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

CHAPTER I

THE FIRST SCIENTIFIC INVESTIGATIONS ON THE CEMENTATION OF STEEL

We have already seen that the theoretical conclusions drawn at the beginning of the eighteenth century by Réaumur concerning the variations which the chemical composition of the iron undergoes during the process of cementation were, although based on scrupulously exact experimental investigations, totally erroneous, on account of the erroneous hypotheses, then accepted by all, of the nature and chemical composition of the materials which experience seemed to indicate as being the most efficient for the transformation of iron into steel. The only fact established with certainty by Réaumur, and later fully confirmed, is the increase in weight of the iron when it is transformed into steel by means of the process of cementation, a fact which Réaumur interpreted as proof that the iron, in passing into steel, *absorbs* some substance. But we have also seen that the true nature of the substance which, combining with iron, transforms it into steel, was identified only sixty-four years later by Vandermonde, Berthollet and Monge, who, in 1786, interpreting on the basis of the new chemical theories of Lavoisier the results of the investigations carried out a few years before by the Swedish chemists Bergman and Scheele, were able to establish with certainty that steel differs from soft iron essentially because it contains a greater quantity of carbon, and that the process of cementation is nothing but a process of diffusion of the carbon of the cement into the mass of the iron.

The views of the three French scientists on the nature of the process of cementation, like the other theories formulated by them to explain various other siderurgical processes, were repeatedly confirmed by the numerous experimental investigations to which the most important siderurgical processes were subjected during the last years of the eighteenth century and the first half of the nineteenth. But we must come to the close of the period just mentioned, and after the proposal and adoption on the large scale by manufacturers of a large quantity of empirical "recipes" for the most varied and complex cements (some of which we have already mentioned), to find serious attempts, carried out along rigorously scientific lines, to establish *in what way* the diffusion of the carbon into the mass of the solid iron takes place, a diffusion to which it was then quite certain that the process of cementation was exclusively due.

One of the first ingenious hypotheses proposed to explain the "mechanism" of the diffusion of the carbon into the solid steel is due to Leplay, who, in a memoir published in 1841 in the *Annales des Mines*, attempted to explain the carburizing action of wood charcoal, then generally used as a cementing material, by assuming that the oxygen of the air which surrounds the particles of the wood charcoal contained in the cementation boxes reacts with the carbon itself, forming first carbon dioxide and then carbon monoxide. The carbon monoxide would then yield to the iron half of its carbon, again passing over into carbon dioxide, and this would again be immediately reduced to carbon monoxide by the action of the carbon used as cement. In this way the cycle of reactions would be reproduced indefinitely, and the carbon monoxide would act as a *carrier* causing the penetration of the carbon into the solid metal.

We shall see later how the hypothesis of Leplay has been clearly confirmed within very recent times. It was not, however, then accepted by all, and Gay-Lussac, in a memoir published in 1846 in the *Annales de Chimie et de Physique*, raised many objections not only to the hypothesis of Leplay but also to the later one of Laurent, according to whom it is not the solid carbon but its vapor, formed at high temperatures, which penetrates into the steel during the process of cementation. Gay-Lussac concludes that there is no reason for excluding the possibility that the carbon can act simply *by contact*, dissolving directly in the iron without the intervention of any gas or vapor, and that many other facts prove that all substances are capable of reacting with each other when brought into contact, whatever may be their state of aggregation, even though the solid state must, to be sure, be considered the least favorable for the operation of phenomena dependent upon chemical affinity.

The objections raised by Gay-Lussac against the hypotheses of Leplay and of Laurent opened the discussion, which has continued actively to the present day, concerning the part played by gases in the process of cementation. And we shall see later how it is precisely with this discussion that are related the greater part of the experimental researches carried out within the last fifty years on the cementation process, researches which, after a long series of contradictory deductions that, as we shall see later, can be explained perfectly well, have now led to the recognition of the fact that both the action of gases and the diffusion of solid carbon by simple contact intervene, although with varying intensity, in the process of cementation.

The hypothesis that free carbon, simply placed in contact with solid iron, at a high temperature, could diffuse into the metallic mass without the intervention of some gaseous substance *capable of penetrating easily into the pores of the metal, dilated by the action of the heat*, appeared, in spite of the just observations of Gay-Lussac, so difficult of acceptance that many other hypotheses were proposed, besides those of Leplay and Laurent to which I have already referred, to explain the diffusion of the carbon into the iron by the intervention of various gaseous carburetted compounds.

