cementation of carbon steels, Guillet completes the series of his practical rules by indicating the conditions which a good cementation furnace must satisfy.

As an example of a rational equipment for the cementation of mechanical pieces, he gives an interesting description, accompanied with photographs and plans, of the equipment adopted by the firm of Fichet and Heurtey in the shops of the Dion-Bouton automobile factory. To these practical data, with which we shall deal later, the author adds some considerations on apparatus for the measurement of temperature in the cementation furnaces; among such apparatus he recommends, for its accuracy and practicability, Féry's pyrometer, which he used in his experiments.

Of the use of this and other pyrometers I shall speak later.

Finally, Guillet passes to the study of the cementation of special steels, and establishes at once that the addition of 2% of nickel to an ordinary cement steel causes the disappearance of the brittleness which such a steel usually shows after cementation.

We shall see later how the great advantages which nickel steels show, as compared with ordinary carbon steels, compensate largely, in fact, for the somewhat higher cost of the former steels as compared with that of the latter.

The author then studies "the influence of various elements on the velocity of penetration of the carbon," subjecting to cementation, all under identical conditions, many special steels containing the same quantity of carbon (about 0.15%).

The results obtained are collected into the following table:

Proportion of foreign metal	Velocity of penetration in tenths of a millimeter	Proportion of foreign metal	Velocity of penetration in tenths of a millimeter
2.0% of nickel	7	2.0% of molybdenum	11
5.0% nickel	5	1.0% titanium	8
0.5% manganese	11	2.0% titanium	7
1.0% manganese	12	0.5% silicon	6
1.0% chromium	10	1.0% silicon	5
2.0% chromium	11	2.0% silicon	4
0.5% tungsten	9	5.0% silicon	0(*a*)
1.0% tungsten	9	1.0% aluminium	4
2.0% tungsten	12	3.0% aluminium	2
1.0% molybdenum	9		

(*a*) No cementation.

Under the same conditions a carbon steel showed a penetration of nine-tenths of a millimeter.

On the basis of these data Guillet considers it proved that "the substances which retard cementation are those which are found in solution in the iron (nickel, titanium, silicon and aluminium)," and that "the substances which accelerate cementation are those which seem to exist in the state of double carbides, substituting a part of the iron of the cementite (manganese, chromium, tungsten and molybdenum)."

Examining separately, next, the behavior of the various types of special steel subjected to cementation, Guillet communicates some interesting observations which I summarize briefly, deferring the discussion of a part of them:

1. Cementation of Nickel Steels.—The author lays stress on the observation (already published by him before[1]) that on cementing a steel containing more than 7% of nickel in such a way as to obtain at the periphery a carbon content higher than 1%, there is obtained a superficially cemented zone which, even when not subjected to tempering but allowed to cool slowly, possesses the martensite structure and the hardness characteristic of tempered steels.

This procedure, patented in various countries by the Dion-Bouton Works, makes it possible to abandon the hardening of cemented pieces and hence to avoid all the disadvantages which accompany this operation, such as deformations, fracturing, etc. Extending, then, the carburization so as to reach 1.5% of carbon at the periphery, there can also be obtained a superficial layer, superimposed on the martensite zone, containing γ-iron, easily admitting of polish without loss.

The author reproduces various micrographs of nickel steels cemented by these processes and gives notice that he is prosecuting investigations of this nature.

2. Cementation of Manganese Steels.—These steels behave like nickel steels except that, on cementing, for example, a steel with 5% of manganese so that the external layer contains 1% of carbon, "*a pearlite core is obtained, then a little martensite is seen*," but the periphery is "*characterized by a great abundance of troostite*" and is not, therefore, as hard as that of steel with 7% of nickel. The author adds the diagram of structure of steels with various amounts of manganese and carbon. I do not reproduce this diagram because, together with other analogous ones traced by Guillet for other special steels, it is well known, owing to its importance, to all who deal with special steels.

3. Cementation of Chromium Steels.—By cementing a steel with 5% of chromium there can be obtained a martensitic steel, and by sufficiently extending the cementation there is obtained, in the surface layer, a double carbide of iron and chromium.

4. Cementation of Tungsten Steels.—The cementation of these steels, which have no practical interest whatever as cemented steels, produces the appearance of the doube carbide of iron and tungsten, or increases the proportion of it in the cases in which it already exists.

5. Cementation of Silicon Steels.—Steels containing more than 7% of silicon or those which, while containing a smaller amount of silicon, have been

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[1] I have already reviewed this work on p. 44.

heated sufficiently long, contain all the carbon in the state of graphite; such steels can not be cemented.

6. Steels Which do not Cement.—Besides the silicon steels, whose carbon content (as we have just seen) does not increase on cementation, there are steels whose hardness does not increase, and sometimes diminishes, as the result of cementation followed by quenching. Thus, on cementing a martensitic nickel steel, there is obtained an external layer of γ-iron, considerably less hard than the original steel.

7. Steels which Cement at Low Temperature.—In an earlier publication which I summarized above,[1] Guillet had shown that a γ-iron steel can be cemented even at 450° C. by using as cement potassium cyanide, whose melting point is lowered by the suitable addition of alkali and alkaline earth chlorides. Now he shows that the diffusion of carbon into γ-iron takes place even at ordinary temperature; in fact, a γ-iron steel which, cemented at 1000° C., contained at the surface 1.22–1.35% of carbon, after six months contained (always at the surface) only 0.85–0.92% of carbon; the carbon of the pheriphery had therefore continued dissolving into the mass.

