the steel possessing a different structure or "grain." Thus in Fig. 30, which represents another surface of fracture of the same drill, the variation of the "grain" is visible at the upper edge of the surface of fracture, by chance so obtained as to avoid exfoliation.

FIG. 31.

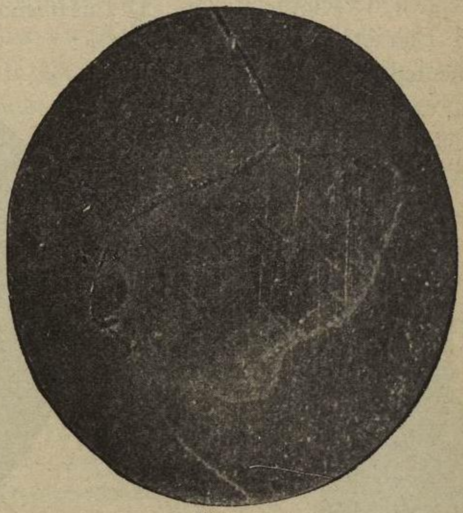

FIG. 33.

FIG. 32.

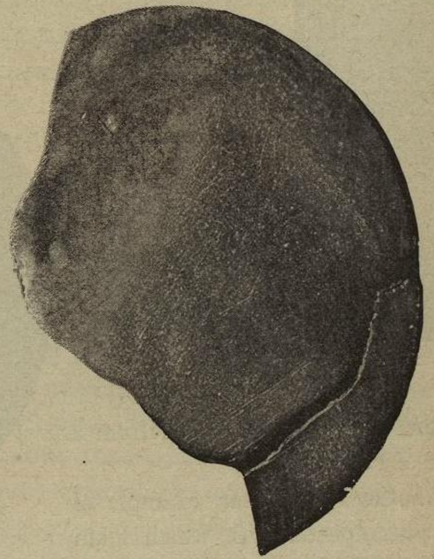

FIG. 34.

Since it is known that steels of different composition, hardened under identical conditions, show surfaces of fracture characterized by different structure or "grain" it was quite natural to suppose that the exfoliation of steels cemented and subjected to a homogeneous hardening would correspond with sudden variations in the composition of the steel. A more accurate study of the phenomenon has fully confirmed this hypothesis, showing that sudden variations in the composition of the steel are certainly the cause of the exfoliation of the cemented steels, and that the variations in composition producing these effects are sudden variations in the concentration of the carbon.

The conclusions thus briefly summarized are the result of a large number of observations, lasting through several years, on cemented pieces which had "exfoliated" in service.

In making observations, the metallographic examination of the pieces studied has been of valuable, if not indispensable, assistance. For example in Figs. 31 and 32 are reproduced (about natural size) two fragments of cemented and quenched soft steel, the axle of the rear wheel of a bicycle. The appearance of the fracture of this piece, broken in service, is exactly characteristic of the "exfoliation" of steels cemented and hardened homogeneously.

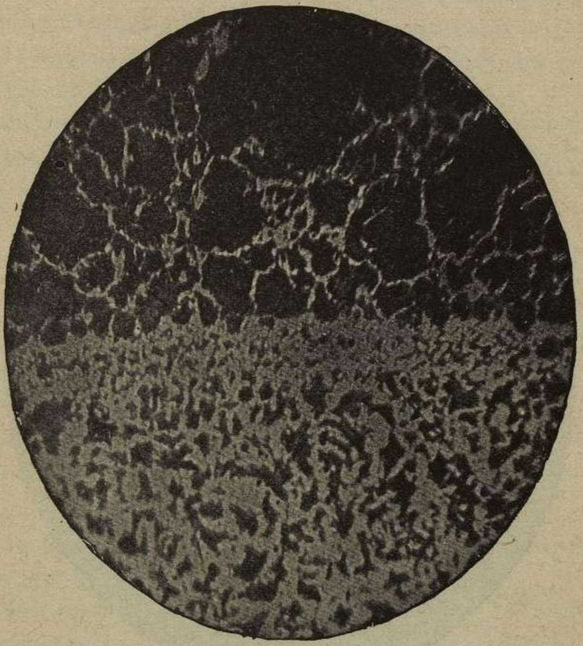

FIG. 35.

Fig. 33 reproduces, with an enlargement of 3.7 diameters, the plane section, normal to the axis of the cylinder, constituting the lower base of the fragment reproduced in Fig. 31. This section was made after having heated the cylinder of steel for about one hour at 900° out of contact with the air; it was polished with chromium oxide and etched with a 5% alcoholic solution of picric acid. In the photograph it is seen clearly that the surface of fracture corresponds to a surface along which the structure of the steel varies suddenly. The same fact comes out even more clearly in Fig. 34, which reproduces (with an enlargement of 3.7 diameters) the section, made and prepared in a manner analogous to the preceding, which forms the upper base of the piece reproduced in Fig. 32.

In both sections, the variation in the structure is especially evident at the points to which the fracture has not yet extended, and at these points it is easy to recognize that the line of separation between the zones of different structure is but the continuation of the line of fracture.

The two figures, 35 and 36, represent with a greater enlargement (60 diameters) two short stretches of the line of demarcation between the two zones of different structure of the section reproduced in Fig. 33. The first reproduces a part of this line to which the fracture has not yet extended, while the second reproduces a part in which the fracture has already begun. In both micrographs, the proportion between the areas occupied by the pearlite and by the ferrite, respectively, shows that the sudden variation in the structure of the steel which manifests itself along the surface of fracture corresponds to a sudden variation in the concentration of the carbon. In the special case to which I am now referring, the concentration changes rapidly across the surface of fracture, from 0.6–0.7% (toward the periphery) to less than 0.2% (toward the nucleus of the cemented piece).[1]

Fig. 36.

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[1] For greater details on the characteristic structures of the micrographs just reproduced, see F. Giolitti and G. Tavanti, *Ricerche sulla fabbricazione dell'acciaio cementato*, VII (*Atti della R. Accademia delle Scienze di Torino*, 1910).

Since, as already stated, I have observed similar coincidences in a large number of cases between the surfaces of exfoliation and the surfaces corresponding to sudden variations in the concentration of the carbon in the cemented zones, the importance of a more precise study of these variations in concentration by gravimetric analyses of the successive layers of these zones was evident.

