

CHAPTER IV

THE LATEST STUDIES ON THE PROCESS OF CEMENTATION

I have already given at the beginning of the preceding chapter the reasons which led to concluding with 1907 a period, clearly distinct from the others, of scientific investigations on the process of the cementation of steel.

We will now review the work done since 1907.

Having had occasion to carry out myself during 1905-1907 a long series of experimental studies on the industrial application on a large scale of the processes of cementation,¹ I very soon realized that the scientific fundamentals of these processes as then known were anything but certain and complete, so that after having for some years prosecuted my industrial investigations I saw the necessity of taking up again the scientific study of cementation; this I have been able to do with the kind collaboration of various other persons.

Since these studies, the results of which I began to publish in the summer of 1908, have made it possible to clear up various interesting points of the theory of cementation and have furnished a useful guide for the industrial application of the processes of cementation, I will give here the results of my investigations, together with the researches contemporaneously carried out by others. A part of my investigations have recently been summarized by Portevin in the *Revue de Métallurgie*.

The first publication² contains only a small part of the results of the investigations carried out on a large scale in the works, chosen from among the few which I am allowed to publish, with the essential object of pointing out how it is possible in practice to produce a variation of the *distribution* of the carbon in the cemented zones, not only by using cements of definite nature but also by simply varying the conditions under which the cementation is effected. In these is systematically taken into account the *distribution* of the carbon in the cemented zones, by determining analytically the carbon in a series of successive layers of these zones. The data of such analyses, reproduced in a "concentration-depth" diagram (by representing on the axis of abscissas the distance of the median surface of the analyzed layer from the external surface of the cemented specimen of steel and as ordinates the

¹ Of these studies, carried out in great part at foreign industrial establishments, I can report (for reasons easy to understand) almost nothing.

² F. Giolitti, *Ricerche sulla fabbricazione dell'acciaio cementato*, Note I: *Gazzetta Chimica Italiana*, 1908, Vol. XXXVIII, Part II.

carbon contents obtained from the corresponding analyses), furnish a clear diagram of the "distribution" of the carbon in the cemented zone, and we shall see how this information can lead to interesting theoretical and practical results.

A first series of experiments, intended to furnish reference data on the "velocities of penetration" of the carbon which can be obtained with the processes usually employed in industrial practice, were carried out by cementing at various temperatures, under the conditions usually adopted in indus-

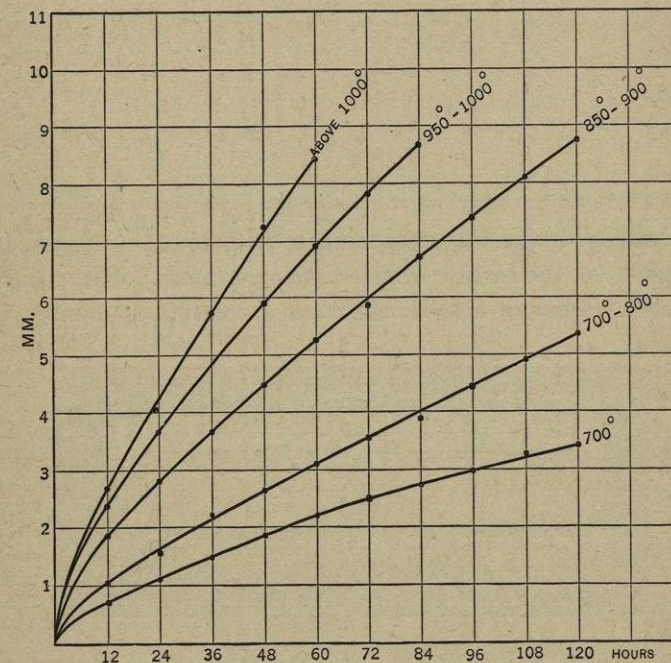


FIG. 19.

trial establishments, bars of soft Martin-Siemens steel in the form of parallelepipeds $40 \times 40 \times 200$ mm. There was used as cement one of the mixtures most frequently employed in practice, consisting of ground wood charcoal treated with 5% of potassium ferrocyanide and mixed with an equal weight of dry barium carbonate. The results obtained are reported in the table reproduced herewith and represented graphically in the diagram reproduced in Fig. 19. In the diagram, ordinates correspond to the depths of cementation, in millimeters, measured on sections of the bars from the edge to the point at which the cementation of the carbon is reduced to 0.2%, while abscissas represent the duration of the cementation, in hours.

The results obtained, aside from their evident practical interest, serve as useful terms of comparison for later experiments carried out with cements

of various natures. I shall omit, for the present, the theories to which these first results have given rise, since the later experiments furnish more precise and interesting data.