Thus Caron, in a series of memoirs published from 1860 to 1864 in the *Comptes Rendus de l'Académie des Sciences*, thought that he had been able to establish, on the basis of many experiments, that the process of industrial cementation is always due *exclusively* to the action of volatile cyanides, partly confirming and partly extending the theory formulated in 1851 by W. Stein, according to whom cyanogen and cyanides have a most important function in industrial cementation, in which they act as "carriers" of carbon to the surface of the iron subjected to cementation.

Since the researches of Caron, and still more the polemics to which they gave rise, may be considered as the starting point of scientific studies on the process of cementation, it seems well to give here a brief summary of their contents. More detailed abstracts of the scientific work of Caron, and especially of his investigations on cementation, can be found in an interesting article by Captain P. Nicolardot, published in the *Revue de Métallurgie*,[1] although it must be said that this article attributes, in general, a somewhat too unqualified value to the evidential value of Caron's experiments.

In his first memoir on cementation (1860), Caron asserts that the compound which gives rise to the carburization of the iron can be none other than a volatile cyanide, capable of penetrating into the pores of the metal dilated by heat. He believed that he proved his assertion on the strength of the fact that, by heating in a porcelain tube bars of iron surrounded by carbon in small pieces and making a current of dry gaseous ammonia circulate through the apparatus, there is obtained in two hours a cemented zone 2 mm. thick; while, on the other hand, if all the other experimental conditions are kept constant, and some other gas (such as hydrogen, carbon monoxide, nitrogen, air, etc.) is made to circulate in the apparatus, no cementation whatsoever is obtained. From this experiment Caron infers first of all that none of the gases which are ordinarily present in metallurgical reactions is capable of cementing iron, and he includes in this category of *inert* gases hydrogen, carbon monoxide, nitrogen, air, etc. We shall see later how this first deduction of Caron is erroneous, and we shall see, moreover, how one of the principal causes of the inexact deductions of Caron is due to the fact that he measured, as many still do to-day, the depth of cementation on the basis of the *grain* of the surface of fracture of the cemented and tempered bars.[2]

The second conclusion which Caron drew from the experiments cited was based on the hypothesis proposed by him to explain the efficient carburizing action exercised on iron, in the presence of carbon, by dry gaseous ammonia. He, in fact, supposed that the ammonia, reacting at red heat with the carbon,

[1] Vol. VI, 1–59 (1909).

[2] Caron says literally (*Comptes rendus*, 1860, 2nd sem., p. 565): ". . . la barre de fer trempée immédiatement, puis martelée pour resserrer le grain et trempée de nouveau, accusait dans sa cassure une cémentation de 2 millimètres de profondeur, parfaitement régulière, et à grain magnifique."

formed ammonium cyanide which alone yielded its carbon to the iron, transforming it into steel, so that the volatile cyanide was the *exclusive* true agent of the cementation. This opinion he believed to be clearly confirmed when, in later experiments, he was able to prove that ammonium cyanide, even when alone, behaves like an active cement, and that the cementation becomes considerably more rapid when the carbon used as cement is impregnated with an alkali or with an alkaline earth and a slow current of air is made to circulate in the apparatus used for the cementation. These last facts possess so much the greater value for the hypothesis of Caron in that he claims to be able to establish that the only alkalis and alkaline earths which are effective (in the sense just indicated) are those which (according to earlier investigations of his) can form, under the conditions prevailing in his experiments on cementation, volatile cyanides. Thus, while potash, soda and baryta had been found effective, lime, on the other hand, appeared to be entirely inert.

In the meantime, the Englishman Saunderson published the results of a series of investigations from which he drew the conclusion that to carburize iron it is *necessary* to have recourse to the simultaneous action of nitrogen (for example, in the form of ammonia) and of carbon (for example, in the form of ethylene), while cementation could not be effected by the action of *pure and isolated* carbon, carbon monoxide, ammonia or ethylene. And Caron (1861), observing that under the experimental conditions used by Saunderson ammonium cyanide must be formed, drew from the researches of the English technologist a new confirmation of his hypothesis.