The analyses of layers 0.5 to 1 mm. thick could not furnish sufficiently precise data, for they could indicate only the *mean* composition of layers in each of which the concentration of the carbon often varied *discontinuously* from the exterior toward the interior; this follows clearly from the data collected in the tables of pages 78–81. Thus, for example, the eutectic zone has a thickness ranging from 0.1 to 0.3 mm., so that it is certain that by taking for the analyses layers 0.5 mm. thick, material of adjacent zones was included in the analysis. *Not one* of the layers analyzed gave the value of constant carbon concentration (0.9%) characteristic of this zone. To be able to establish on the "concentration-depth" diagrams the important discontinuity, characterized by a horizontal portion corresponding to the composition of the eutectic zone joined more or less abruptly with the steeply inclined arms of the curve corresponding to the adjacent hypo-eutectic and hyper-eutectic zones, it is evidently necessary that *two or more* of the layers analyzed should fall entirely within the eutectic zone.

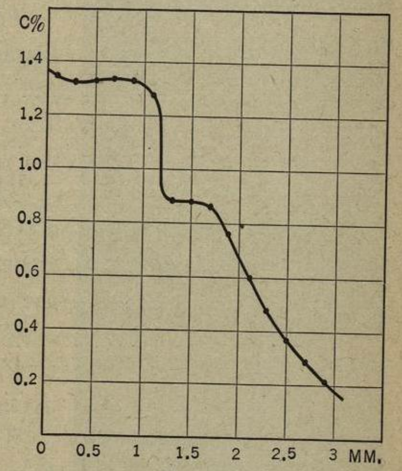

Fig. 37.

It is clear, therefore, that the curves which I have reproduced above can not show with sufficient distinctness the discontinuities characteristic of the cemented zones. For this it is necessary to analyze successive layers of these zones not thicker than 0.1–0.2 mm.

A first series of carbon gravimetric determinations, made on the material obtained from successive layers (0.2 mm. thick) of a cemented zone obtained by carburizing a cylinder of soft steel (0.08% of carbon) for four hours at 1050° C., and then allowing it to cool very slowly, showed at once the phenomena of discontinuity. The results of these analyses, which I communicated in a preliminary paper presented before the Chemical Society of Rome in 1908, are collected in the manner which I have already explained in the "concentration-depth" diagram reproduced in Fig. 37.

It is easy to see how this diagram confirms fully the results of the microscopical examination. To become convinced of this, examine the micrographs Fig. 26 (cementation five hours at 1000° C. with ethylene, followed by slow

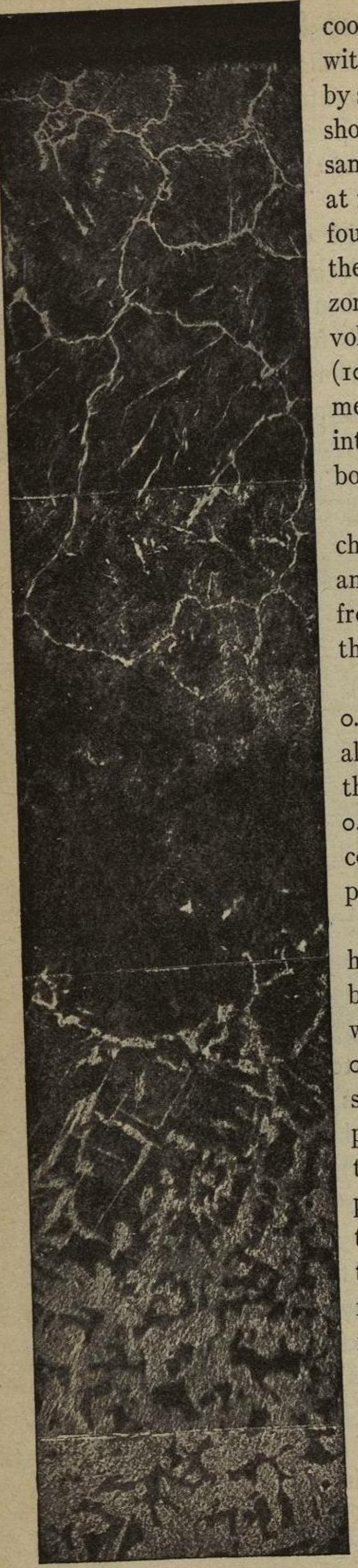

Fig. 38.

cooling), Fig. 18 (cementation seven hours with acetylene at 1050° C., likewise followed by slow cooling) and Fig. 38. This last figure shows a cemented zone obtained under the same conditions as that of Fig. 37 (ethylene at 1050° C.) but during five hours instead of four. From the micrographs as well as from the diagram it is evident that the carburized zones obtained by cementing soft steel with volatile hydrocarbons at a high temperature (1000–1100° C.) and then allowing the cemented pieces to cool slowly, are subdivided into three strata characterized by their carbon content and by their microstructure.

The first layer, clearly hyper-eutectic, is characterized by the presence of cementite and pearlite; in it the carbon content varies from 1.27% to 1.33%, markedly higher than the value for pearlite (0.9%).

The second layer, generally less than 0.5–0.6 mm. thick, is formed of pearlite alone; in it, therefore, the concentration of the carbon is uniform and equal to about 0.9%. This layer appears clearly in Fig. 37, corresponding to the intermediate horizontal portion of the "concentration-depth" curve.

This second layer is followed by a third, a hypo-eutectic layer, characterized, therefore, by the presence of pearlite and ferrite, in which the carbon content (always less than 0.9%) diminishes at first rapidly, then more slowly, toward the interior of the cemented piece. The sudden variations in the concentration of the carbon in the layers of the passage between the hyper-eutectic zone and the eutectic zone and between the latter and the hypo-eutectic zone are evident either from the micrographs (Figs. 18, 26 and 38) or from the diagram, Fig. 37. Thus, referring to the diagram, in which the values of the concentration of the carbon are shown with greater precision, we see that the carbon content at first remains almost constant for a thickness of more than a millimeter, oscillating only between 1.27 and 1.33%, then falls from 1.27 to 0.88% in the space of a quarter of a millimeter, then again remaining almost absolutely constant between 0.88% and 0.86% in the eutectic zone, more than half a millimeter thick, and diminishes rapidly from 0.86% to 0.61% in the successive four tenths of a millimeter.

