in other countries so also in England, this manufacture began to develop extensively only after the labors of Réaumur had placed at the disposal of manufacturers rules for its execution which were much more precise and efficacious than the secrets jealously guarded from the first by a few manufacturers, and thus wrested from the latter the monopoly of an industry which at that time still yielded large profits. Newcastle and Sheffield became the principal centers of the manufacture of cement steel in England; here the manufacture was carried out in furnaces of the type of those shown in Figs. 4, 5, and 6, based on the same principle as those proposed by Réaumur and not differing much from those still used in some establishments. The pieces of iron, in the shape of thin, elongated rectangular bars, were placed in boxes made of slabs of refractory material and surrounded with simple powdered carbon, closely packed around them. The boxes, also in the form of rectangular parallelopipedons about 3 m. in length by 70 cm. in width and in depth, were placed with their longest sides parallel, on two sides of the furnace, leaving between them a space about 50 cm. long occupied by the hearth. The charge of every furnace was about 10 tons of iron, and the operation was completed after five or six days running at full heat.

The bars of steel, after removing the ends, (which were forged in fagots and sold as *hard steel*) were placed on the market at about 600 francs ($120) per ton under the name of *blister steel*. This name, referring to the small

blisters which characterize the surface of the bars of cement steel, is still used to-day in England to designate this product, as also the term *blister bar*.

The superiority of cement steel manufactured in England was due essentially to the superlative quality of the iron used as raw material, an iron which the English manufacturers procured almost exclusively in Sweden, purchasing the entire production of some of the best Swedish iron works. It was very natural, therefore, that another result of this was the springing up and the development of the industry of cement steel in Sweden. The industry, however, did not attain either in Sweden or in Norway (where, also, it began to develop at that time) the state of perfection reached in England.

In America also, after a period of unsuccessful attempts, the manufacture of cement steel began to develop in the second half of the eighteenth century, but it did not attain marked importance until the beginning of the nineteenth.

The manufacture of cement steel reached a still greater development in England when an English clockmaker, Benjamin Huntsman, discovered in 1740 and afterward made practically workable on a large scale the crucible process of melting steel. After many unsuccessful attempts the difficulties were gradually overcome and, beginning with the last years of the eighteenth century, Swedish bar iron converted into cement steel constituted the raw material for the best English crucible-fused steels.

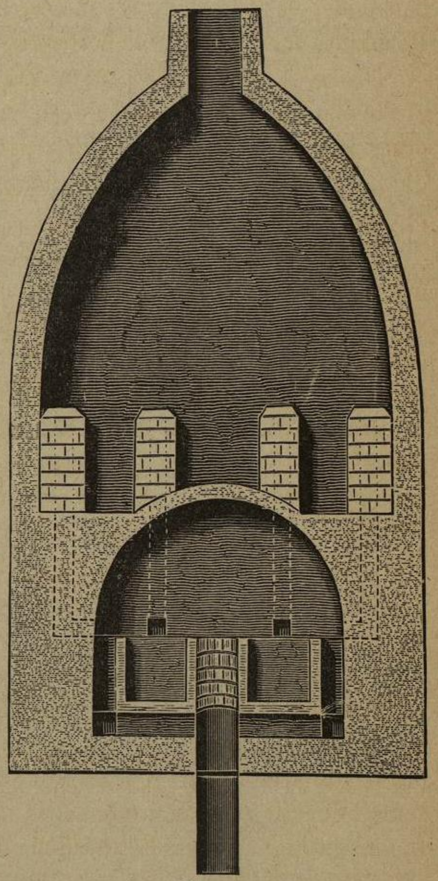

Fig. 4.

The manufacture of cement steel then developed rapidly in almost all the countries of Europe and in America during the first half of the nineteenth century. In France the manufacturers of cement steel began to obtain good results only when, having given up their determination to use only French iron, they adopted Swedish iron as raw material and, while following almost all the rules developed by Réaumur, substituted for the complicated mixtures recommended by him the simple powdered wood-charcoal already used with so much success in England.