The same results, confirmed by some later experimental data, analogous to those just referred to, are summarized in a note presented five months later by Guillet before the "Académie des Sciences.[2]

In October of the same year Charpy published in the American Journal *The Iron and Steel Magazine*,[3] under the title, "Notes on Cementation," a memoir in which are developed at greater length the considerations contained in the two notes which I have reviewed in the preceding pages,[4] presented by him in the preceding year before the "Académie des Sciences." Of this new paper, I shall review only the part which relates to facts and considerations of which the author had not spoken in the preceding papers which I have summarized.

Charpy begins by calling attention to the fact that in the study of the solubility of carbon in iron it is necessary to take into account, besides the solubility of the cementite, that of the graphite also, which is now known with absolute certainty.

Taking up again, then, the attempts, thus far fruitless, like those of Mannesmann, to determine the solubility of cementite in iron, by means of cementation tests, Charpy reports the results of four series of experiments carried out by cementing a wire of soft steel (with 0.04–0.09% of carbon) by means of four cements: wood charcoal, illuminating gas, potassium cyanide and cyanogen.

Notwithstanding all the precautions taken in the execution of these experiments, the results are extraordinarily irregular; the concentrations of carbon obtained vary irregularly from minima of 0.15–0.24% to maxima of 3.5–3.9% without its being possible to find any connection between these values and the conditions of temperature, of quenching, etc., under which the cementation was carried out.

Moreover, some of the cemented specimens contain an excess of cementite; others, an excess of graphite. From these experiments it seems that it is not possible in cementation to reach a limit of saturation; nor is it, therefore, possible to determine in this way the solubility of cementite.

Here Charpy recalls his reasoning, which I have already referred to in the preceding pages (see p. 42) to explain the separation of the excess of cementite and acknowledges that, unknown to him, Osmond (see p. 32) had already used (as we have seen) the same reasoning to explain the analogous results of some experiments of Saniter. (See p. 31.)

In confirmation of these deductions, Charpy reports the results of the experiments (which I have already summarized on pp. 42–43) in which filings and fine wires of iron are totally transformed into cementite by means of cementation with potassium cyanide, and others in which the cementation of the same materials with illuminating gas and with carbon monoxide gives rise to the formation of considerable proportions (more than 8%) of graphite.

From these data it follows that the segregation of the cementite and of the graphite occurs only near the point of saturation, and it does not, therefore, present itself in the practice of cementation. But since ordinary cementation is not automatically limited (as follows from the experiments cited), it is necessary in practice, in order to obtain a predetermined result, to work under definite conditions (of composition of the cement, of temperature, etc.) determined, in each case, empirically.

And here Charpy calls attention to the fact that it is possible to imagine conditions in which the cementation is *automatically limited;* this happens, for example, when using gaseous cements whose decomposition products have the tendency to decarburize the metal. Such cements are carbon monoxide, cyanogen and the hydrocarbons.

Granted this, Charpy reports the results of his experiments on the cementation of a fine wire of iron by means of carbon monoxide, results and experiments already published a year before in the note which I reviewed in the preceding pages. (See p. 45.) On the basis of these experiments and of the considerations already developed, extended to cyanogen and to the hydrocarbons, whose gaseous decomposition products (nitrogen and hydrogen, respectively) act as decarburizers of the steel, he deduces that "the cementation may be executed in such a way that the quantity of carbon absorbed is regulated automatically, and this *by using as cementing substance a continuous current of a gaseous mixture containing definite proportions of*

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[1] See p. 44.

[2] *Comptes Rendus*, 1904, 1st sem., Vol. CXXXVIII, p. 1600.

[3] *The Iron and Steel Magazine*, Vol. VIII, No. 4, p. 309.

[4] See p. 44 *et seq.*

either carbon monoxide and carbon dioxide, cyanogen and nitrogen or hydrocarbons and hydrogen."

We shall see later how the conception expressed in indefinite form in these sentences of Charpy is not susceptible of practical application; this, moreover, is easy to understand when we think of the enormous practical difficulty of adjusting the mixture of carbon monoxide and carbon dioxide in which, to obtain appreciable cementations at temperatures sufficiently high so that the process may go on with sufficient rapidity, the proportion of carbon dioxide must be below 1% and determined with an accuracy greater than one part in a thousand.

We shall also see, however, how, taking into account the various elements (such as the distribution of the carbon in the cemented zones, the relation between the velocity of penetration of the carbon monoxide and of the carbon dioxide into the iron, the velocity of the reactions which take place in the process of cementation, the conditions of equilibrium between the gases in the cementing atmosphere and in the mass of the steel, etc.) which Charpy could not consider in his experiments,[1] it is in reality possible to obtain in practice the result whose possibility Charpy foresaw. But, I repeat, this result can be obtained under conditions of *industrial feasibility* only by means quite different from those suggested by Charpy, based on the use of gaseous mixtures in definite proportions. Of such means we shall treat later; for the present I only wish to point out how Charpy's preconceptions relative to the use of hydrocarbons to "limit" the cementation do not seem confirmed by more recent experiments.