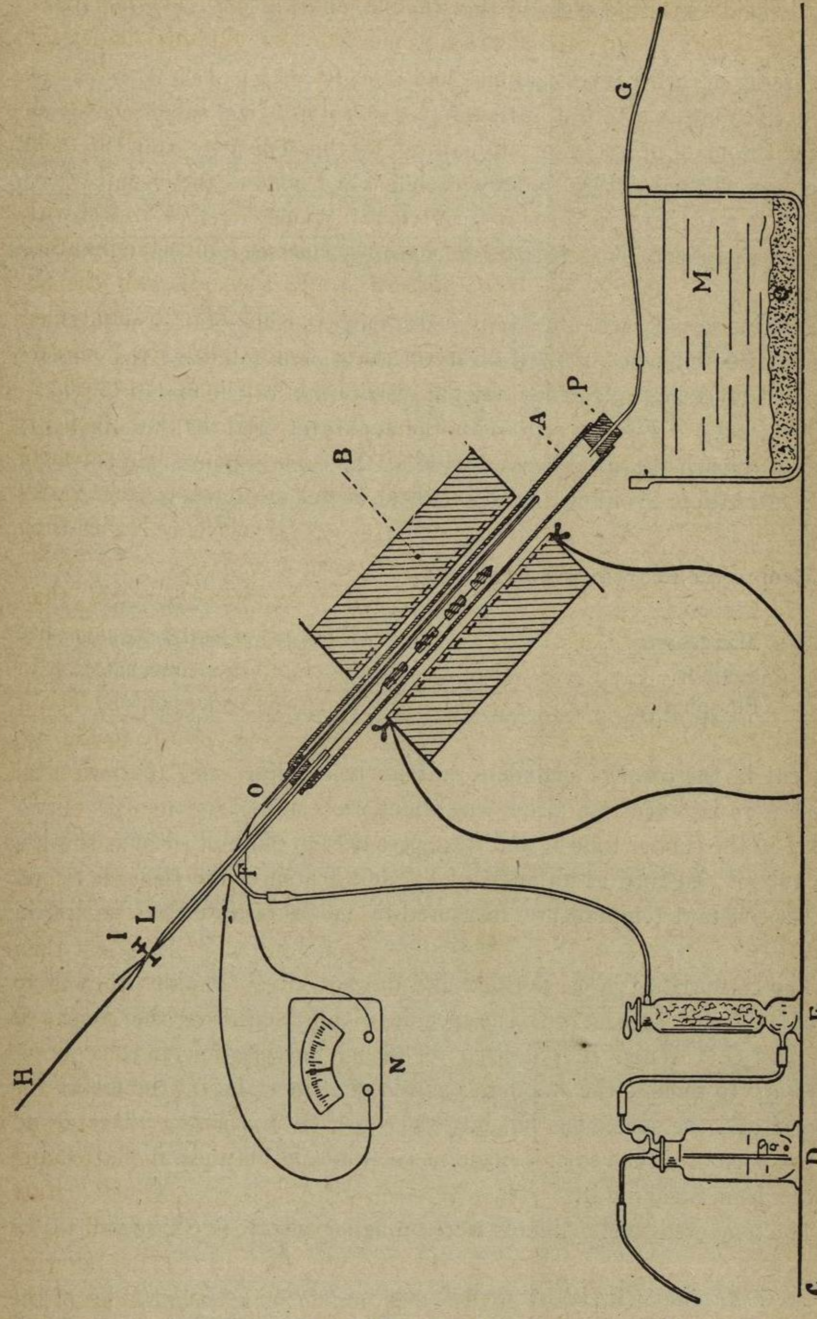

Fig. 39.

There are thus established accurately the phenomena of discontinuity in the "distribution" of the carbon in the cemented zones, to which, as I have already said, experiment shows that the "exfoliation" of cemented steels is due.

A series of earlier investigations[1] had already led me to explain some analogous phenomena manifesting themselves in cast iron (malleableized castings) by the theory of processes of "liquation" of the cementite and the ferrite, which are effected during the slow cooling which follows the chemical treatment. It was therefore quite natural that I should attempt to determine whether the phenomena observed in cemented steel are not due to the same cause.

Positive results were obtained by studying, in collaboration with Doctor Tavanti, the influence of the velocity of the cooling following the cementation and preceding quenching, on the distribution of the carbon in the cemented zones.[2] Fig. 39 represents the apparatus used for these investigations to quench the specimens of steel at the same temperature as that of the cementation, avoiding any slow cooling before the quenching.

Steel of the following composition:

Carbon	0.26 percent.
Manganese	0.54 percent.
Sulphur	0.02 percent.
Phosphorus	0.02 percent.

was cut in the form of cylinders 10 mm. in diameter and 100 mm. long. These were fastened to a nickel wire which was clamped by the screw pinchcock *I* in the rubber tube *L*, and thus were held in place in the glazed porcelain tube *A*, inclined at an angle of 45° and heated in the Heraeus furnace *B* at a constant temperature, measured by means of an electric pyrometer *OFN*.

The carburizing gases, purified and dried in *C*, *D*, *E*, pass through the tube *A*, come in contact with the specimens to be cemented, and issue from the tube *G*. When it is desired to quench the specimens, it is merely necessary to remove the stopper *P* and loosen the clamp *I*; the nickel wire is freed and the specimens fall into the vessel *M* containing water at 12°. On the bottom of the vessel is placed a layer of sand to prevent the cylinders of steel from breaking it.

The tempered steel cylinders were brought back for five minutes to 700°, out of contact with the air;[1] then, after they had been straightened, and adjusted in the lathe, co-axial layers 0.1 mm. thick were removed, and the carbon in them determined by combustion.

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[1] See F. Giolitti, *Sulla fabbricazione della ghisa malleabile*, I (*Rend. della Società Chimica di Roma*, 1908); and F. Giolitti, F. Carnevali and G. Gherardi, *Id.*, Note II (*Atti della R. Accademia dei Lincei*).

[2] F. Giolitti and G. Tavanti, *Ricerche sulla fabbricazione dell' acciaio cementato*, III (*Gazzetta Chim. Italiana*, 1909).

Seven such experiments of cementation and quenching were carried out under different conditions, especially as regards the relations between the temperature of cementation and that of the corresponding quenching and, therefore, the extent and length of the slow cooling following the cementation and preceding the quenching, as is indicated in the following table:

Number	Gas used as cement	Length of cementation (hours)	Temperature of cementation	Length slow cooling following cement. and preceding quenching (min.)	Extent of interval of cooling	Temperature of quenching in water at 12° (degr. C.)	Volume of carburizing gas used (liters)
1	Ethylene	4	1000° C.	32	250° C.	750°	6.6
2	Ethylene	4	1000°	0	0	1000°	6.25
3	Ethylene(*a*)	1	1000°	15	200°	800°	3.0
4	Ethylene	4	800°	0	0	800°	6.25
5	Mixture of CO with 3.1% of ethylene.	4	1000°	22	250°	750°	6.25
6	Mixture of CO with 3.1% of ethylene.	4	1000°	0	0	1000°	6.0
7	Mixture of CO with 3.1% of ethylene.	4	800°	0	0	800°	6.25

(*a*) The steel used in this 3rd experiment contained only 0.04% of carbon.