As the result of his experiments and his hypothesis, Caron proposed (1861) the use of a cement (still employed to-day) consisting of a mixture of three parts of carbon with one part of barium carbonate, finely powdered, the efficiency of which, inexhaustible by use, he attributed exclusively to the formation of barium cyanide. This is very slightly volatile, hence less liable to escape from the cementation boxes, and is formed by the simultaneous action of the carbon and of the nitrogen of the air occluded in the powdery mass. We shall see later how the formation of barium cyanide is but a secondary reaction among those to which Caron's cement owes its effectiveness.

As to the carburizing action of the cements usually employed in the industry, and consisting essentially, and sometimes exclusively, of wood charcoal, Caron also attributed it to the cyanides of alkali metals or alkaline earth metals formed by the simultaneous action of the carbon and the nitrogen of the air occluded in the mass of the cement on the alkalis and the alkaline earths constituting the ashes of the carbon used.

Moreover, Caron was the first to observe the existence of a relation between the *decomposability* of carburetted compounds which, under given conditions, give rise to cementation, and the concentration of carbon in the cemented zones obtained with them. Thus he draws attention to the fact that ammonium cyanide is, of the various cyanides, the one which, when used as cement, shows in the most marked degree the inconvenient property of excessively carburizing the iron, transforming it quite easily into cast iron instead of steel, while this fact does not manifest itself when barium cyanide is used. This is because ammonium cyanide is, of all the alkali cyanides, the one which is the most easily decomposed.

But if Caron was able to feel sure that in the processes of cementation used the sole agent of the carburization of iron is cyanogen with its compounds, he had to abandon his theory in some special cases, being compelled to recognize, for example, that in the cementations obtained by means of pure methane it is not possible to assume the intervention of cyanides. He maintains, however, that the hydrocarbons used as cements, on account of their too easy decomposability, always carburize the iron too much, transforming it into cast iron instead of steel. Therefore the *only* compounds capable of producing in practice a true cementation proper (or a transformation of iron into *steel*) are the alkali cyanides, which he considers as "the only compounds of carbon which are undecomposable and volatile."

Meanwhile Frémy, in a series of memoirs also published in the *Comptes Rendus de l'Académie des Sciences*, believed that he had been able to establish by means of a large number of observations that the importance of the function of nitrogen in the process of cementation was by far still greater than was attributed to it by Caron. In fact, he believed that he could extend the results of the earlier researches of Faraday, Schafhäutl and Marchand (who had revealed the presence of nitrogen in steel and in cast iron) and could show[1] that nitrogen is, together with carbon, a *necessary* constituent of steel, so that "on peut dire qu'on acière du fer en l'*azotant* en présence du carbone, et qu'on le *désacière* en le *désazotant* par l'hydrogène." ("One may say that iron is made steel by absorbing nitrogen in presence of carbon, and that steel is changed to iron by removing its nitrogen by hydrogen.") Therefore, according to Frémy the function of the nitrogen of the air in industrial cementation is not only that of forming volatile and difficultly decomposable alkali cyanides, considered by Caron as the sole *agents of cementation*, capable of "carrying the carbon in a state of combination into the pores of the iron, where the latter absorbs it in the nascent state," but that more complex one of simultaneously serving as a *vehicle* for the penetration of the carbon into the iron and taking part directly in the formation of the steel, combining with the iron and with the carbon, "forming a kind of cyanide compound which appears to be an essential constituent of steel."

The investigations of Frémy, the contents of which are summarized by the author himself in the phrase "steel is therefore not a simple carbide, but a nitrogenized-carburized iron," excited the most lively interest among scien-

[1] See *Comptes Rendus*, 1861, 1st sem., p. 626 *et seq.*

tists, as is evident from the animated discussions which always followed, at the Academy of Sciences, the communications of Frémy.

But very soon the investigations which Caron was rapidly carrying on at the same time as Frémy, led him to results which it would have been difficult to harmonize with the theory of Frémy, whence arose a lively polemic between the two scientists. The discussion ended with the proof of the unreality of Frémy's theory, but the cementation experiments with pure hydrocarbons made by Caron to demonstrate the lack of foundation of his opponent's theory constrained their author himself to modify (as we have already seen) his original theory and to admit that certain volatile carburetted compounds (as, for example, various hydrocarbons) can cement iron, even without the intervention of nitrogen.

Three years later (July, 1864) a new scientific discussion was precipitated by Margueritte concerning the results of Caron's earlier work; but the latter, in the meantime, although continuing his interesting studies on the composition of steel, on the nature of the process of tempering steel, etc., had made no further experimental studies on cementation, considering (as he says in one of his Memoirs of 1864) that the question was now completely solved on the basis established by him.