Charpy's memoir concludes with some interesting observations on the action of carbon monoxide on manganese and on chromium. These metals, and especially chromium, when subjected to the action of carbon monoxide, absorb its oxygen, being transformed into mixtures of their oxides and of free carbon. Chromium preserves this property even when it is alloyed with other metals; for example, in chrome steels. "When a chrome steel is subjected to the action of carbon monoxide, a certain cementation occurs, but at the same time an oxidation also manifests itself. This, however, seems to be limited to the chromium, and does not proceed beyond the surface zone, because the oxide of chromium formed does not diffuse into the metal." We shall have occasion to see later how these facts can be clearly explained on the basis of the results of a series of most interesting investigations by

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[1] This is due, above all, to the fact that Charpy almost always used in his cementation experiments (except in a few cases) the iron in the form of wires or filings, in which it is evidently impossible to take into account the distribution of the carbon.

From the considerations which I shall have occasion to develop later, it will appear clear that the investigations of Charpy, carried out with the ability and acumen which distinguish the author, would certainly have led to the most interesting results (especially from the practical point of view) if the author had placed himself under such experimental conditions as to have been able to study the *distribution* of the carbon in the cemented zones.

Schenck, and how these investigations make it possible to determine with precision the course of the reactions which take place between carbon monoxide and the various metals.

Following the chronological order, we find a work of J. Lecarme, published in 1905 by the *Revue de Métallurgie*.[1] Although the contents of this work do not bear strictly on the process of carburization of cemented zones, but rather on the transformations which take place in the "heart" of the cemented pieces (to which, at least apparently, the carburization does not extend), yet the conclusions to which they lead, if the experimental facts on which they are based should ever receive more certain confirmation, would be of great importance for the study of cementation, as well from the theoretical as from the technical point of view.

Lecarme reports the results of several series of comparative bending tests, made on various samples of the same steel, some of which had been cemented and quenched under definite conditions while others had been subjected in a neutral medium or in the presence of substances capable of impeding the cementation (substances which Lecarme calls "anti-cements," keeping their composition secret), to the same thermal treatment to which the cemented specimens had been subjected.

From the brittleness of the cemented pieces, which was always greater than that of the others, Lecarme believes he can conclude:

1. "That the brittleness of the cemented soft steels is not due to the heating which accompanies the cementation;

2. "That the surface carbon cementation is accompanied by a chemical transformation of the center of the metal, which appears homogeneous throughout its whole mass. The new metal thus produced, when treated by the ordinary methods, that is, simply quenched at about 800° C., becomes brittle."

Lecarme adds that "with thermal treatment executed under suitable conditions, it is possible to suppress, in part, the brittleness of cemented soft steels without harm to the hardness of the surface layer," but concerning such useful treatment he furnishes no precise information.

The practical importance which these results would have, if they were ever confirmed, is evident. As to their theoretical importance, the fact of a chemical transformation *due exclusively to cementation* and manifesting itself in the metal lying *below the carburized* zone would show beyond doubt the marked intervention of gases in the process of cementation, or, at least, would be a proof that the process of cementation does not consist simply, as was supposed by Margueritte and later by Ledebur, in a process of solution of the solid carbon in the iron.

In a note immediately following Lecarme's work, Le Chatelier points out

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[1] J. Lecarme, *Sur la fragilité des aciers doux cémentés* (*Revue de Métallurgie*, 1905, Vol. XI; *Mémoires*, pp. 516–525).

that the conclusions of that work are very interesting but that they are "not based on any precise experimental proof." Le Chatelier insists above all on the fact that in the bending tests on the cemented bars "the fracture of the cemented zone produces a crack, equivalent to a very sharp cut, the presence of which is sufficient to cause the breaking, through brittleness, of the greater part of soft steels. It would have been necessary, therefore, in order to obtain comparable results, to carry out the comparative tests on non-cemented bars after having made in them a cut as sharp as possible," which Lecarme did not do.

Le Chatelier adds that "it must, however, be acknowledged that Braune's experiments on the harmful influence of nitrogen lend a certain probability to the facts announced by Lecarme, *for in the usual processes of cementation the nitrogen is the carrying agent of the carbon.*"

As to the possibility, alluded to by Lecarme, of regenerating steel made brittle by cementation, Le Chatelier says he long since pointed out to various works a process capable of producing such an effect. We shall treat of this later.

Answering briefly Le Chatelier's observations,[1] Lecarme admits their justice but adds that he has been able to establish by means of a series of experiments that the difference in brittleness between the cemented bars and those simply heated persists, though to a less marked degree, even when the bending tests are executed on specimens obtained by removing, with an emery wheel, the brittle carburized zone. The later data reported by Lecarme are, however, absolutely insufficient to establish either the importance or even the reality of the phenomena. Precise investigations on this line would certainly be of great use.

On January 15, 1906, appeared an article by Ledebur,[2] in which the celebrated German metallurgist harshly criticises the work (reviewed a few pages back[3]) published two years before by Guillet in the *Mémoires de la Société des Ingénieurs Civils de France.*

Ledebur states that he has not read Guillet's work in the original text and that in his criticism he refers to the review of that article published about a year and a half before in *Stahl und Eisen.* He then explains the delay in the appearance of his criticisms by a long illness which he has suffered in the meantime and by the long time required by investigations on an industrial scale, which he has thought necessary to make as a basis for his objections, not considering as sufficient experiments carried out in the laboratory on a small scale.