The results of these experiments are represented graphically, in the manner already explained, in the seven "concentration-depth" diagrams reproduced herewith (Figs. 40–46).

Since a very large number of earlier experiments (some of which I have in part summarized[2]) have shown that the variation in the concentration of the carbon in the cemented zones obtained by the action of gaseous hydrocarbons such as ethylene is analogous to that which is observed in the cemented zones obtained by means of the solid cements usually employed in practice, containing organic substances and cyanides, we can apply to the study of the phenomena of exfoliation which manifest themselves in practice the deductions drawn from the results of the first four of the experiments just given.

The examination of the first diagram (Fig. 40), representing the variations in the concentration of the carbon as functions of the depth in the specimen cemented with ethylene at 1000° and quenched at 750° after having slowly cooled to this temperature, shows directly a characteristic

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[1] In the original memoir (through a typographical error) the temperature of heating is given as 900° instead of 700° C.

[2] See Giolitti and Carnevali, *Ricerche sulla fabbricazione dell'acciaio cementato*, II (*Gazz. Chim. Italiana*, 1908, Part II).

phenomenon which differentiates clearly the cemented zone obtained by this treatment from that which is obtained when, all the other conditions remaining equal, the cemented specimen is quenched at the same temperature as that at which the cementation was effected.

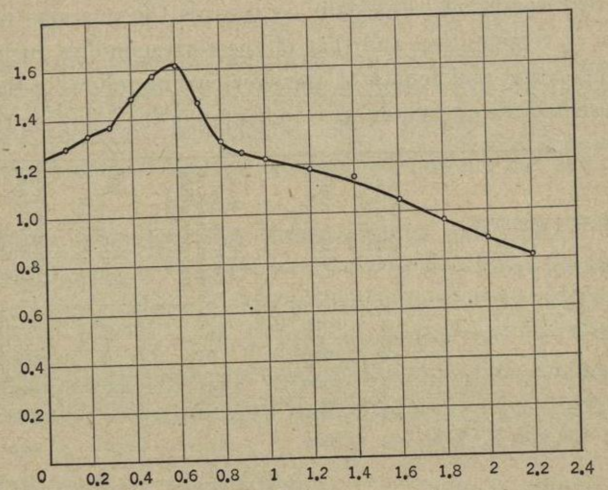

FIG. 40.

Comparing the diagram of Fig. 40 with that of Fig. 41, we see that while in the latter the concentration of the carbon *decreases* continuously and uniformly as we proceed from the surface toward the axis of the cemented

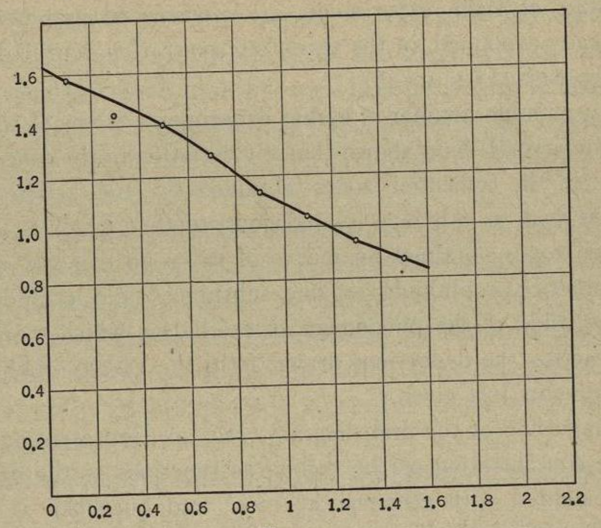

FIG. 41.

cylinder, in the first (proceeding in the same direction) the concentration, on the contrary, increases at first until it reaches a maximum at a depth of 0.6 mm., and then diminishes rapidly up to a depth of 0.8 mm., then decreasing considerably more slowly, so that in the whole succeeding interval of 1.4 mm. the concentration varies only between 1.2% and 0.81%.

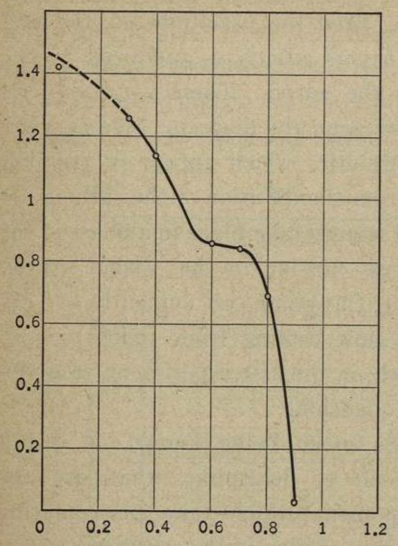

FIG. 42.

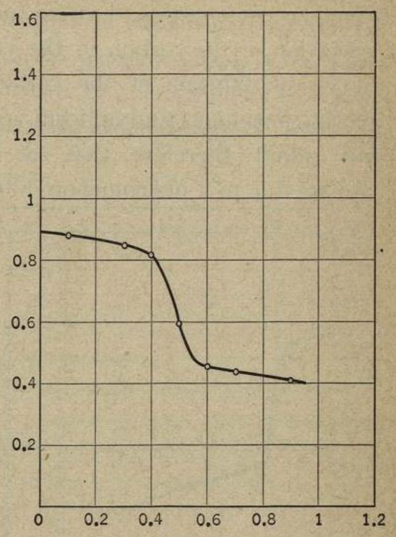

FIG. 43.

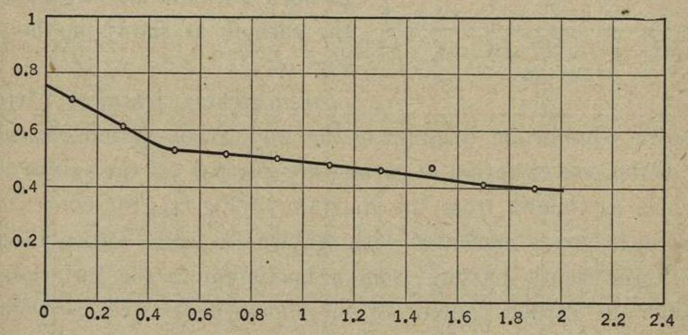

FIG. 44.