Very soon, however, the introduction of new methods for the manufacture of steel, capable of furnishing a product of good quality at a considerably lower price, began to produce a decrease in the importance of the manufacture of cement steel proper, gradually limiting the application of this process to the production of the material necessary for the manufacture of the finer and more expensive crucible-melted steels. Such was the effect of the introduction into industrial practice of the manufacture of puddled steel, which occurred about 1830, and still more that of the marvelous development attained in the second half of the nineteenth century by the processes for the manufacture of fused steel which bear the names of Bessemer, Thomas, Martin and Siemens, and, in recent times, by the electric steel processes.

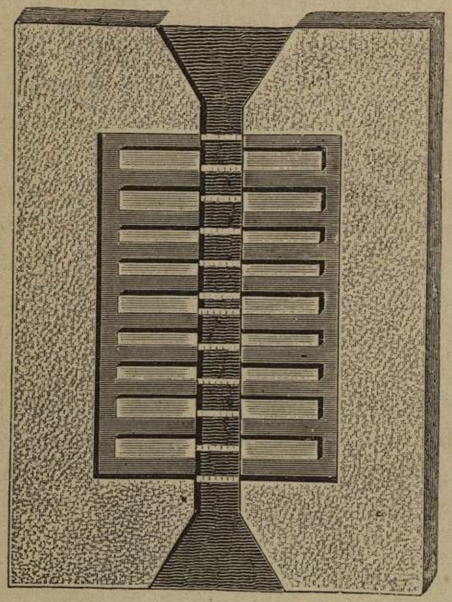

FIG. 5.

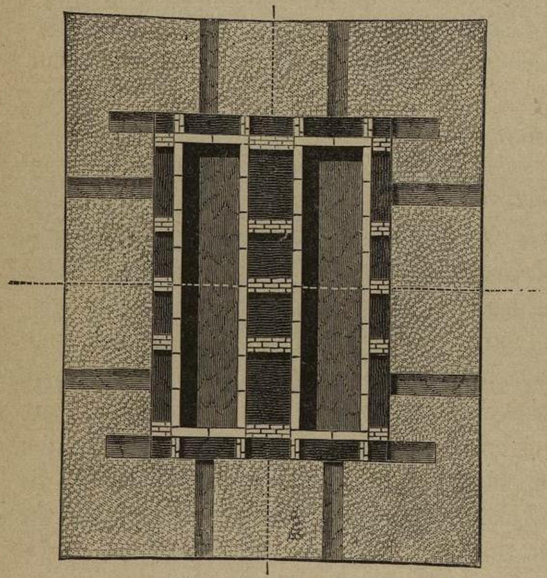

FIG. 6.

For these reasons on the one hand and, on the other, to satisfy the demands of the mechanical industries which were in course of rapid development and improvement, the industry of the cementation of steel has tended, within the last few years, to assume a character closer to that it possessed at its beginning rather than to that which it had in the period of its greatest development. In fact, if cement steel proper (to be worked up at once, or after melting) can no longer compete in price with

steels manufactured by the new processes, it nevertheless still possesses its great superiority in *quality*, so that its new uses, necessarily limited to those cases in which the high quality of the material is considered above all else, have constrained manufacturers to study the process of cementation so as to obtain by it the best product at the least cost. On the other hand the rapid improvement in mechanisms, placing at every moment before the producer of the metal used in them the problem of obtaining in a large number of parts the maximum superficial hardness combined with minimum aggregate brittleness, resulted in causing the process of surface cementation of finished objects of soft steel to assume great importance, especially the process known by the name of *case hardening*, which, as we have seen, was already known and applied at the end of the sixteenth century.

A consequence of the facts just mentioned is the recent progress, especially since the close of the nineteenth century, made both in the theoretical study and technical applications of the process of cementation, at present carried out on a large scale and according to precise and delicate rules, for the surface carburization of machine parts made either of carbon steel or of definite types of those special steels which have found such wonderful application in mechanisms.

We shall study further on the most recent processes of cementation and the chemical theories on which they are based, and limit ourselves here to noting briefly the historical development of each up to the middle of the nineteenth century.