The very full review of Guillet's work to which Ledebur refers[4] is compiled by Bauer, who reports the data and arguments contained in Guillet's memoir with great precision and in an entirely impersonal manner. The compiler allows himself, however, to set forth here and there some of his personal views, which he always takes care to distinguish clearly from Guillet's, and it must be admitted that many of his observations are justified. Such, for example, is the just criticism by Bauer of a statement of Guillet (which I have quoted, in italics, on p. 53) to the effect that in manganese cemented steels we pass, proceeding from the surface toward the interior, from a troostite layer to one of martensite and from this to a pearlitic one; it is, in fact, difficult to explain how this can happen when we remember the fact that troostite constitutes one of the end points of the passage of martensite to pearlite.

Ledebur begins by upbraiding Guillet for having made use only of metallography and not of chemical analysis when studying the course of a process essentially chemical, such as that of the diffusion of carbon into iron. Then, against the conclusion of Guillet that the velocity of cementation is independent of the carbon content of the steel subjected to cementation, he cites the experiments of Saniter (which I have already briefly reviewed) which, on the basis of chemical analyses, showed that the velocity of cementation *diminishes* as the concentration of the carbon increases in the steel.

Ledebur denies, then, any scientific value whatever to the second series of Guillet's experiments, relative to the influence of time on the depth of cementation, since the results of those experiments are irregular, uncertain and, moreover, inconsistent with those obtained by other experimenters; for example, with those of Mannesmann.[5]

As to the third series of Guillet's investigations, relative to the influence of temperature on the course of cementation, Ledebur admits that they present marked interest. In fact, the earlier experiments of Arnold and MacWilliam,[6] which had already proved that below 750° C. the migration of carbon into iron does not take place, and that the velocity of this migration increases with rise in temperature, related to the passage of the carbon from a mass of steel in which its concentration was high to another in which it was low, rather than to the true process of cementation, properly so called. On the other hand, in the researches of Mannesmann,[7] which had proved that the cementation is more rapid the higher the temperature, the measurements of the temperature were certainly inexact.

But there is one point on which Ledebur declares himself to be of an opinion entirely contrary to that of Guillet; this relates to the "mechanism" of the process of cementation. In fact, Ledebur maintains that, on the basis of the

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[1] *Revue de Métallurgie,* 1905, pp. 720–721.

[2] *Stahl und Eisen,* 1906, Vol. XXVI, pp. 72–75.

[3] See p. 46 *et seq.*

[4] *Stahl und Eisen,* Sept., 1904, pp. 1058–1064.

[5] These results of Mannesmann are briefly summarized in the first chapter of this book (see p. 19 and especially the figure).

[6] See pp. 34–37.

[7] See p. 14 *et seq.*

exceedingly numerous and conclusive experiments of many able experimenters—among whom he cites Margueritte, Roberts-Austen, Hempel and Mannesmann (whose experiments are already summarized in preceding chapters) —it is now absurd to admit the theory of Caron and Guillet that cementation can not be effected directly by the action of solid carbon but is always produced by cyanides formed by the action of the nitrogen of the air on the alkalis contained in the ashes of the wood charcoal used as cement.

Ledebur censures Guillet for having carried out the experiments to prove his assertion only in the laboratory, on a small scale,[1] continuing the duration of the cementations only up to eight hours and limiting himself to measuring the depths of the cemented layers without determining, by chemical means, their carbon content. He proposes to show, by means of experiments carried out on an industrial scale, that the cementation is effected by the direct action of the solid carbon placed in contact with the iron, independently of the intervention of volatile carburizing substances.

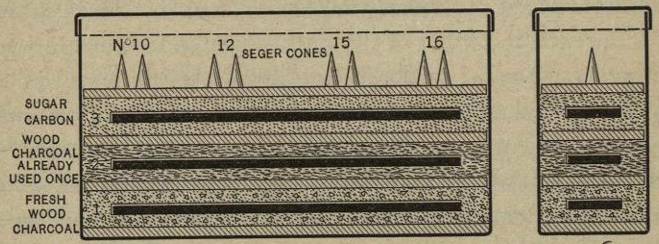

FIG. 17.

Ledebur's first group of two comparative experiments, carried out by cementing Lancanshire iron in closed graphite crucibles, using as cements wood charcoal and sugar carbon, did not give clear-cut results because even the sugar carbon contained considerable quantities of ash, quite rich in alkali.

A new series of three experiments was carried out in the "Bergische Stahlindustrie" foundry of Remscheid, by cementing bars of Lancanshire iron, 35 cm. long, 8 cm. wide and 1.5 cm. thick. The iron bars were placed in a well-closed sheet-iron box in the manner indicated in the accompanying figure (see Fig. 17), surrounding each one with a cement and separating with refractory bricks the spaces occupied by the individual cements. The cement filling the lower space was "new" powdered wood charcoal; the intermediate chamber contained wood charcoal already used once as cement; finally, the cement used for the upper chamber was sugar carbon, previously washed with acids. In the free space remaining in the upper part of the sheet-iron box were placed Seger cones, corresponding to temperatures of 950°, 890°, 800° and 770° C.