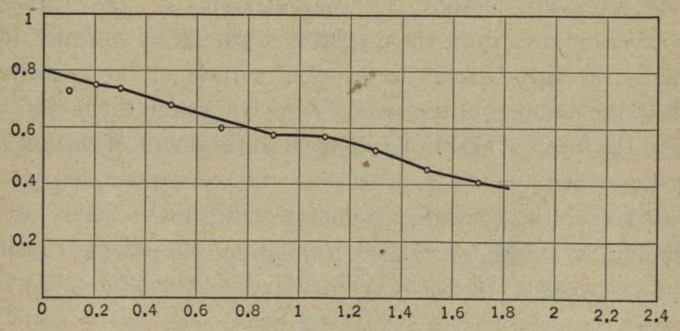

FIG. 45.

We evidently can not admit that this discontinuity in the concentration of the carbon can be due to the essentially *continuous* phenomenon of the diffusion of this carbon. Moreover, this discontinuity was not produced in the second experiment (Fig. 41), in which the cementation was carried out under identical conditions and in which the quenching at 1000° immediately after the cementation, has, so to speak, fixed the variations in the concentration of the carbon in the various layers exactly as produced by the process of diffusion of the carbon into the γ-iron. These variations are clearly continuous and uniform, as follows from the diagram, Fig. 41. We must admit, therefore, that the discontinuities which appear in the first case are due to a phenomenon different from the diffusion of the carbon and that it must take place in a phase of the process missing in the second experiment; this phase can evidently be only the slow cooling from 1000° to 750° which, in the first experiment, precedes the quenching.

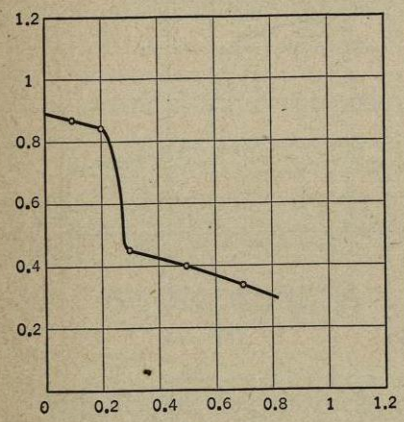

FIG. 46.

So much being known, it is not difficult to determine what are the phenomena which take place during the slow cooling of the cemented pieces, giving rise to the special distribution of the carbon, as shown in the diagram, Fig. 40.

For greater clearness, I refer to the well-known equilibrium diagram of the iron-carbon system, on which the values of the concentration of carbon are plotted on the axis of abscissas. And since, as follows from the diagram of Fig. 41, the concentration of the carbon in pieces cemented with ethylene at 1000° varies about inversely with the depth, passing from a maximum in the surface layer to a minimum (the carbon content of the homogeneous steel used) in the extreme internal limit of the cemented zone, we can make use of the abscissas to represent, besides the concentrations of the carbon in the various layers of the steel, the distances of the layers to which these concentrations correspond from the external surface of the cemented piece, noting that the numbers of the second series will run in the inverse direction to those of the first. Thus, in Experiment 2, the points of the line *AB* (Fig. 47)[1] corresponding to 1.63% of carbon will correspond also to the external surface of the cemented cylinder, while those of the vertical *PQ*, corresponding to 0.26% of carbon (content of the original homogeneous steel) will correspond also to the deepest layer to which the cementation has extended.

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[1] In the figure the relations of the segments representing the concentrations have been altered, so as not to render the figure too disproportionate. Thus, for example, the straight line *AB* should be more toward the right. The figure would correspond, therefore, to a shorter cementation.

The points of the verticals intermediate between these two will represent (at the various temperatures) the successive layers of the cemented zone and the corresponding concentrations of the carbon. All this holds as long as the continuity in the variations of the concentration of the carbon between the successive layers subsists; that is, as long as the temperature is, in the whole cemented zone, higher than the values represented by the points of the curves *CE* and *EN*, corresponding to the crystallization of ferrite and of cementite, respectively.

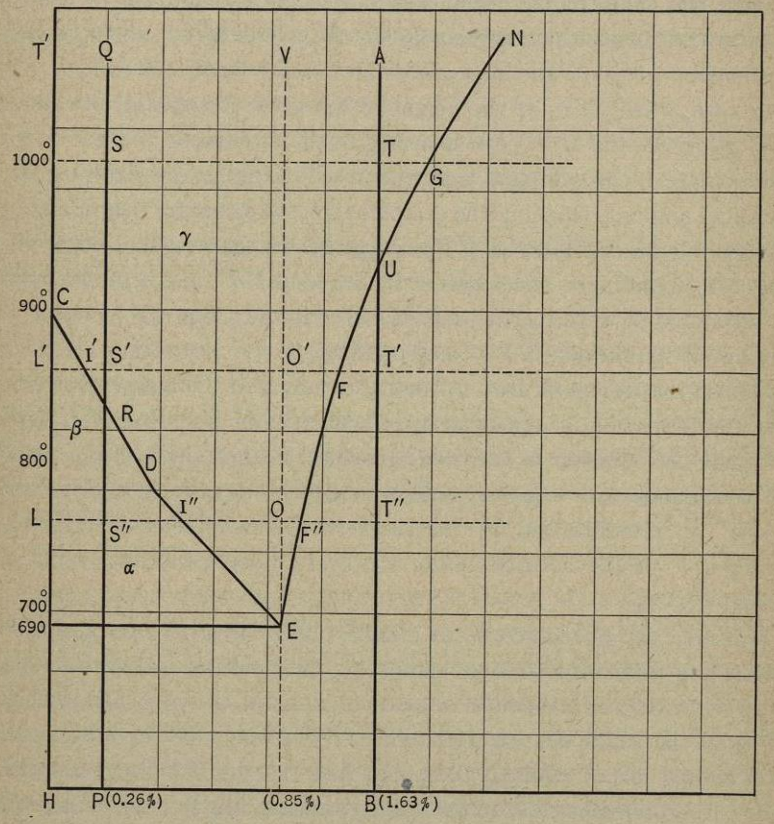

FIG. 47.

What happens when the temperature slowly falls below these limits, that is, below the point corresponding to the intersection of at least one of the two verticals *AB* or *PQ* with the corresponding crystallization curve *EN* and *CE*?