As we have already seen, the theoretical conclusions drawn by Réaumur, on the basis of his numerous and painstaking experiments regarding the nature of the process of cementation, contained, together with a large part which was true, grave errors, which, however, were the inevitable result of the chemical theories universally accepted at the beginning of the eighteenth century.

But very soon, more precisely in the second half of the eighteenth century, the Swedish chemist Bergman began by showing that malleable iron, steel and cast iron are nothing but compounds of pure iron with variable proportions of graphite. He, however, still considered graphite as a compound with phlogiston as base. Later, in 1779, Scheele (also a Swede), on the basis of accurate combustion experiments, established that the graphite contained in cast iron is nothing but a species of *mineral carbon*, formed from *fixed air* (carbon dioxide) and phlogiston. When, in the last years of the eighteenth century, the classical researches of Lavoisier showed that the theory of phlogiston was false and cleared up the true chemical nature of a large number of substances, the obstacle was removed which had prevented Réaumur and other scientists from drawing from their investigations, although conscientious and deep, exact theoretical conclusions, and Vandermonde, Berthollet and Monge, in a memoir presented in 1786 before the Academy of Sciences of Paris, taking up again the results of the investigations of

Réaumur, of Bergman and of Scheele and interpreting them on the basis of the new theories, were easily able to show that the foreign substance which, when combined with pure iron in various proportions gave rise to steel and to cast iron, was none other than the element carbon. In doing so they made use precisely of the phenomenon, already observed by Réaumur, of the increase in weight of iron when it is transformed into steel by means of cementation in the presence of wood charcoal alone and protected from contact with air and moisture, thus showing that such a transformation can be due only to the gradual *absorption* of the carbon by the iron.

The investigations of Vandermonde, Berthollet and Monge, which treat with equal clearness many of the most important problems of siderurgy, were followed by a large number of analogous researches carried out by other scientists, all on the basis of the new chemical theories, and the rapid development of the latter, at the end of the eighteenth and in the first half of the nineteenth century, brought about the result that very soon the greater part of siderurgical processes could be clearly interpreted and explained on the basis of sure analytical data. All these investigations, which still form the basis of that scientific study of iron which Jüptner calls *siderology*, confirm the fact that the process of cementation consists simply in the gradual diffusion of the carbon into the mass of the iron.

After the establishment of this fundamental fact, which permits of the reinstatement of cement steel, from the point of view of its chemical constitution, in the same category to which belong steels obtained by other processes, the history of the development of the theoretical knowledge concerning the nature, the properties and the intimate structure of cement steel no longer forms a special chapter in the history of siderology, but is a part of the general theory concerning steel, knowledge which it would be neither possible nor opportune to discuss here and which I must assume as being already known.

It is quite proper, therefore, to say that, since the investigations of Vandermonde, Berthollet and Monge, the task of one wishing to study the history and the present state of our knowledge regarding the *modus operandi* of cementation is limited to the study of the phenomenon of *diffusion* of carbon (or other elements) into solid steel.

Although the investigations to which I have called attention had, since the last years of the eighteenth century, completely cleared up the nature of the process of cementation, and the continued progress shown, during the whole of the nineteenth century, in the knowledge regarding the structure and chemical composition of steels had continually furnished new material adapted to serving as the basis of scientific investigations concerning the process of the diffusion of carbon into solid steel, yet the study of this process was always, up to very recent times, carried out with methods and data so little in conformity with scientific accuracy as to render the ideas extant, even recently, in this field of siderurgy nothing but a confused mass of disorderly, discordant and often unfounded individual opinions. We shall see this better later on; I mention the fact now only because it alone can explain the absolute empiricism which thus far has dominated and still dominates the industrial application of the processes of cementation, and this, too, while the technology of almost all other siderurgical processes was ever gaining new scientific data from the systematic and rigorous study of the chemical phenomena on which those processes are based.

We have already seen that the mixtures, in general quite complex, recommended by Réaumur as "cements" were quickly abandoned by English manufacturers who, while largely taking advantage of the rules developed by the French scientist for the construction of his furnaces, the carrying out of the heating and, in general, the conduct of the various operations, adopted as cement simple powdered wood charcoal. The example of the English was very quickly followed by manufacturers in other countries.