Not convinced of the exactness of the hypothesis of Caron, Margueritte began an experimental study of the process of cementation and published the results obtained in a series of communications presented before the Academy of Sciences of Paris, beginning in July, 1864. The experiments on which Margueritte bases his thesis, contrary to the hypothesis of Caron, both of the possibility of *direct* cementation by means of carbon alone and by simple contact, and of the possibility of cementing iron by means of pure carbon monoxide, merit brief mention, for many of the discussions which have since taken place on the same argument spring from these experiments and those brought out in opposition by Caron.

In his first communication[1] Margueritte declares that the old experiments by Clouet (referred to by Guyton-Morveau), thought to show the possibility of cementation by simple contact, are not decisive because in them an iron crucible in which the diamond was heated remained exposed during the whole time of ignition to the carburizing action of the gases of the furnace, so that to the action of these gases rather than to that of the diamond might be attributed the transformation of the iron crucible into steel. To avoid such a cause of error Margueritte placed a thin sheet of iron (first ignited for a long time in a current of pure dry hydrogen "to cause it to lose its sulphur and its nitrogen" on the edges of a porcelain boat; on the sheet of iron he placed a diamond and introduced the boat thus prepared into a porcelain tube glazed inside and out; then he circulated for two hours through the cold porcelain tube a current of very pure and perfectly dry hydrogen so as to totally dis-

[1] *Comptes Rendus*, LIX, p. 139.

place the air from the apparatus. This done, he rapidly raised the temperature of the tube to bright redness and kept it so for some time, then, still without interrupting the current of hydrogen, let the apparatus cool. Removing the boat from the tube, the experimenter was able to note that the diamond had perforated the sheet of iron and had fallen into the boat, together with a small globule of cast iron. After having repeated the same experiment with diamonds and sheets of iron of various dimensions and having always obtained the same results, Margueritte heated in the same apparatus and under identical conditions (always in a current of hydrogen) an iron wire 1 1/2 mm. in diameter, immersed for half of its length in diamond dust in a platinum boat; the experiment being finished, he could easily note that the part of the wire which had been in contact with the diamond dust was cemented while the other part was not and remained insensible to tempering. Analogous, but still more conclusive results were furnished by a similar experiment in which graphite or sugar carbon, first ignited for a long time in a current of hydrogen, was substituted for the diamond dust.

Margueritte justly observes that if the hydrogen used in his experiments had reacted with the carbon to form acetylene or any other volatile hydrocarbon to which might be attributed the cementing action observed, the iron wire ought to have been cemented along its whole length. And since such was not the case, Margueritte considers it as proved that iron is carburized, passing into steel or cast iron, when it is heated in contact with carbon and that the transformation of iron into steel takes place even without the intervention of nitrogen.

In a second note[1] Margueritte describes a series of experiments carried out by heating pure iron in a porcelain tube glazed inside and out, through which he circulated a current of very pure carbon monoxide.

His experiments, executed with minute care, led him to maintain, contrary to what Laurent and Leplay, and more recently Caron, had asserted, that pure carbon monoxide markedly cements iron. As to the possible objection which might have been raised against the correctness of his deductions, on the basis of the hypothesis proposed by Caron, who had attributed to the silicon contained in the steel the partial carburization observed by himself in his cementation tests with carbon monoxide, a simple calculation, based on the amount of silicon contained in the iron which he had used, enabled Margueritte to show that "the influence of silicon on the cementation with carbon monoxide, though actually detectable, has played, in the samples of iron used by him, merely an almost insignificant part."

It is well to call attention now to the fact, the importance of which we shall see later, that Margueritte had used for these experiments iron in the form of *fine wire*, *powder* (obtained by reducing iron oxalate in a current of hydrogen) or *very thin sheets*.

[1] *Comptes Rendus*, LIX, p. 185.

In his new experiments Margueritte found a further proof against the hypothesis of Frémy on the function of nitrogen in the process of cementation.

To the two notes just cited Margueritte added a third,[1] in which, on the basis of the data from his own researches and those of other experimenters, he formulates his theory of cementation in the following phrase: "Iron combines with carbon and is transformed into steel by contact or cementation, and also by the decomposition of a carburetted gas; these two causes of carburization are present and act simultaneously in the cementation box."

I shall have occasion later to again refer to the correctness of these words.