Referring to the case of our first and second experiments the analysis of the successive layers of the specimen quenched at 1000° (Experiment 2) shows us (Fig. 41) that for the cementation carried out with ethylene at 1000° we can apply the method of graphical representation just noted, so that the points of the segment of the line *ST* will represent the concentrations of the carbon and the corresponding depths of the various layers of the cemented zone as long as the temperature remains at 1000°. If, now, we cool the specimen very quickly, we shall "fix," so to speak, this state of affairs; this, precisely, manifests itself in the second experiment. Let us, on the contrary, allow the cylinder to cool very slowly; the representative segment ST will then fall parallel to itself in the diagram until first its extreme points and then the points contiguous to these intersect, successively, one of the two crystallization curves CE or EN, or both. (In the case represented by our drawing, the first curve intersected by the horizontal segment is EN.)

From this moment the formation of crystals of ferrite or of cementite begins in the layers which correspond to the points of ST which at any instant happen to fall on the intersection of ST with either CE or EN. Thus, in our case, when ST is at the height of the point U, crystals of cementite begin to form in the layer corresponding to the abscissa of U (that is, in the exterior layer of the cylinder); and when the cooling has proceeded a further very small amount, reaching the temperature, for example, corresponding to the value of the ordinates of $S'T'$, cementite will have separated in all the layers corresponding to the points of the segment $F'T'$, and in all these layers the concentration of the carbon still dissolved in the γ-iron will have the value represented by the point F', corresponding to the saturation of the solid solution at that temperature. A further lowering of the temperature should cause the formation of new crystals of cementite in F'. However, while at this point the solution is still homogeneous, in the points of the segment $F'T'$ contiguous to it exist crystals of cementite already formed, acting as "germs" of crystallization, so that the new crystals of cementite, instead of forming in F' proper, form at points which are more toward the right of the segment $F'T'$.

And since this phenomenon can manifest itself along EN during the whole slow cooling from 1000° to 690° (point E), there results an "accumulation" of the cementite, and therefore a great increase in the concentration of the carbon, at the points nearest to the line AB (that is, in the external layers of the cemented piece), while at the points near the line EV the concentration of the carbon remains close to the value corresponding to the abscissa of this line (0.85%), this being the value toward which the concentrations of the successive points F', F'', etc., tend.

The same remarks can be made on the separation of the ferrite, which, beginning to crystallize at the points at which ST successively intersects the curve CDE, "accumulates" at the points near the line PQ, greatly diminishing there (and hence at the deeper points of the cemented zone) the concentration of the carbon.

Granted this, it is clear that when the cooling is very slow, so as to make as complete as possible this kind of "liquation" which gives rise to the accumulation of the cementite at the external edge of the cemented zone and of the ferrite in its deeper layers, and when the cooling is extended below the point E (690°), there must be a great increase (as compared with the values of the diagram of Fig. 41, which represents the distribution of the carbon at 1000°) in the concentration of the carbon in a zone near the line AB and to the left of this, a great decrease in the concentration of the carbon in a zone near PQ, but to its right, and, finally, a zone around EV in which the carbon has a concentration resulting from the absence of the ferrite and of the cementite (accumulating to left and right, respectively), that is, the concentration of the eutectic pearlite, equal to 0.85%, abscissa of the point E.

This is precisely the distribution of the carbon which we have seen characterizes the carburized zones obtained by cementing soft steels with volatile hydrocarbons (ethylene, acetylene, etc.), and letting the cemented pieces cool slowly to ordinary temperature.

I have given most evident examples of this in the preceding pages, such as those which correspond to the micrographs reproduced in Figs. 18, 26 and 38 and to the diagram of Fig. 37.

When, on the contrary, the specimen is not allowed to cool slowly to ordinary temperature but is quenched in cold water at a temperature higher than 690°, a somewhat different distribution of the carbon is obtained.

Thus, for example, by cementing at 1000° and quenching at 750° (as in our first experiment), instead of the central zone of constant concentration (0.85% C), we shall have a zone corresponding to the segment $I''F''$ (Fig. 47), in which the concentration of the carbon must still diminish about as in the corresponding zone of the specimen cemented and quenched at 1000° (Experiment 2). This is because the points of the segment $I''F''$ have not intersected, in the slow cooling, the crystallization curves CE and EN. This distribution of the carbon appears most clearly in the specimen obtained in the first experiment; in fact, from the diagram (Fig. 40) is to be seen the great increase (as compared with the diagram of Fig. 41) of the concentration of the carbon in the external regions of the cemented zone, due to the accumulation of the cementite in these regions. In the succeeding region (between 1 mm. and 2.2 mm. in depth, corresponding to the segment $I''F''$) the concentration of the carbon varies considerably more slowly.

In the first experiment the cementation had extended too near to the axis of the steel cylinder to make it possible to remove on the lathe the deeper layers of the cemented zones.

The third experiment, carried out under conditions analogous to the preceding but limiting the length of the cementation to one hour, allows a study of these deeper layers. In the diagram obtained from the analyses of the successive layers of this specimen (see Fig. 42), the accumulation of the cementite in the external layers naturally appears less evident, on account of the greater thinness of the cemented zone, but on the other hand the sudden decrease in the concentration of the carbon in the last and deepest layers of the cemented zone (between 0.8 and 0.9 mm. in depth), which could not be shown in the preceding case, is now seen very clearly; a decrease due (according to what I have just explained) to an "accumulation" of the ferrite toward the "nucleus" of the specimen.

Let us see, now, how we can explain the irregular concentration of the carbon in the fourth experiment (see diagram, Fig. 43). Here we evidently can not attribute the sudden decrease in the concentration of the carbon which manifests itself in the intermediate layers of the cemented zone to phenomena of liquation, because the quenching was carried out at the same temperature as the cementation (800°), and was not preceded by any slow cooling during which liquation could have been produced. The explanation of the phenomenon must, on the contrary, be sought in the fact that the cementation was carried out at a relatively low temperature, and at a temperature during which, noting the initial concentration of the carbon in the specimen subjected to the cementation, the iron of this specimen was still present in the state of β-iron.

A phenomenon entirely analogous, though less marked, is observed in the "concentration-depth" diagrams of the experiments which I have reported on pp. 73 and 74, carried out on a large scale with solid cements at relatively low temperatures (850°–880° C.).

