700° C., at which a true cementation does not take place because iron-iron carbide mixed crystals can not be formed. We can, therefore, in a first approximate examination of the course of the phenomena in the experiments cited above, limit ourselves to a consideration of the diagram consisting of the first five curves.

Since in the experiments which I have cited we always started with gaseous systems rich in carbon dioxide, working in the presence of wood charcoal (to which form of carbon Curve 5 of our diagram is meant to refer), therefore, in the case in which variations in temperature do not take place and the formation of metastable states is assumed to be excluded, the only regions of the diagram which we must take into account would be those situated to the left and below Curve 5. We will begin by examining this case.

From the diagram we see clearly how the course of the process varies radically with variation in the pressure, and in the following way:

(*a*) At pressures above those corresponding to the point *O*[1] (intersection of the Curves 4 and 5) there are formed simultaneously ferro-ferric oxide and mixed crystals Σ, in the presence of the wood charcoal.

(*b*) At pressures between that corresponding to this point *O* and that corresponding to the point *Q* (intersection of the Curves 3 and 5) there are formed simultaneously ferrous oxide and mixed crystals Σ, still in the presence of the wood charcoal.

(*c*) At pressures lower than that corresponding to the point *Q*, there are formed only mixed crystals Σ, still in the presence of the wood charcoal.

It is therefore only for pressures lower than that corresponding to the point *Q* that the process of cementation with the "mixed cement" can take place alone, without being accompanied by the oxidation of the metal. On this basis it must be foreseen that, by sufficiently raising the pressure of the gas in the cementation with the mixed cement, there must be obtained, even with pure iron or ordinary carbon steel, phenomena analogous to those observed by Charpy for chrome steels.

This is fully confirmed by Experiments I, II, III and IV (Table I). For the first two of these the pressure (15 kg. per sq. cm.) is lower than the pressure corresponding to the equilibrium point *Q* (for the temperature at which the cementation is carried out); while for the other two the pressure (25 kg. per sq. cm.) has a value higher than that which the ordinate of *Q* assumes at the temperature chosen for the experiment (900°–1000° C.).

In the first two experiments, therefore, the process of cementation alone takes place; while in the other two the process of cementation (formation of mixed crystals Σ) is accompanied by a strong surface oxidation of the metal.

The state of the cemented and oxidized steel cylinders merits closer examination. The cylinder cemented in Experiment 3 is covered with a compact layer of oxide about 0.7 mm. thick, in which have remained solidly fixed the pieces of granular carbon which were in contact with the surface of the metal. The metal lying beneath the oxide is intensely carburized.

This combination of facts, which on first superficial examination might appear bizarre and contradictory but which, on the contrary, are explained perfectly by the principles which I have developed, is illustrated by the three accompanying photographs (see Figs. 64, 65, and 66).

FIG. 64.

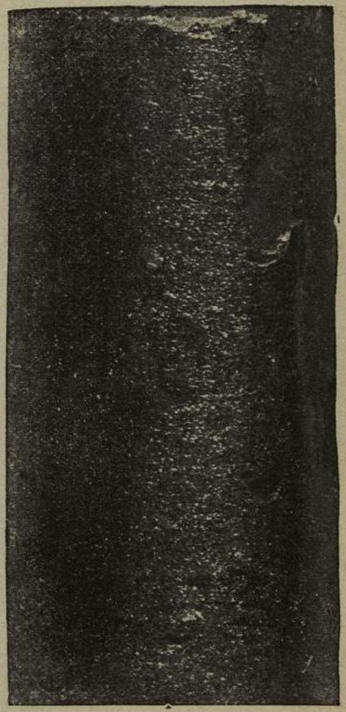

FIG. 65.

The first two photographs reproduce (enlargement 4 and 4.5 diameters, respectively) the external appearance of two regions of the cemented and oxidized cylinder; in the first are seen the fragments of carbon fixed in the iron oxide; in the second the thickness of the layer of oxide appears clearly, in the zone in which it has been broken so that the part removed has left exposed the metal lying beneath.

The third photograph reproduces (enlargement 65 diameters) a section normal to the axis of the cylinder of the steel lying directly below the layer of oxide; the appearance of this section (polished and etched with a 5% alco-

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[1] It must be remembered that in the experiments cited here the pressure is kept constant during the whole operation by the entrance of fresh gas into the apparatus. For, if the quantity of gas were limited, it is well known that the initial minimum pressure of the carbon dioxide at which the ferro-ferric oxide is formed would be lower than the pressure corresponding to the point *O*.

holic solution of picric acid) shows that the steel is cemented and that the concentration of the carbon reaches, near the external surface of the cemented zone, about 0.85%.

The examination of the material composing the external zone, easily detachable from the cylinder, showed that it was ferro-ferric oxide (Fe_3O_4) mixed with a small quantity of carbon.[1]

The position of the two invariable equilibrium points *O* and *Q*, the significance of which we have just seen, varies with variation in the temperature and in the composition of the steel subjected to the cementation. Let us examine briefly the course of these variations.[2]

As regards the variations in the two equilibrium pressures due to variation in the temperature, let us note that the three curves 3, 4 and 5 of Fig. 63 are all displaced toward the right when the temperature rises, so that the variations in the ordinates of the points *O* and *Q* depend on the relations between these displacements. These relations vary with the composition of the steel, but in general they are such that the ordinates of the points *O* and *Q* (minimum pressures for each of the two degrees of oxidation) increase when the temperature rises.


FIG. 66.