Nevertheless, even though the researches of Vandermonde, Berthollet and Monge had confirmed the reasonableness of the English method, showing, as we have already seen, that the process of cementation consists in the diffusion of *carbon alone* into the iron, yet the opinion continued to exist that by the addition of suitable foreign substances to the wood charcoal or by means of more complex carburizing substances it was possible to greatly shorten the time necessary for a given amount of cementation.

Such an opinion, which, as we shall see further on, has in some respects been confirmed scientifically within the last few years, gave rise during the whole of the nineteenth century to an immense number of attempts to perfect the known processes of cementation, attempts which had as their exclusive object the discovery of the substances or mixtures most efficient as cements, and which were (and in part still are) conducted along exclusively empirical lines.

The first one who tried to use cements essentially different from those proposed by Réaumur was Prof. Vismara of Padua, who in the first years of the nineteenth century showed that excellent cement steel can be obtained by using as carburizing materials gaseous hydrocarbons instead of wood charcool. It appears that Vismara was the first to propose the use of gaseous cements.

An analogous process of cementation, based on the use of illuminating gas obtained by the distillation of fossil carbon, was later patented and applied industrially for some time in England by MacIntosh, in 1825. But neither process found wide application until many years later, when it became possible to exclude air completely from the cementation boxes.

Later, in America, Prof. A. K. Eaton proposed to increase the efficiency of solid cements by means of the action of cyanogen. His process consisted in heating the bars of iron in contact with a mixture of wood charcoal and potassium ferrocyanide, powdered together. We shall see later, from some examples, that among the innumerable substances which have been, and are now, employed to increase the efficiency of cements of any kind (solid, liquid and gaseous), the compounds of cyanogen occupy one of the most important places, but we shall see that their real efficiency is considerably less than is generally attributed to them. Thus Caron, in proposing in 1861 a new process of cementation (still widely in use to-day) based on the use of powdered mixtures of wood charcoal and barium carbonate, attributed the efficiency of the latter substance to its tendency to form, with the nitrogen of the air, cyanogen compounds. In reality (as we shall see later) the function of the barium carbonate is, in this process, quite different from that attributed to it by the theory of Caron, a theory which, however, is still believed to be exact by many "experts," and referred to as correct in many manuals.

Some success was obtained in the United States of America, about 1870, by a process of "liquid cementation" based, like that described by Agricola and by Biringuccio, to which I have called attention, on the use of molten cast iron as cement. This process, however, did not attain wide use.

Meanwhile, for reasons which we have already seen, while the production of cement steel proper, intended to be subsequently worked up, was decreasing, the importance of the industry of partial cementation or "case hardening" of finished mechanical pieces was constantly increasing. Now, contrary to what is needed in the manufacture of steel intended for melting, in which it is merely a question of obtaining maximum carburization in minimum time, the application of the process to the partial cementation of finished pieces intended to furnish products which, without any further working up and solely as the result of cementation and temper, must satisfy by their mechanical properties certain given conditions often quite difficult to realize, presents a large number of complex problems, the solution of which requires precise knowledge of the methods of treatment best adapted to obtain, from a given raw material, a product having exactly the desired properties.

The complexity of such problems, which we shall take up later, explains the active researches and the innumerable attempts made in the second half of the nineteenth century to perfect the *technique* of the processes of partial cementation of finished pieces, processes which extended rapidly to many branches of industry, as, for example, the manufacture of tools for the working of wood and of metals, machine parts, armor for ships, etc.

Coming to the last decade, however, we see the investigations on cementation assuming a new, truly scientific direction, due essentially to the introduction of metallographical methods. These methods, in fact, furnish an easy and sure means for determining rapidly a large number of data, such as the depth of the cemented zone, the concentration and distribution of the carbon in this zone, the structure of the carburized zone, etc., which are essential to obtaining a product possessing exactly defined properties.

Having thus briefly noted the transformations through which the industry of the manufacture of cement steel passed before reaching its present state, we will now examine the development of the theoretical and practical knowledge on which are based the cementation processes of to-day.

PART FIRST

THE CHEMISTRY OF CEMENTATION PROCESSES