It follows clearly, from the 1st, 2nd and 3rd diagrams of Fig. 21 on p. 75 (which refer to these experiments) that the curve which represents the concentration of the carbon as a function of the depth of the analyzed layers presents at first a portion slightly inclined toward the horizontal, then a portion in which the concentration of the carbon decreases rapidly, and finally a third portion again slightly inclined toward the horizontal. In all these cases the course of the "concentration-depth" curves is easily explained as follows:

At a temperature of 800° the iron of the bar with 0.26% of carbon is in the state of β-iron, or, according to the length of the heating during which the equalization of the concentration of the carbon in the mass of the metal is effected, has passed into the state of γ-iron in the zones containing pearlite at ordinary temperature. At any rate, the carbon dissolves in it only with great slowness. No sooner, however, has the carbon content of the first external layers of the bar increased a little as the cementation proceeds, so as to reach the value at which the iron passes from the state of β-iron into γ-iron (which is known to occur at about 800° for 0.3–0.4% of carbon), than these layers begin to cement rapidly. Thereafter the concentration of the carbon in these increases rapidly, while in the contiguous layers, in which the iron has not yet completely passed into the γ-state, the cementation proceeds with the original slowness as long as in these, too, the concentration of the carbon has not reached the value 0.3%. In this case, therefore, the cementation proceeds as follows: the concentration of the carbon in a given layer first rises very slowly up to the value 0.3–0.4%, then increasing rapidly as soon as this value is reached. Thus there must always manifest itself a large difference in the concentration of the carbon between the last layer in which it has reached the value 0.3–0.4% and has thereafter rapidly increased, and the succeeding layer, in which this value has not yet been reached. This is precisely the sudden variation in concentration which is observed in the diagram of Fig. 43.

We must therefore recognize that the causes of the sudden variations in the concentration of the carbon in the cemented zones belong to two distinct groups of phenomena. The first, which manifest themselves when intense cementation is effected at a high temperature, and the cemented pieces are allowed to cool slowly through a more or less wide interval of temperature before quenching them, consist of a true "liquation" of the cementite and of the ferrite during their segregation from the iron-carbon solid solutions. The others, which manifest themselves when the cementation is effected at temperatures below 900° or, more generally, below the point Ar_3 of the steel subjected to the cementation, are due to the varying solubility of the carbon in the three allotropic modifications of the iron.

It is easy to understand, then, why the discontinuities in the distribution of the carbon in the cemented zones are considerably less marked in very deep cemented zones than in thin ones. Thus, for discontinuities of the first class, due to the liquation of the cementite and of the ferrite, we have already seen that the pearlitic zone—their most characteristic feature—does not occupy, in general, more than 1 mm., so that it does not appear clearly if layers thicker than 0.3 mm. are analyzed; and the 5th, 6th and 7th diagrams of Fig. 21 show that this feature does not manifest itself appreciably in the "concentration-depth" curves traced on the basis of analyses of layers several millimeters thick, obtained from cemented zones deeper than 10–15 mm.

The 4th diagram (cementation of 360 hours at 850°-880°) of the same Fig. 21 shows next that the discontinuities due to the second class of phenomena (cementations carried out below 900° C.) also appear but slightly in very deep cemented zones.

The causes of the sudden variations in the concentration of the carbon in the cemented zones having been determined, it was interesting to study the ways of preventing them in order to avoid the phenomena of brittleness connected with them.

The elimination of a first series of discontinuities—those due to the liquation of the cementite—can evidently be obtained by carrying out the cementation in such a way as to avoid the formation of a hyper-eutectic layer containing free cementite. We have already seen on pp. 84–85 that this result can be obtained by carrying out the cementation with carbon monoxide mixed with definite quantities of gaseous hydrocarbons and working under definite conditions of temperature and of pressure.

Experiments 5, 6 and 7 of the table on p. 99, the results of which are reported in the diagrams of Figs. 44, 45, and 46, show the results which can be obtained in this way.

Experiment 6, in which quenching at 1000° (the temperature at which the cementation is effected) "fixes," so to speak, the distribution of the carbon due to the cementation before it is modified by other succeeding phenomena, shows how, by working under the conditions described (of temperature, of pressure and of composition of the gaseous mixture), the hyper-eutectic zone is entirely avoided. And Experiment 5 shows how, the hyper-eutectic zone being absent, the highly supercarburized layer formed in the first experiment is no longer formed during the slow cooling from 1000° to 750°, thus confirming again the correctness of the views set forth.

In Experiment 7 (cementation at 800° and quenching at the same temperature) is seen again the same sudden variation in the concentration of the carbon in the last layers of the cemented zone which manifested itself in 4, carried out under the same conditions of temperature, both as regards the cementation and the quenching.

This confirms still better what we then stated, *viz.*, that this phenomenon is due to the fact that the cementation was effected at a temperature at which the iron of the specimen was still—at least partially—in the state of β-iron.

I have already said that the coincidence of the surfaces of fracture of cemented steels with the surfaces of separation between layers of different carbon content is proved from a very large number of observations analogous to those which I have cited in the preceding pages (see pp. 90–95).[1]

But, even aside from such observations, it is easy to find a reason for this coincidence. In fact, it is known that there is a point of variation in carbon content in a hardened steel corresponding to a variation, equally sudden, of the hardness and of the other mechanical properties, and hence a point of lesser resistance to mechanical forces, due to the different mechanical properties of the two qualities of steel which meet there. The phenomenon manifests itself most acutely over the surface of junction between the eutectic zone and the hypo-eutectic zone when the concentration of the carbon in the latter falls suddenly below the minimum value necessary for the steel to "harden," which is exactly what often occurs in practice, ordinary cemented steels hardening at temperatures between 750° and 800°. In this case the eutectic zone (together with the hyper-eutectic zone) becomes hard and relatively brittle, while the hypo-eutectic zone lying beneath remains tough and easily deformable. It is easy to understand then how the first zone, forming, so to speak, a "brittle crust," sharply separated from the much more malleable nucleus lying beneath, must easily break under the action of mechanical forces which produce in the nucleus a deformation which the "crust" can not follow on account of its hardness and rigidity. The "crust" must then break and "flake off" from the nucleus, which is exactly what characterizes the phenomenon of exfoliation.

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[1] An interesting example of this coincidence of the zone of separation between the hyper-eutectic layer and the eutectic layer is cited and illustrated by a micrograph (without, however, an explanation of the cause) in the work of Bannister and Lambert to which I have already referred (*Journ. of the Iron and Steel Institute*, 1907, Vol. III, p. 117).