It follows from this that the higher the temperature of cementation the higher the pressure above which the oxidation which accompanies the process of cementation begins to manifest itself, in its two degrees. In other words, the higher the temperature the wider is the range in pressures within which the cementation can be carried out with the certainty that the oxidation of the metal will not be produced.

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[1] While it is easy to separate the iron oxide from the larger pieces of wood charcoal, it is not possible to separate it completely from the pulverulent carbon which is always mixed with it.

[2] From the practical point of view, the only one of these two points which presents interest is the lower one (*Q*), because this corresponds to the minimum pressure at which the oxidation of the metal to *ferrous oxide* (FeO) begins to manifest itself. The second point (*O*) corresponds simply to a change of the "*degree of oxidation*" of the metal, in the sense that at pressures higher than that corresponding to it the stable oxide is no longer the ferrous oxide FeO but the ferro-ferric oxide Fe_3O_4. It seems now, from the practical point of view, that this change is not of much importance.

A comparison of the results of the experiments already cited, taken two by two from those carried out with the same steels, confirms this assertion.[1]

The same fact is shown very clearly by the following experiment:

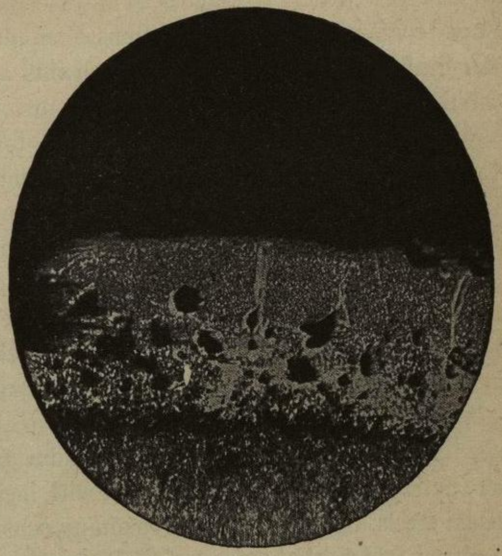
FIG. 67.

A cylinder of ordinary soft steel 60 cm. long and 1 cm. in diameter was subjected to cementation for about three hours in the usual apparatus and with the usual mixed cement, under a pressure of 15 kg. per sq. cm., care being taken to surround it completely, along its whole length, with granular carbon. The temperature, kept constant between 980° and 1035° C. for a zone of about 20 cm. near the central part of the cylinder, decreases gradually (owing to the way in which the apparatus which I have described is constructed) toward its ends until it reaches at the ends about 500° C.

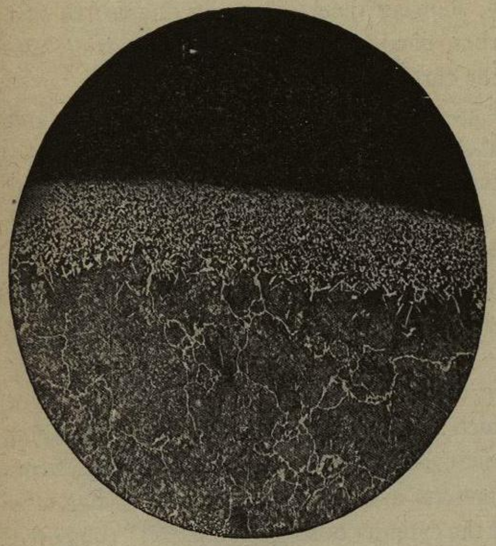
FIG. 68.

The surface of the cylinder thus treated, which is distinctly cemented throughout all the portion in which the temperature has exceeded 800° C., is perfectly unchanged in the central, hottest part (which is also the most intensely cemented), while it is covered, in the parts heated to a lower temperature, with the characteristic layer of compact oxide, in which are fixed the fragments of carbon. Beneath the layer of oxide the steel is still cemented in all parts in which the temperature has exceeded 750–800° C.

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[1] Thus, for example, compare the results of Experiments VII and VIII, and note that in the latter the velocity of the gaseous current is double that in the former.

The two equilibrium pressures vary also, as I have already said, with variation in the composition of the steel subjected to the cementation. Since in this case the curve 5 undergoes no displacement whatever, because it must always correspond to the conditions of equilibrium of the gaseous mixture with the wood charcoal, the displacements of the points *O* and *Q* will be determined exclusively by the displacements of the two straight lines 3 and 4 of Fig. 63.

Now, it is known that these two straight lines are displaced farther toward the left the more chemically inactive the metal subjected to the action of the gaseous mixture. And, since the displacement of the lines 3 and 4 carries with it the raising of the points *O* and *Q*, it follows that the more inactive the metal used the wider is the range of pressures (lower than that corresponding to the point *Q*) within which the cementation can be carried out with the certainty of not producing oxidation of the metal.

Among the metals which frequently form alloys with iron, forming mixed crystals with it, are manganese, chromium and nickel. The first two are more active metals than iron, so that with increase in their concentration in special steels, the temperature remaining constant, the two pressures *O* and *Q*, above which the cementation is necessarily accompanied successively by the two degrees of oxidation of the metal, gradually become lower. For chromium steels a relatively low chromium content (about 2–3%) is sufficient for these pressures to become (for not too high temperatures) less than ordinary atmospheric pressure. This explains the results of the investigations of Charpy (*loc. cit.*), showing them not to be due to the fact that the gaseous mixture of carbon dioxide and of carbon monoxide acts "separately on the iron and on the chromium."

Nickel, alloyed with steel, has an effect opposite to that of chromium and manganese, imparting to the solid solution with the iron, of which it forms a part, the characters of a metal less active than pure iron, so that the higher the nickel content of the steel subjected to the cementation the higher are the pressures which can be reached with the "mixed cement" without the oxidation of the metal manifesting itself.