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[1] I shall have occasion to bring out later how unjustified is this reproof of Guillet by Ledebur.

The box remained in the furnace during 408 hours of firing. When removed from the fire, three of the Seger cones had melted completely, while the fourth, corresponding to 950°, had merely suffered a slight softening; the maximum temperature reached by the box was therefore 950°.

The analyses of the bars and of the cements gave the following results:

Lancashire iron, before cementation	0.144% of carbon
The same, cemented with "new" wood charcoal	1.45% of carbon
The same, cemented with used wood charcoal	1.23% of carbon
The same, cemented with sugar carbon	1.38% of carbon
Percentage of ashes (as residue in the combustion):	
"New" wood charcoal	2.00%
Used wood charcoal	10.75%
Sugar carbon	0.75%

The ashes of the sugar carbon were almost completely free from alkali and consisted of almost pure iron oxide. Nevertheless, the carburizing action of the sugar carbon was almost equal to that of the "new" wood charcoal and higher than that of the wood charcoal already used. These experiments show anew that for the cementation of iron the intervention of gaseous carburizing compounds is in no wise necessary and that, instead, the carbon can penetrate directly into the iron and diffuse into it until it reaches a limit of saturation depending upon the temperature.

This does not mean, naturally, that carburizing gases or vapors, and especially hydrocarbons and cyanides, do not cement iron *even more rapidly;* this is a fact known for a long time and applied in industry for superficial cementation and, more recently, in the manufacture of armor for ships.

Ledebur then observes that, at least in the form in which the author expresses himself, the assertion of Guillet that "the use of too high a temperature in the cementation may give rise to a decarburization of the iron" is inexact; in fact, Ledebur remarks justly that all the experiments show with the greatest certainty that cementation carried out at too high a temperature can produce only an excessive carburization of the iron, and that the decarburization can manifest itself only as the result of the exhaustion of the cement and of consequent access of air to contact with the metal.

Ledebur concludes with some considerations on the probable causes of the known phenomenon of the decrease in the efficiency of cements with use. He does not consider as correct the explanation of the phenomenon advanced by Margueritte and by Mannesmann, who attribute it to the increase in "compactness" or in "density" which manifests itself in the particles of wood charcoal subjected to a long heating. If this were so, it should be possible to distinguish with the microscope "new" carbon from that already used, which, however, he has never succeeded in doing. Moreover, contrary to the hypothesis of Margueritte is the fact, shown by experiment, that various very dense carbons cement iron more intensely than others which are considerably lighter. Ledebur holds, rather, that the cause of the phenomenon lies in the ashes, the proportion of which in the carbon increases (as the experiments cited by the author, and others, show) with use of the latter, and this for two reasons; the first is that in every cementation a little of the carbon burns up on account of the air occluded in it; the second is the fact that during the various operations a little sand, coming, especially, from the cover of the boxes, becomes mixed with the powdered carbon. So that, first, the quantity of efficient carbon is diminished by the presence of these foreign substances, and, in the second place, the basic components of the ashes of the carbon and the siliceous sand fallen into it form a mass fusible at the temperature of the cementation, which covers the grains of carbon, diminishing their contact with the iron.

A lengthy summary of Ledebur's memoir was published a few months later by the *Revue de Métallurgie*[1] and followed, in the same number of the French Review, by a brief reply by Guillet,[2] who answers successively the three principal criticisms directed against him by Ledebur, as follows:

1. To the criticism of having determined the course of the cementation by means of microscopical examination instead of by chemical analyses, Guillet answers that Ledebur would not have made that criticism if, instead of the summary of his work published by *Stahl und Eisen*, he had read his original memoir.

Now, leaving aside the consideration that even in the summary of *Stahl und Eisen* mention is made, *as in the original memoir*, of gravimetric determinations of the carbon *in the surface layers* of the cemented pieces and that, therefore, Ledebur's opinion would not have been modified by reading the original memoir, Guillet's statement that he can not see what interest the use of chemical analysis can present in determining *the velocity of penetration of the carbon* seems somewhat immoderate. In fact, we shall see later how analyses of the successive layers of the cemented zones furnish most interesting data on the mechanical properties of the cemented pieces, due to the "distribution" of the carbon in these zones. Moreover, the observation of Ledebur assumes the very greatest importance as regards the cementation of special steels, for which, as we shall see later on the basis of practical examples, the measure of the depth of cementation made by means of microscopical examination furnishes, in the majority of cases, but uncertain and inexact data.

2. As to the experiments of Saniter cited by Ledebur, Guillet observes very justly that they do not at all contradict his own; he, in fact, determined the *velocity of penetration* of the carbon, finding it constant for steels containing from 0 to 0.5% of carbon, while Saniter had shown that the velocity with which the *concentration* of the carbon increases as the result of cementation diminishes when this concentration has reached the value 1.64%.

And here, to this correct observation of Guillet, it may be added that Saniter, working on fine iron wires, could certainly not determine the "depth" of cementation and, therefore, neither the "velocity of cementation" in the sense in which this datum is meant in Guillet's experiments.

3. Guillet holds that the only interesting criticism advanced against him by Ledebur is that regarding the way of considering the course of the cementation.