At the surface of junction between the hyper-eutectic zone and the eutectic zone the phenomenon of exfoliation under the action of mechanical forces is less intense, because the differences between the mechanical properties assumed as the result of the quenching of the steels constituting the two zones are not so great. In fact, both of these steels harden under the same conditions as cemented steels ; there enters into play only the different "intensities" of this hardening, due to the different carburizations of the two steels and the different variations in volume which the two differently carburized zones undergo as the result of the hardening. This last phenomenon is the cause of the well-known "internal tensions," to which "hardening cracks" are due.

In the exfoliation of the hyper-eutectic zone, however, there enters into action another cause of brittleness, consisting in the scales of cementite which, being quite thick under the conditions which prevail in practice, do not pass completely into the state of solid solution during the heating which precedes the hardening and, remaining even after the hardening in the hyper-eutectic zone, render the latter much more brittle than the eutectic zone lying beneath, which does not contain crystals of primary cementite. This is another important cause of exfoliation "by difference of concentration of carbon."[1]

Granted this, it was evident that the best proof of the correctness of all the theories set forth consisted in cementing and hardening specimens of soft steel under various conditions where the experiments reported in the preceding pages show that the phenomena of exfoliation manifest themselves; also in verifying whether these phenomena are really produced always and only under the circumstances stated. A series of experiments carried out along these lines has fully confirmed the predictions. The results are set forth in detail in the last part of the paper which I have just been considering, but it seems superfluous to me to summarize them here.

As conclusions from the observations and the considerations reviewed in the preceding pages, we can then formulate two general rules to avoid, or at least to reduce, in the cemented and hardened zones, the sudden variations in the concentration of the carbon to which are due the phenomena of exfoliation:

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[1] We have seen (see p. 51) how Guillet had already pointed out the great practical importance of this fact. He had, however, not taken into account the still more important effects of the liquation of the cementite.

1. Avoid effecting the cementation at too low a temperature and, in any case, cement at a temperature higher than that of the point Ar_3 of the steel used.
2. Avoid slow cooling after the cementation and before the quenching.

The first rule is simple and precise and does not require more detailed explanation. Some remarks on the second, however, seem opportune.

It is well known that in the practice generally followed in works for surface cementation of machine pieces, or case-hardening, there is always a slow cooling of the cemented pieces, starting from the temperature of the cementation and before the quenching. In fact, aside from the method adopted in many works of letting the cemented pieces slowly cool in the cementation boxes themselves, then heating them again in salt or lead baths to the hardening temperature, slow cooling ordinarily occurs during the time necessary to withdraw the cementation boxes from the furnace and remove from them one by one the cemented pieces in order to harden them; and, in fact, with a slowness amply sufficient to produce the phenomena of liquation which we have studied.

We shall see later how, in the majority of cases, the disadvantages just mentioned can be avoided by means of a "double quenching," executing the first in water or oil at a temperature but slightly different from that of the cementation. This can be done very easily, especially when the cementation is not effected in the usual boxes but with mixed cements in fixed cementation chambers. The second quenching is performed after having brought the pieces by the usual salt or lead bath to the temperature suitable for final quenching.

Finally, it is evident (and we shall see that experiment fully confirms it) that the sudden variations in the concentration of the carbon produced by the phenomena of the liquation of the cementite and of the ferrite must be the more marked the more rapid the variation of the concentration of the carbon in the cemented zone, before the slow cooling which precedes the quenching, and as long as the temperature remains about constant during the cementation.

In fact, as we have seen, these sudden variations in the concentration of the carbon are, so to speak, but an "exaggeration, localized in definite layers," of the continuous and uniform variation of this concentration which manifests itself before the slow cooling, in the cemented zones, at temperatures higher than the point Ar_3 of the steel used.

The importance of working so as to obtain cemented zones in which, before the cooling, the concentration of the carbon decreases as slowly as possible from the external layers to the deeper ones is therefore evident; in this way the effects of the sudden variations in this concentration which may be produced afterward by the liquation of the cementite and of the ferrite will be reduced to a minimum.

We have already seen (see p. 85) how this result can be obtained by carrying out the cementation under definite conditions with carbon monoxide, pure or mixed with small quantities of hydrocarbons, and the results of the experiments collected in the table on page 99 show the efficacy of such methods (see summary and discussion on pages 107–109).

We shall see later how the use of cements based on the special cementing action characteristic of carbon monoxide may find, for the same reasons, useful practical applications. Moreover, we shall see that the use of cements of this class makes it possible to avoid the formation of hyper-eutectic zones, with their dangerous brittleness, in cases in which it is not necessary to obtain extraordinary hardness on the surface of the cemented pieces, such as is very rarely required in practice.[1]

The practical importance of the facts to which I have just referred is shown by the value attributed by experts to cements which they call "gradual," as compared with "violent" cements. This distinction, which experts make from purely empirical data and without knowing the reasons for it, finds its exact explanation in the considerations which I have set forth and which permit of proceeding more rationally in the choice of cements and of the most suitable conditions for their use.

In the meantime, in May, 1909, Charpy published another memoir[2] on cementation, in which, together with a few new experiments, he reviews many of his preceding experimental researches and gives many remarks on the behavior of carbon monoxide in cementation. This paper contains very little new material, and gives the impression of being written chiefly for practical purposes.

Charpy, after having pointed out how he had shown in 1903 that carbon monoxide cements iron, begins by examining the results of the experimental investigations on the same subject preceding his, and dilates especially on the polemic between Caron and Margueritte (of which I have already spoken in Chapter I). He tries to explain by various arguments (some of them not entirely exact) the causes of the false deductions which Caron had drawn from his experiments, both as regards the carburizing action of carbon monoxide on iron and as regards the supposed necessity of the intervention of alkali cyanides in industrial cementation.

In the second part, Charpy repeats the account of previous experiments,

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[1] We shall see that in practice it can be useful to obtain concentrations of carbon higher than 0.9% only in certain special types of very thin cemented zones, the use of which is limited to rare cases of little importance. In the very large majority of practical cases, a maximum concentration of 0.9% gives a hardness (after quenching) which is amply sufficient and sometimes even excessive. In Part II of this volume we shall see that devices which permit of lowering the maximum concentration of the carbon in the cemented zones below 0.9% are sometimes useful in practice.

[2] G. Charpy, *Sur la cémentation du fer et de ses alliages par l'oxyde de carbone* (*Revue de Métallurgie*, May, 1909, Vol. VI, pp. 505–518).