All these deductions are fully confirmed by the results of the experiments reported in Table I.[1]

For the special steels, therefore, the phenomena with which we are dealing show effects analogous to those which I have described for the ordinary carbon steels. Thus, for example, the micrograph reproduced in Fig. 67 represents (with an enlargement of 185 diameters) a portion of the external edge of a plane section normal to the axis of the cylinder of the steel "Cr-Ni" cemented in Experiment XXIV.[2] Here, too, the cemented metal is covered with a layer of oxide in which are fixed particles of carbon.

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[1] Compare, for example, Experiment VI with XVIII, XI with XV, XVI with XXIV, etc.

[2] Etched with a 5% alcoholic solution of picric acid.

Figs. 68 and 69 (made under the same conditions as the preceding, with an enlargement of 65 diameters, after having removed the layer of oxide adhering to the cylinder) show the intense cementation which the chrome steels of Experiments XVIII and XX have undergone, although at the same time, as already observed in Table I, they have been strongly oxidized.

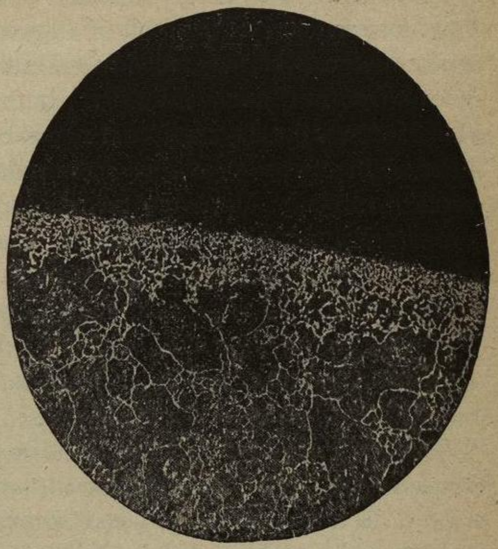

FIG. 69.

The same facts are observed in the nickel steels when working under pressures sufficiently high to produce the oxidation of the metal. This is clearly shown by the micrograph, Fig. 70 (Experiment VII), made under the usual conditions, enlargement of 65 diameters.

It is therefore evident that the course of the cementation of the special steels with the "mixed cement" having carbon monoxide as base is subject to the same rules which govern this process for the carbon steels. The differences for the various steels are, as we have seen, only "*quantitative*," both as regards the pressures of oxidation and as regards the concentrations of the carbon in the mixed crystals in equilibrium (along the curve 5) with the gaseous mixture ($CO + CO_2$), which, in its turn, is in equilibrium with the wood charcoal.

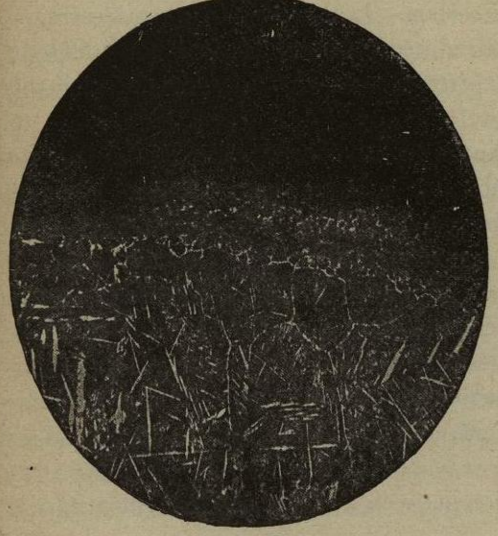

FIG. 70.

All the principles thus developed are valid as long as phenomena of metastable equilibrium do not manifest themselves, and on condition that the temperature remains constant during each cementation.

Now, both conditions are very difficult to realize experimentally, and it can be said that they are almost never realized in industrial practice. This leads to the possibility that in one or more of the phases of the cementation the point representing the system in which the reactions are effected may fall in a field of the diagram in which stable equilibrium has not been reached. Thus, for example, as the result of a lowering of the temperature, the said representative point may fall in the field situated to the right of or above the curve 5 (see the diagram of Fig. 63). In this case reactions other than those which we have thus far considered may take place; for example, the decomposition of the carbon monoxide, accompanied by the separation of free pulverulent carbon.[1] Moreover, the representative point may meet one of the two curves 1 and 2, which in their turn undergo wide displacements as the result of the variations in the temperature. In this last case the reactions which may take place are much more complex.

Before leaving this subject I wish to remark that many useful practical rules for the cementation of special steels with the mixed cement may be drawn from the information just given.

Thus, the cementation of steels of a rather high chromium content, over 4 or 5%, with the mixed cement at temperatures not higher than 1000° C., is accompanied by a marked oxidation of the metal, even when working under ordinary atmospheric pressure. But, the considerations developed in the preceding pages suggest immediately means of avoiding this oxidation; it suffices, in fact, to reduce the pressure of the gaseous carburizing mixture ($CO + CO_2$) below the minimum pressure of oxidation, Q, peculiar to the alloy at the temperature used. This can be obtained in many cases by simply diluting with air the carbon dioxide which circulates through the mass of the granular carbon. In this way the gaseous carburizing mixture acts under a partial reduced pressure, because it is "diluted" with the nitrogen of the air. Experiment confirms fully the efficacy of this method.