While Ledebur maintains that carbon is the agent of the cementation, Guillet "believes that he has shown that the active agent in every industrial cementation *is a cyanide or a carbide.* He insists, however, that carbon alone does not cement."

As to the experiments of Margueritte, of Roberts-Austen, etc., Guillet holds that cementation experiments carried out with diamonds in a current of hydrogen[3] prove nothing, since hydrogen is not the desired inactive medium. As to the assertions of several authors that in various experiments, carried out under definite conditions, cementation had manifested itself only at the points where the carbon was in contact with the iron, Guillet wonders if it is "possible to verify such facts." But we shall see further on how he himself later had occasion to state such facts.

Guillet adds here the results of two other experiments. In the first, carried out by heating sugar carbon in contact with iron for twenty-four hours in a vacuum, not the least cementation detectable by the microscope or by chemical analysis manifested itself. In the second "industrial" experiment, carried out by cementing iron for 300 hours at 1000° C. in sugar carbon, there was formed only a carburized layer 2/10 mm. thick, which Guillet attributes to the action of small quantities of ashes. Under the same conditions the mixture of wood charcoal and barium carbonate gave a "penetration" of 20 mm.—Guillet finally affirms—and in this (as we shall see) he is evidently reasonable—that Ledebur's experiments do not certainly prove that carbon by itself can cement.

He supports his assertion by the fact that in the majority of cases the carbon used by Ledebur contained quantities of ashes sufficient to explain the cementation by the intervention of cyanides, and in the single experiment in which the ashes of the sugar carbon consisted solely of almost pure iron oxide, he admits that the vessels might have yielded substances (and especially alkaline bases) useful in the cementation. We shall see later, however, that the lack of proof by Ledebur's experiments lies in causes quite different from those just indicated.

Guillet then invites Ledebur to prove the exactness of his theory by

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[1] *Mémoires*, 1906, pp. 222–226.

[2] *Mémoires*, 1906, pp. 227–228.

[3] It is well to note that some of the cementations of Roberts-Austen were carried out *in a vacuum.*

making a prolonged cementation *in a vacuum* in the presence of sugar carbon perfectly purified by preliminary treatment with chlorine at red heat.

4. Guillet does not know in what part of his memoir Ledebur found the phrase, which we saw criticised by him, the text of which (according to Ledebur) is: "too high a temperature, *in the process of surface hardening*, gives rise to a decarburization of the iron."

Now, in truth, the text of Guillet's work (here, as in all other points, faithfully reported in the summary of *Stahl und Eisen*) does not contain exactly the phrase given by Ledebur. In fact, it is in speaking of the effects of heating *in general* that Guillet says that "if the temperature is too high, a decarburization of the metal may manifest itself." But since this phrase forms part of the views of Guillet on the disadvantages which the use of too high temperatures may produce in cementation, considerations which led Guillet to conclude that it is necessary to cement at the lowest possible temperature, it was natural enough that Ledebur should consider that the observations of Guillet referred to the heating which accompanies the cementation. At any rate it would have been useful if, in his answer, Guillet had cleared up better the mistake due merely to the inexact interpretation of his sentence.

In one of the first pages (p. 154) of the same number of the *Revue de Métallurgie*, the Editor makes some observations on the polemic which had arisen between Guillet and Ledebur regarding cementation. These observations, which, from their clearness and the breadth of the views which they contain, are certainly due to the pen of Le Chatelier, are worth noting here.

The Editor holds that the disagreement between Ledebur and Guillet is due in great part to the fact that the former means to indicate by the word *cementation* the process for the manufacture of steel founded on the total carburization of relatively thick bars of iron heated for very long times in contact with carburizing substances, while the latter deals only with surface cementation, limited to the formation of carburized layers of small thickness (1 or 2 mm.). It is evident, in fact, that the difference of these two points of view results in the two experimenters giving a totally different signification to the expression "velocity of cementation"; while to Ledebur this velocity refers to the increase in *concentration* of the carbon, to Guillet it refers to the *depth* to which the carbon penetrates.

The Editor adds, that "notwithstanding the quite widely prevalent contrary opinion, it is very difficult, not to say impossible, to admit that the cementing action of carbon monoxide is *nil*. *It must be extremely slow*, as its dissociation into carbon and carbon dioxide is arrested as soon as the smallest trace of this latter gas is produced; this must again be reduced in contact with carbon in order that the operation may begin again."

Le Chatelier, holds, then, that it may be admitted as certain:

1. "That many gaseous substances permit the rapid transport of carbon to the iron, without direct contact of the two substances.

2. "That the diffusion of carbon placed in intimate contact with iron is likewise possible. The disappearance of temper-carbon on heating is the proof of it."

And he concludes:

"The only point on which there can be any discussion is as to whether, in practice, this second method of penetration of carbon into iron takes place in the industrial processes of cementation. The experiments of Ledebur are not sufficient to prove it, as it would have been necessary to work in an absolute vacuum and with materials freed from the last traces of alkalis, such as with carbon first heated to white heat in a current of chlorine." We shall see later how these last observations contain exactly the key to the problem.