Margueritte ends his third Memoir by explicitly showing again that his experiments constitute a new demonstration of the lack of foundation of Frémy's theory and summarizes his views on the nature of steel, deducing them from his investigations on cementation, in a few sentences which merit being quoted in full as epitomizing, in advance, our present ideas on this question:

"The truth is that no one can to-day prove that steel is exclusively a nitro-carbide rather than a phospho-carbide, a chromo-carbide, a silico-carbide, a mangano-carbide, a titano-carbide, a tungsto-carbide of iron, etc. But among these classes of steel, so numerous and of such varying quality, it is the *typical steel*, the *ferro-carbide steel*, which is formed and disappears together with the carbon, and which generates the other steels, changing under the influence of all the metalloids or the metals which can combine with it."

Meanwhile, before the third note of Margueritte had been read before the Academy of Sciences, Caron had presented to the same Academy[2] a communication in which he reports some new experiments intended to show how pure carbon monoxide *does not cement iron at a bright red heat*, while *at a lower temperature* (not high enough to soften glass) it decomposes, passing, in contact with iron, into carbon dioxide and carbon. Granting this, according to Caron, the cementation (always slight) observed by Margueritte was not produced during the heating *at redness* of the iron in a current of carbon monoxide but only during the brief period in which, during the cooling of the apparatus, the temperature of the system had passed through the interval in which the decomposition of the carbon monoxide can take place. From all this Caron concludes that, while it must be recognized that carbon monoxide, under special conditions of temperature, can carburize iron, it is necessary to maintain that this can take no part in industrial processes of cementation, which are carried out at a high temperature.

As to the fact that the carbon monoxide issuing from Margueritte's apparatus always contained carbon dioxide, even during the whole period of heating at *redness*, Carbon explains it by assuming that the carbon monoxide used by Margueritte had not been purified with sufficient care.

[1] *Comptes Rendus*, LIX, p. 376.

[2] *Comptes Rendus*, LIX p. 333.

We shall see later how the results of Caron's experiments are explained perfectly without in any way weakening the validity of those of Margueritte.

To Caron's observations, Margueritte made answer one month later,[1] again citing his earlier experiments but adding concerning their execution more details, by which the objections of Caron are clearly refuted.

The answer of Caron[2] is based first of all on the consideration of the well-known fact that the carbon employed in industrial cementation becomes *exhausted* with use, becoming incapable of carburizing iron. Such a fact could not be explained, according to Caron, if the assertion of Margueritte were exact that "carbon and carbon monoxide (formed by the reaction between the carbon of the cement and the oxygen of the air occluded in it) must be considered as the most abundant and most active elements in industrial cementation." In fact, it is clear that, however much the carbon may be used, neither the carbon nor the air occluded in it can suffer any diminution. Caron maintains, on the other hand, that it is evident that since, from the carbon already used for cementing, the alkalis (contained in the ashes and capable of giving rise to the formation of cyanides) have been removed, volatilizing for the greater part, the diminished carburizing efficiency of used carbon is proof of the preponderant action of cyanides in the process of cementation.

To this observation Caron adds the results of some experiments in which iron bars in the form of parallelepipedons, $10 \times 10 \times 300$ mm.,[3] heated twelve hours to redness in a current of pure carbon monoxide, did not show a trace of cementation, while identical bars of the same iron, cemented (under identical conditions) with one of the ordinary cements, were strongly carburized to a depth of about 3 mm.

Margueritte again answers in two notes, presented before the Academy of Sciences at the meetings of October 31, and November 14, 1864. In the first Note[4] he merely communicates the results of new experiments (analogous to his earlier ones), from which it appears that by heating at a *high temperature* (from cherry-red to light orange) *powdered iron*, or *iron wires* having at the most a diameter of 3.5 mm., in a current of pure carbon monoxide strong cementations are obtained.

He observes clearly that the content in carbon of the iron wires cemented under such conditions is smaller the higher the temperature at which the cementation takes place.

In the second Note[5] Margueritte opposes to the arguments of a technical nature advanced by Caron in support of his theory of cyanides various other

[1] *Comptes Rendus*, LIX, p. 518.

[2] *Comptes Rendus*, LIX, p. 613.

[3] We shall see later the importance of the dimensions of the samples of iron subjected to cementation in explaining the discordance between the experiments of Caron and those of Margueritte.

[4] *Comptes Rendus*, LIX, p. 726.

[5] *Comptes Rendus*, LIX, p. 821.