Finally, I shall close this chapter by citing some experimental data not referring to methods usually employed in the *normal* practice of industrial cementation, but which serve to clear up facts which sometimes present themselves accidentally in such practice, and which may occasionally also find useful technical application. The first series of these data[2] comprises the phenomena of abnormal increase in the concentration of the carbon in the cemented zones due to the formation of free cementite. I will shortly show that the occurrence of these phenomena, where under ordinary conditions the formation of free cementite can not take place, is due to the oscillations of temperature of cementation.

Exact knowledge of the relation between formation of free cementite and variation of temperature during the cementation, while it indicates the cause of the abnormal increases sometimes found in the concentration of the carbon in the cemented zones, also furnishes a means for carrying out the heating during the cementation in such a way as to purposely cause, with certainty, the formation of free cementite when it is desired to obtain cemented zones capable of taking an exceedingly high degree of hardness by quenching without its being necessary that their brittleness be reduced to a minimum.

The phenomenon of the formation of free cementite in the processes of the direct carburization of iron in the solid state constituted for a long time one of the most important arguments[1] cited against the hypothesis of the metastability of cementite, but more recently[2] it has been recognized, on the contrary, to constitute an argument rather in favor of than against this hypothesis. An explanation had already been proposed, by Osmond[3] and Charpy,[4] and more recently and in more complete manner by Benedicks, which attributed the formation of free cementite to the oscillations in the temperature which inevitably manifest themselves during industrial cementation. Their conclusions were not founded on any *direct* experimental datum; more recent experimental studies, to which I shall now refer, have confirmed the fundamental fact assumed by those experimenters, but have shown that the "mechanism" of the phenomenon is markedly different from that imagined by them.

We have already seen how a series of cementations, carried out with cements whose activity is due to the specific action of carbon monoxide, have established with certainty the maximum values which the concentration of the carbon can reach when working under definite conditions at a constant temperature. It is clear how this result, never before attained, constitutes a sure point of departure for verifying experimentally the theory of the formation of the cementite just enunciated. It suffices, in fact, to establish a combination of conditions such that, carrying out the cementation at any *constant* temperature within a definite range, it would be quite certain (on the basis of the experimental and theoretical principles to which I have just referred) that the maximum concentration of the carbon in the cemented zones thus obtained could not exceed a given value, and especially that free primary cementite could not be formed. Given this, it is sufficient to carry out a cementation under conditions identical with the preceding but at *variable* temperatures, oscillating within *the above definite interval*, and thus find out whether in this last case the maximum concentration of the carbon in the cemented zone reaches values higher than those obtained in the pre-

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[1] The appearance of this new form of free carbon produces in its turn a displacement of the curve 5.

[2] See F. Giolitti and G. Scavi, *Sulla formazione della cementite* (*La Metallurgia Italiana*, September, 1911).

[1] See, for example, Bakhuis Roozeboom, *Journ. of the Iron and Steel Institute*, 1904, I, p. 257.

[2] See especially Carl Benedicks, *Ueber das Gleichgewicht und die Erstarrungsstrukturen des Systems Eisen-Kohlenstoff* (*Metallurgie*, Vol. 3, 1906, Nos. 12–14).

[3] *The Journal of the Iron and Steel Institute*, 1897, II, p. 143.

[4] *Comptes Rendus de l'Académie des Sciences*, 1903, 1st sem., Vol. CXXXVI, p. 1000.

ceding cementations at constant temperature, and whether free cementite is formed in this zone. If this last case is verified, it is clear that the formation of the cementite is due only to the oscillations of the temperature, and the hypothesis supported successively by Osmond, Charpy and Benedicks would have to be considered as confirmed experimentally.

The hypothetical explanation proposed by Benedicks to represent the details of the "mechanism" of the phenomenon with which we are dealing would also then be considered as probably correct.

This was proved by the experiments now to be reported:

The cementations were carried out with the usual apparatus already described in detail in the preceding pages,[1] using as carburizing substance pure carbon monoxide (supplied continuously at 1 liter per hour per square decimeter of the surface of the steel subjected to cementation) in the presence of a "granular" mass of wood charcoal, freed from ashes by washing with hydrochloric acid and placed in contact with the surface of the steel.

The cementation material was soft steel of the following composition:

Carbon	0.12 percent.
Manganese	0.36 percent.
Silicon	0.03 percent.
Sulphur	0.01 percent.
Phosphorus	0.016 percent.

Numerous experiments reported in the preceding pages show with entire certainty that when carrying out the cementation under the conditions just indicated the maximum concentration of the carbon in the cemented zones never exceeds 0.9%, and that not the smallest trace of free primary cementite is formed in these zones when working for a period not longer than six hours at any temperature between 900° and 1100° C. which is *kept constant during the whole cementation.*

Assuming this, we will now give the results of cementations carried out[2] under the conditions indicated above but *making the temperature oscillate* within the limits just indicated. In order to define in the best way the course of the thermal treatment for every experiment without digressing into minute descriptions, I give for every operation a heating diagram with abscissas proportional to the time (length of heating) and ordinates proportional to the corresponding temperatures.

These various diagrams are collected in Fig. 71.

I. Cementation of three hours at temperatures oscillating between 900° and 1000°, as indicated in Diagram I.

In the cemented zone examined under the microscope appear no traces

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[1] See p. 115.

[2] See F. Giolitti and G. Scavia, *Sulla formazione della cementite* (*La Metallurgia Italiana*, September, 1911).

of primary cementite, but only a eutectic zone 0.45 mm. thick and a hypo-eutectic zone in which the concentration of the carbon falls to 0.2% in an interval of 0.25 mm.