We wish to point out now, however, that the causes of disagreement between the conclusions of Guillet and those of Ledebur can be understood better if it is observed that, while the former experimenter proposed to determine the course of the process of carburization of solid iron by effecting it under the simplest and most rigorously defined conditions, and by considering it as a chemical process capable of a theoretical explanation, Ledebur sought, instead, to establish in what way the process takes place under the conditions of industrial practice. But Guillet's hypothesis, founded on the intervention of gases, is precisely that which applies (suitably modified) in the process of industrial cementation, while the explanation accepted by Ledebur does not hold, therein, except to a very small degree. Ledebur's hypothesis, in fact, enters into play to a marked extent only in cases in which the experiments are carried out under rigorously defined experimental conditions analogous to those adopted by Guillet.

Later the journal *Metallurgie* published a paper by R. Bruch[1] in which the author undertakes the accurate study of the course of cementation carried out with gaseous cements. The experiments are carried out under well-defined conditions, using carefully dried gases and cementing cylinders of steel 10 mm. in diameter, placed in tubes of glazed procelain kept at constant temperatures determined with a Le Chatelier pyrometer, and using a tubular electric furnace with platinum ribbon, made by Heraeus. Moreover, the author determined the carbon by chemical analysis of five successive layers (each $\frac{1}{2}$ mm. thick) turned on the lathe from the cylinders of cemented steel, and subjected his specimens to an accurate microscopical examination. The gases used were: the illuminating gas of the city of Aachen, petroleum vapor, acetylene, and pure carbon monoxide. The iron

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[1] *Ueber Zementierversuche mit gas-, resp. dampfförmigen Zementiermitteln* (*Métallurgie*, 1906, Vol. III, pp. 123–128).

subjected to the cementation was a very pure, extra soft iron (with 0.03% of carbon).

The experimental conditions were therefore very good, and could easily have led Bruch to draw most interesting conclusions regarding the process of cementation if he had subjected the results of his experiments to a rational study. However, he makes use of his numerous carbon determinations, made on the successive layers of the cemented cylinders, only to study how the velocity of penetration of the carbon varies with variations in the temperature. He thus merely reaches the conclusion, not at all new, that this velocity increases with increase in temperature; we shall see later that the results of these analyses could have led to valuable conclusions if he had made use of them (confirming them by a more exact metallographical examination) to determine the *distribution* of the carbon in the various cemented zones.

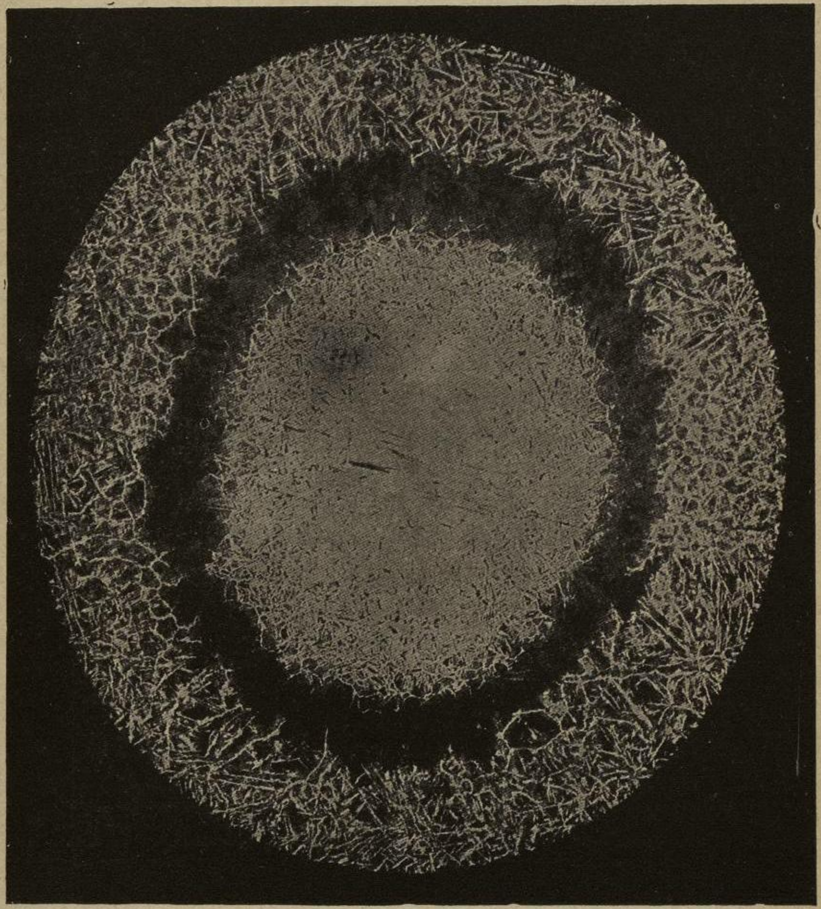

Fig. 18.

Besides the conclusion mentioned, Bruch also concludes that gases cement iron at temperatures below 700° C.

However, besides these two observations, Bruch makes two others which would certainly be more important if they were not evidently erroneous. The first refers to the cementing action of carbon monoxide, an action which Bruch holds is absolutely *nil*. We shall see later that Bruch was wrong, also the probable explanation of his error.