II. Cementation of three hours at temperatures oscillating between 1000° and 1100° C., as indicated in Diagram II.

In the cemented zone observed under the microscope appears an external hyper-eutectic layer 0.4 mm. thick containing primary cementite in proportion corresponding to about 1.1% of carbon, a value confirmed by a gravimetric analysis. This layer is followed by a eutectic layer about 0.7 mm. thick, and finally by a hypo-eutectic layer in which the concentration of the carbon falls to 0.3% in an interval of about 0.65 mm.

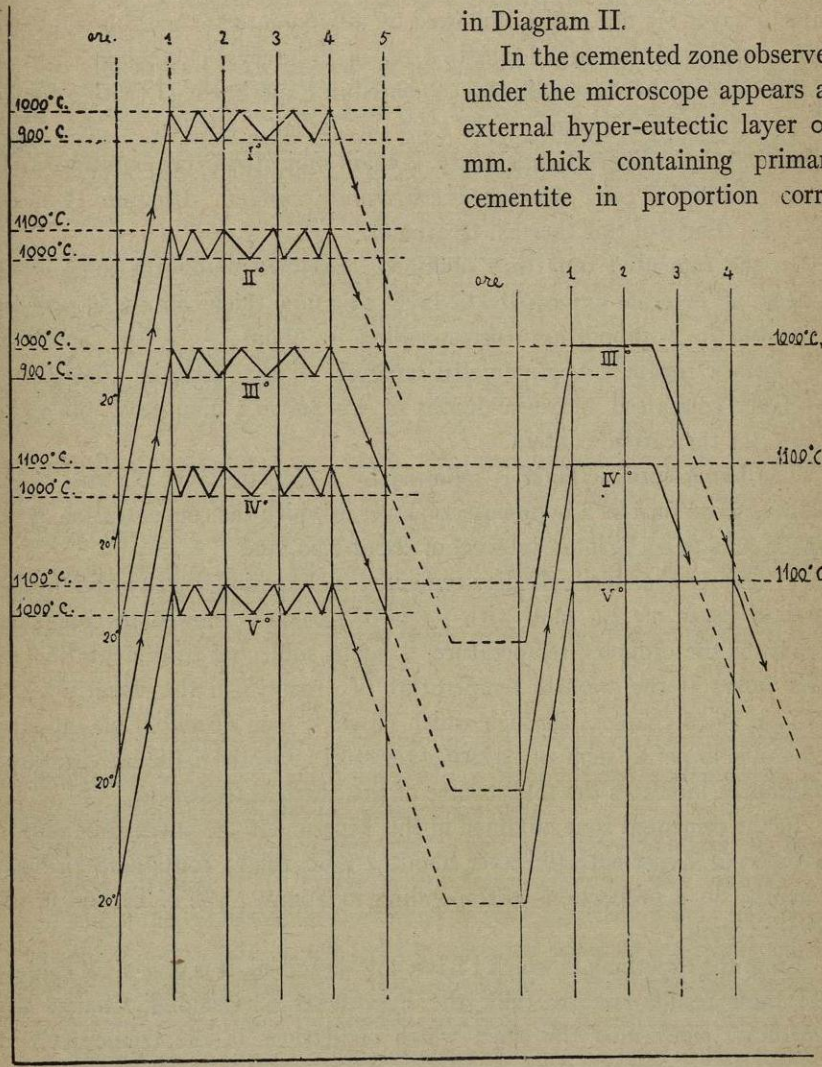

FIG. 71.

III. One of the steel cylinders cemented in Experiment I (free from primary cementite), allowed to cool completely to the ordinary temperature, is again subjected to cementation for one hour and a half at 1000° C., *keeping the temperature constant*. Diagram III shows the total course of this thermal treatment.

In the cemented zone thus obtained, examined under the microscope, no traces of primary cementite appear. The zone is formed of an external eutectic layer 0.5 mm. thick, followed by a hypo-eutectic layer in which the concentration of the carbon falls to 0.2% in an interval of 0.7 mm.

IV. One of the steel cylinders cemented in Experiment II (with a hyper-eutectic layer of 0.4 mm. with 1.1% of carbon), allowed to cool completely to the ordinary temperature, is again subjected to cementation for an hour and a half at 1100°, *keeping the temperature constant*. Diagram IV shows the total course of this thermal treatment.

In the cemented zone thus obtained, examined under the microscope, appears an external hyper-eutectic layer 0.95 mm. thick containing primary cementite in a proportion corresponding to about 1.5% of carbon in the surface region. A gravimetric analysis of the material constituting the layer comprised between depths of 0.2 and 0.3 mm. gave the value 1.46% for the carbon content.

The hyper-eutectic layer is followed by a eutectic layer 0.4 mm. thick, followed in its turn by a hypo-eutectic layer in which the concentration of the carbon falls to 0.3% in an interval of about 0.60 mm.

V. One of the steel cylinders cemented in Experiment II (with a hyper-eutectic layer of 0.4 mm. with 1.1% of carbon), allowed to cool completely to the ordinary temperature, is again subjected to cementation for three hours at the *constant* temperature of 1100° C. in the usual mass of granular wood charcoal through which passes *a slow current of air* (about 2 liters an hour per sq. dcm. of surface of the steel subjected to the cementation). Diagram V indicates the total course of this thermal treatment.

In the cemented zone obtained in this experiment the microscope reveals an external hyper-eutectic layer about 2 mm. thick, containing primary cementite in a proportion corresponding to about 1.4% of carbon in the surface region.

From the experiments which I have now described, it is first of all evident that these results confirm fully the hypotheses of Osmond, Charpy and Benedicks, concerning the effect which oscillations in the temperature of cementation exercise in the formation of primary cementite.

The exactness of this assertion is seen from the results of Experiments II, IV and V. In these, in fact, is shown abundant formation of primary cementite, under conditions where the earlier investigations[1] have excluded the possibility of such formation taking place when carried out at constant temperature.

We can, however, see that an accurate examination of the results of these experiments leads to modifying and completing in various parts the hypotheses of Osmond, Charpy and Benedicks. We will, therefore, subject these results to still further discussion.

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[1] See p. 135.

First, a comparison of the results of Experiments III, IV and V at once shows the effect which the presence of pre-existing quantities of primary cementite, formed during a period of cooling, exercises on the further formation of cementite. In this effect there is certainly to be seen the phenomenon of the difference between the velocity of the solution of cementite in γ-iron and the velocity with which carbon passes into solution in iron by cementation. This is exactly the phenomenon to which Benedicks attributed in greater part the large increase in the concentration of the carbon and the abundant formation of cementite at oscillating temperatures.

In Experiment III, in which the cemented zone obtained in the first phase of the operation does not contain the hyper-eutectic layer, all the iron carbide liberated as the result of the cooling preceding the second phase is in the secondary state (lamellæ of pearlite); that is, in the form best adapted to making it rapidly soluble in the iron as soon as this reaches, as the result of the succeeding heating, the "γ" state. In this case, therefore, the phenomenon indicated by Benedicks (to which we have just referred) can not be produced. This our Experiment III most clearly confirms, for in its second phase (cementation of one hour and thirty minutes at 1000° C.) the concentration of the carbon has not increased in the least.

This confirmation is still clearer when we take into account the results of Experiments IV and V, in which the cementation is carried out similarly to that of Experiment III, but in such a way that by cooling between its two phases there is formed in the cemented zone a certain quantity of primary cementite, which is more slowly soluble in the γ-iron formed during the second period of heating than is the secondary cementite.

Now, in this case there is manifested in the second period a large increase in the concentration of the carbon of the cemented zone, even when in the second phase the cementation is effected under conditions which, in normal "continuous" procedure, would furnish cemented zones of a carbon concentration *lower* than that reached in the first phase. This is especially evident in Experiment V, in which the second period of the operation is carried out under conditions in which other experiments[1] have shown "continuous" cementation to furnish carburized zones containing a maximum of about 0.7–0.8% of carbon. These phenomena are explained clearly by the hypothesis of Benedicks.

But, on the contrary, this same hypothesis no longer suffices to explain

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[1] See the note already cited, and especially F. Giolitti and G. Scavia, *Sull'impiego dei forni a muffole orizzontali per la cementazione dell'acciaio con cementi misti* (*La Metallurgia Italiana*, August, 1911, pp. 332–348). See also the second part of the present volume.

the differences between the results furnished by Experiments I and II as regards the concentration of the carbon and the formation of the primary cementite in the cemented zones.

In the first place, we can exclude *a priori* the supposition that the increase in the concentration of the carbon in the cemented zone obtained in Experiment II, up to the formation of a hyper-eutectic layer in the cooled specimen, can be due to a process analogous to that indicated by Benedicks—for the minimum of the oscillating temperatures is quite distant from the maximum temperature at which primary cementite separates in a carbon steel with 1.1% of carbon.

In the second place, if the cause of the formation of the cementite were exclusively that indicated by Benedicks, this same formation should manifest itself with greater intensity in Experiment I, in which the minimum of the oscillating temperature of cementation is considerably nearer than that of the following experiment to the maximum temperature at which primary cementite can begin to separate.

A plausible explanation of the phenomenon to which I have just referred, and, in general, of the increase which the oscillating temperatures exercise on the carbon of the cemented zones (even when the minimum temperature reached in these oscillations is kept distant from the maximum values at which the separation of the primary cementite from its solid solution in γ-iron can be manifested) is furnished by an accurate consideration of the equilibrium of the systems constituted by iron, carbon, cementite, the mixed iron-carbon crystals, carbon monoxide, carbon dioxide, and the oxides of iron.

The equilibrium isotherms of the various systems formed of the components mentioned above, in groupings corresponding to the reactions which can take place, have been studied recently with great care by Schenck, mostly on the basis of the experimental investigations carried out by himself and his students.

It would lead too far to review here in detail the conclusions of Schenck; I shall assume, therefore, that his results are known.[1]

Among all the cubical hyperbolas (a_1, a_2, etc., see Fig. 72) of the form

$$\frac{x^2}{1-x}\,P = K$$

(in which, as is well known, x represents the concentration of the carbon monoxide in the gaseous phase, P the total pressure of this gaseous phase, and K an equilibrium constant) which, for a definite and constant temperature, represent, for various values of K, the conditions of equilibrium of the gaseous phase with mixed crystals of various concentrations, one presents to us a special interest. When the operation is carried out in the presence of a large excess of wood charcoal, the constant K has the same value that the equilibrium constant of the system CO_2, CO, C (wood charcoal) assumes at the same temperature.

This curve (which coincides throughout its whole length with the corresponding equilibrium isotherm of the system *wood charcoal*, CO, CO_2) *fixes*, in fact, the maximum concentration which the carbon can reach in the cemented zone when the cementation is carried out in the way we have indicated at a definite temperature *kept constant during the whole operation.*

Now, it is known that any variation in the temperature produces a displacement of all these curves a_1, a_2, etc. (Fig. 72). An increase in the temperature produces a displacement of these curves toward the right, while a decrease displaces the curves toward the left. It is clear that any relative retardation in the variations of concentrations of the mixed crystals and gaseous phase gives rise to states of *false equilibrium*, protracted for a more or less extended period of time according to the amount of retardation and the duration of the variations in the temperature. When, then, many opposite variations in the temperature alternate with each other, the final state of the system can be independent of these states of false equilibrium only when the retardations occur to an identical extent in two opposite directions. When this identity is absent, these retardations, caused by the oscillations in temperature, will markedly influence the final state of the system.