The second erroneous observation of Bruch refers to the way in which the concentration of the carbon varies in the successive layers of the cemented zones. Bruch maintains that the microscopic examination of his cemented specimens confirms the hypothesis that cementation consists in a process of "diffusion" or of "*solution*" of the carbon, for it shows that in these specimens there is "a *continuous and uniform* increase in the carbon content as we pass from the nucleus to the periphery."

It is sufficient to examine Fig. 18 to become convinced that the conclusions which can be drawn from the examination of Bruch's cemented specimens are quite different from those drawn by Bruch himself. This is but the reproduction of the microphotograph contained in Bruch's work to which Bruch refers to confirm his assertion. In this photograph (which reproduces, enlargement 10 diameters, the polished and etched section of a soft steel cylinder cemented by acetylene gas at 1050° C. for seven hours) is clearly seen the sudden transition from the external hyper-eutectic zone, rich in cementite, to the intermediate eutectic zone, formed of pure pearlite; and from this to the hypo-eutetic nucleus.

Moreover, since it is certain (and the micrograph and the analyses of Bruch prove it) that the carbon content increases from the center to the periphery of the steel cylinder, and it is no less certain that this content is constant (and equal to 0.9%) in the whole dark zone formed of pure pearlite, it is evidently absurd to say that the concentration of the carbon increases "in a continuous and uniform way" from the nucleus to the periphery.

We shall see later that these discontinuities are not due to the cementation but to phenomena following it. So that, if the proof offered by Bruch has no value, the hypothesis, independently of it, might nevertheless be correct. With this we shall have occasion to deal later, basing our remarks on more precise experimental data.

We may cite a work on the same line, published in the same year (1906), by Partiot in the *Revue de Métallurgie*.[1] This, while contributing no new facts, contains some clear observations on the preceding investigations. Thus the author, subjecting to a brief critical examination the experiments on which Guillet and Ledebur had based their conclusions, points out how

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[1] Partiot, *Sur quelques points obscurs de la théorie de la cémentation*. *Revue de Métallurgie*, 1906, pp. 535-540.

these two experimenters had not taken into account two important data, the influence of which was especially strong in the experiments of Ledebur, carried out by heating large masses during very long intervals of time. These data are: the time necessary to reach the constant temperature of cementation, and the "exhaustion" of the cements used.

The paper of Partiot then contains remarks on the need of carrying out experimental investigations on the substances which he, like others before, calls "anti-cements," *i.e.*, those capable of impeding the carburization of definite zones of steel objects subjected to cementation, and on the phenomena of brittleness and deformation which manifest themselves in pieces subjected to cementation.

Among the investigations on the cementation of steel published during the following year (1907), we must mention a work of Braune, which appeared in the *Bihang till Jernkontorets Annaler;*[1] a summary of this (to which alone I can refer) is published in *Stahl und Eisen.*[2]

The interesting researches of Braune on the influence of the nitrogen contained in steel on its mechanical properties are well known.

In the memoir with which we are now dealing, he reports the results of a series of investigations on the absorption of nitrogen by iron subjected to cementation, and on the effect of this absorption on the mechanical properties of the cemented steel.

A series of cementations, carried out under various conditions of temperature and of time, with various cements (wood charcoal, animal charcoal, etc.), revealed an absorption of nitrogen by the steel subjected to cementation, in amounts varying with the conditions under which the cementation is effected and with variations in the nature of the cement used. Braune's experiments do not yet seem, however, to indicate with accuracy the relations which exist between the phenomenon of nitrogen absorption and the special mechanical properties acquired by the steel subjected to cementation.

Two memoirs on the surface cementation of steel were presented at the meeting of the Iron and Steel Institute[3] held in Vienna in September of the same year (1907).

The first, by C. Shaw Scott, does not contain new experimental data worthy of note. In it the author repeats (for example, on the intervention of nitrogen in the process of cementation) many of the observations and remarks made by other experimenters and contained in the publications summarized in the preceding pages. Further, his experiments can give no exact information, since they were carried out with a cement (carbonized leather) of very indefinite chemical composition.

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[1] 1907, No. 3, pp. 191–204.

[2] 1907, pp. 1395–1398.

[3] *Journal of the Iron and Steel Institute*, 1907, pp. 120–136.

The second memoir is by C. O. Bannister and W. J. Lambert.[1] This contains the results of a series of cementation tests made with a cement designated by the name of "Red Scintilla," but the composition of which is not given. The authors report also, but not very clearly, the results of the micrographic examination made both on cemented and quenched specimens of steel, and on specimens cemented and allowed to cool slowly. These last observations are a repetition of those of Bruch, which I have already summarized and commented upon.[2]

The micrographic observations on the cemented and hardened specimens led the authors to considerations of very doubtful value on the relations existing between the areas occupied by the pearlite before and by the martensite after the hardening.

The authors also made measurements of the depth of cementation, but for this (if we except one case in which they made four carbon determinations), instead of making use of microscopic examination and chemical analysis, they preferred to use the file, attempting to determine with this the hardness of the successive layers of the cemented cylinders exposed by removing, by means of an emery wheel, definite quantities of steel in coaxial cylindrical zones. We shall see later (in the second part of this volume) how inexact may be the results obtained in such a way.

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[1] *Journal of the Iron and Steel Institute*, 1907, pp. 114–119.

[2] See p. 65 *et seq.*