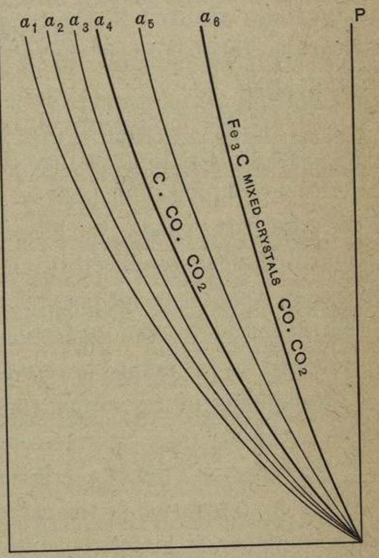

FIG. 72.

The phenomenon is in this latter case perfectly analogous to that considered by Benedicks in the separation of the cementite from the saturated mixed crystals.

To fix our ideas: as the result of a lowering in the temperature, the pencil of curves a_1, a_2, etc., is displaced toward the left, so that the point representing the composition of the gaseous phase will fall for a certain time (the length of which depends on the retardation in the establishment of equilibrium between the gaseous phase and the mixed crystals, by the separation of free carbon from the gaseous mixture) on one of the curves a_1, a_2, etc., corresponding to a carbon concentration greater than that of the curve a_4, on which it first lay.[1] It is possible that for a certain brief time this point may reach

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[1] Rudolf Schenck, *Chimie physique des métaux.* Translated by M. Lallement, Paris, Dunod and Pinat, 1911.

[1] The variations in the temperature produce displacements of the equilibrium curve of the system C, CO, CO_2 concordant with those of the curves of equilibrium of the gaseous

and pass the last curve to the right of the pencil, corresponding to equilibrium with free cementite. If, now, in the succeeding rise in the temperature, during which the representative point of the system will fall temporarily on one of the curves a_1, a_2, etc. (corresponding to a concentration of the carbon of the mixed crystals lower than the initial concentration a_4), the retardation in reaching complete equilibrium with the free carbon (wood charcoal) is less than that manifested in the preceding phase, the local increase in the concentration of the carbon (and the final formation of cementite) occurring in the preceding period will not be compensated. The effect of the oscillation in temperature will therefore be an increase in the concentration of the carbon above the value corresponding to the conditions of equilibrium which would have been realized if the temperature had remained constant.[1] It is also clear that these effects of the successive oscillations in the temperature may be cumulative.

In fact, the mechanism of the phenomena which we have just set forth is identical to that proposed by Benedicks, except that our study of the phenomena of equilibrium between the gaseous phase, the mixed crystals, and the cementite explains the increases in the concentration of the carbon in the cemented zones produced by the oscillations in temperature. Even in the cases in which it is not possible to admit that the separation of the primary cementite, due to the saturation of the mass of the mixed crystals, can be produced by a simple lowering of the temperature below the point Ar_1 corresponding to the normal concentration of carbon for a cementation carried out under these definite conditions, the explanation still holds.

The effect of a definite series of oscillations in the cementation temperature on the concentration of the carbon in the cemented zone depends on such a large number of factors, so uncertain and imperfectly unkown, as to make predictions in this field practically impossible. Among these factors are: the velocity of the dissociation of carbon monoxide mixed with carbon dioxide, while lowering the temperature; the velocity of the diffusion of the gases into the iron at the various temperatures; the velocity of the reaction of the carbon of the mixed crystals upon the mixtures of carbon dioxide and carbon monoxide at the various concentrations and at the various temperatures, etc. The differences between these factors easily explain the differing results of Experiments I and II.

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phase with the iron-carbon mixed crystals. The experiments which I have cited in the preceding pages seem to show that at the various temperatures comprised between 850° and 1200° C. the first curve practically coincides with the curve of equilibrium of the gaseous phase with mixed crystals with 0.9% of carbon. This is under such conditions of approximately complete equilibrium as can be realized in the practice of cementation.

[1] I recall here that the mixed crystals whose concentrations correspond to curves of the pencil of hyperbolas lying to the *right* of the curve a_4 (see Fig. 72) are those for which further cementation can not be effected directly by the action of the carbon, but *only* by means of carbon monoxide.

The experimental data just reported and the principles which I have developed may find useful practical applications where it is desired to obtain free cementite along with an increase in the carbon content of the cemented zones above that normally obtained with a given cement, and this without modifying the chemical nature of the cement used.

It follows that the thermal treatment suitable for obtaining this result consists in an interruption of the cementation, accompanied by quick cooling of the piece being subjected to carburization.

This operation is difficult, and not practicable where the cementation is effected with solid cements in ordinary cementation boxes. It becomes easy, however, when the cementation is carried out with gaseous or mixed cements, working in apparatus specially adapted for their use.

The second group of experimental data are of an essentially theoretical interest, directly confirming the correctness of the principles set forth in the preceding pages concerning the mechanism of the carburizing action of carbon monoxide, alone or in the presence of other carburizing substances. These same data may some day find useful practical applications.

A detailed account of the experimental facts in question may be found in a paper published in *Rassegna Mineraria, Metallurgica e Chimica*, 1910, Vol. XXXIII, under the title "*Sulla fabbricazione della ghisa malleabile*," Paper III. By F. Giolitti, F. Carnevali and G. Tavanti. These facts may be briefly summarized as follows:

If the cementation of an ordinary soft carbon steel is effected with a mixed solid-gaseous cement, in which the solid constituent is composed (instead of the usual wood charcoal) of turnings of a carbon steel of definite carbon content, and the carburizing gas consists of the usual mixture of carbon monoxide with small quantities of carbon dioxide, it is observed that the maximum concentration of the carbon in the cemented zones remains equal to the carbon concentration of the carbon in the steel turnings used, instead of reaching the 0.9% which is obtained normally with granular wood charcoal as the solid constituent of the cement.

These observations confirm the theory which I have developed, according to which the carbon monoxide (and its mixtures with carbon dioxide which are formed as the result of its carburizing action) intervenes in the cementation, when the mixed cements are used, essentially by acting as a vehicle, transporting the carbon from the carburizing medium proper (solid, liquid or gaseous) to the soft steel which it is desired to cement, until the concentration of the carbon in the cemented zone reaches a value such that it is exactly in equilibrium with that mixture of carbon monoxide and carbon dioxide which is in equilibrium with the carburizing agent under the given conditions. This last condition is strikingly realized when the cementation of the steel stops at the concentration of the carbon in the steel acting as carburizer, even when the two steels are not in direct contact.

In these examples, the specific action of the gaseous carburizing mixtures (to which *alone* the equilibrium phenomena observed can be referred) is so evident that it is no longer possible to doubt the very great preponderance of the *direct* action of the carburizing gas in comparison with the direct action of the carbon in contact with the steel or which may be deposited on the surface of the steel as the result of the decomposition of the gas.

The principles which I have developed also allow an explanation of some older observations already referred to. Thus, for example, we easily see the weakness of Mannesmann's reasoning which I have cited on p. 18, based on the alleged absurdity of admitting that the same gas contained in a crucible can on the one hand remove the carbon from the cast iron to yield it on the other to the steel. It is, in fact, quite understandable that a given mixture of carbon monoxide and carbon dioxide should act as an oxidizer on the carbon of the iron-carbon mixed crystals of high carbon content (of the cast iron) and as a carburizer on the mixed crystals of lower carbon content (soft steel). I have already reported the results of experiments which realize very simply and surely just the process considered as absurd by Mannesmann, producing, simultaneously and in the same operation, the decarbonizing of a cast iron and the cementation of a steel.

The same principles explain in a very simple way the phenomenon observed by Forquignon, of the refining of a cast iron ignited in carbon powder, and "therefore subjected to the same treatment which gives rise to the carburization of steel." In fact, my own direct experiments show that certain types of cast irons can be decarburized easily by gaseous mixtures with carbon monoxide as base which are in equilibrium with free carbon.

Finally, I wish to mention the results of some experiments which, on account of their essentially practical interest,[1] I shall examine more in detail in the second part of this volume.

These experiments show that when the cementation with mixtures of carbon monoxide and carbon dioxide in chemical equilibrium with free carbon (for example, with wood charcoal) is carried out under the usual experimental conditions which I have indicated, diluting the gaseous carburizing mixture with nitrogen, there are obtained cemented zones in which the maximum concentration of the carbon is less than that which would be obtained by working under identical conditions but without diluting the gaseous mixture. I shall consider in a subsequent chapter the theoretical and practical importance of this fact.

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[1] F. Giolitti and G. Scavia, *Sull'impiego dei forni a muffole orizzontali nella cementazione dell'acciaio coi cementi misti* (*La Metallurgia Italiana*, August, 1911).

CHAPTER V

THE PRESENT STATE OF THE THEORY OF THE PROCESS OF CEMENTATION[1]

The simple setting forth in the preceding chapters of the theoretical conclusions resulting from the experimental investigations carried out to determine the nature of the process of cementation define the actual state of our knowledge on this subject. It does not, however, seem to me useless to further summarize and briefly classify this knowledge, and to show how the inconclusive and at times apparently contradictory results of the first experimental investigations are clearly explained by results of more recent investigations. This will place still better in evidence the real value of the most recent studies, showing that the experimental foundation of the new theories is considerably more extensive than that on which they were directly constructed.

One of the questions which has been discussed at greatest length and with the greatest interest is the part played in the process of cementation by the various carburizing gases, especially as compared with the *direct* action of the free carbon. And here, it seems to me, one of the prinicipal causes of the discordance of opinions must be sought in the fact that in many cases the various experimenters set themselves, in reality, quite different problems, which could not admit of a common solution. It is easy to see this by examining, for example, the experimental data discussed by Ledebur and by Guillet in their polemic, which I reviewed at length in the preceding pages. Thus, for example, Guillet, among other things, proposed to show that pure carbon, *in the absence of the smallest trace of gas*, can not cement iron, but he admitted explicitly that in industrial practice the carbon monoxide produced by the oxygen of the air contained in the cementation boxes on the carbon of the cement may give rise to a cementation, though "very slow." Now, given this premise, it can not but cause surprise to see Ledebur oppose to Guillet, in proof of the possibility of producing the cementation directly with solid carbon without the intervention of any gas, experiments carried out without the least precaution for eliminating from the medium in which the cementation is effected precisely that gas (air) to which Guillet had, at least partially, attributed the cementation. This fact, otherwise inexplicable, is easily

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[1] The contents of this chapter have already been published in part in a note which appeared in September, 1911, in the *Rassegna Mineraria, Metallurgica e Chimica*. In the present compilation, however, have been added various considerations relative to many researches carried out since that time.