Length of the cementation in hours	Depths in millimeters of the cemented zones at the following temperatures				
	About 700°	750°-780°	850°-900°	950°-1000°	Above 1000°
12	0.75	1.10	1.95	2.45	2.65
24	1.15	1.60	2.85	3.70	4.00
36	1.50	2.25	3.65	5.10	5.80
48	1.90	2.80	4.50	5.90	7.30
60	2.20	3.15	5.30	7.00	8.45
72	2.55	3.60	5.90	7.80
84	2.80	3.95	6.75	8.70
96	3.00	4.50	7.45
108	3.30	4.95	8.10
120	3.45	5.45	8.75

In the same note, these first experiments are followed by others, showing the *distribution* of the carbon in the cemented zones. The cement used in this second series of experiments was a mixture containing 70% of

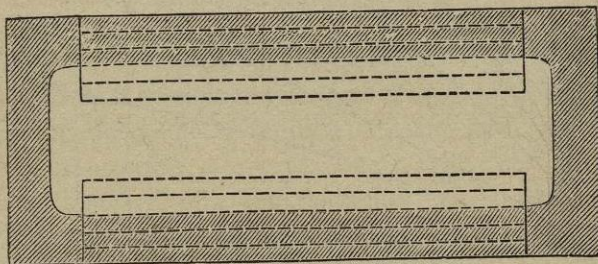


FIG. 20.

wood charcoal and 30% of animal charcoal. The steel was in the form of cylindrical bars or rectangular parallelepipeds, and had the following composition:

Carbon.....	0.05 percent.
Manganese.....	0.28 percent.
Silicon.....	0.011 percent.
Phosphorus.....	0.035 percent.
Sulphur.....	0.042 percent.

Successive layers 1 mm. thick were removed from the slowly cooled cemented bars (on the lathe or on the planer, according as they were cylinders or parallelepipeds), taking care to leave intact the portions near the angles of the specimens. Fig. 20 shows schematically the method followed in removing the successive layers; in it the shaded surface represents the section of the

carbureted zone, while dotted lines bound the sections of the successive layers removed on the lathe or on the planer.

A series of seven cementations, followed by analysis of successive layers, 1 mm. thick, of the cemented bars, gave the results reported in the following tables:

I

Length of the cementation, 36 hours. Temperature, 850°-880° C.

Depth in mm.	Carbon, percent.	Depth in mm.	Carbon, percent.
0.5	1.02	6.5	0.16
1.5	1.00	7.5	0.14
2.5	0.94	8.5	0.12
3.5	0.66	9.5	0.10
4.5	0.43	10.5	0.08
5.5	0.22	11.5	0.07

II

Length of cementation, 60 hours. Temperature, 850°-880°

Depth in mm.	Carbon, percent.	Depth in mm.	Carbon, percent.
0.5	1.03	7.5	0.33
1.5	1.02	8.5	0.24
2.5	1.00	9.5	0.18
3.5	0.95	10.5	0.14
4.5	0.83	11.5	0.11
5.5	0.66	12.5	0.09
6.5	0.50	13.5	0.08

III

Length of cementation, 96 hours. Temperature, 850°-880°

Depth in mm.	Carbon, percent.	Depth in mm.	Carbon, percent.
0.5	1.04	9.5	0.42
1.5	1.03	10.5	0.33
3.5	0.99	11.5	0.27
4.5	0.92	12.5	0.23
5.5	0.84	14.5	0.16
6.5	0.73	15.5	0.14
8.5	0.53	17.5	0.11

IV

Length of cementation, 360 hours. Temperature, 850°-880°

Depth in mm.	Carbon, percent.	Depth in mm.	Carbon, percent.
0.5	1.01	22.5	0.43
2.5	0.95	24.5	0.37
4.5	0.90	26.5	0.33
6.5	0.85	28.5	0.28
8.5	0.79	30.5	0.25
10.5	0.73	32.5	0.22
12.5	0.67	34.5	0.18
14.5	0.62	36.5	0.17
16.5	0.57	38.5	0.15
18.5	0.52	40.5	0.14
20.5	0.47

V

Length of cementation, 24 hours. Temperature, 1050°

Depth in mm.	Carbon, percent.	Depth in mm.	Carbon, percent.
0.5	0.72	6.5	0.29
2.5	0.58	9.6	0.17
4.5	0.43	12.5	0.09

VI

Length of cementation, 36 hours. Temperature, 1050°

Depth in mm.	Carbon, percent.	Depth in mm.	Carbon, percent.
0.5	0.84	10.5	0.27
4.5	0.55	14.5	0.18
7.5	0.39	17.5	0.14

VII

Length of cementation, 96 hours. Temperature, 1050°

Depth in mm.	Carbon, percent.	Depth in mm.	Carbon, percent.
0.5	0.99	10.5	0.50
4.5	0.72	17.5	0.33

These numerical data are reproduced, in the manner which I have just indicated, in the seven "concentration-depth" diagrams in Fig. 21.

From these diagrams it is seen clearly how the temperature at which the cementation is effected and the length of the operation influence strongly the *form* of the curves which represent the *distribution* of the carbon in the cemented zones. I gave a very simple explanation of this phenomenon in the same note which I am now reviewing, but I prefer to speak of it somewhat later, when I shall treat of the results of other experiments, carried out under better defined conditions, which have furnished a surer confirmation of this explanation. I shall then have occasion to refer to the tables and the diagrams which I have here reproduced.

It is well to keep in mind that the experiments which I have summarized were carried out on an industrial scale and the results can not, therefore, represent data as rigorously precise as those furnished by later experimental researches. Nevertheless, even taking into account only the "qualitative" significance, so to speak, of the experiments which I have summarized, we shall see later how the simple "form" of the curve which represents the *variation* in the concentration of the carbon in the various successive layers of the cemented zones has an influence on the mechanical properties of the cemented pieces at least equal to that of the total quantity of the carbon which has penetrated into the steel during the cementation and of the depth reached by this carbon.

Having thus established the fact that in industrial practice marked differences can manifest themselves in the distribution of the carbon in the cemented zones, I undertook a series of investigations in the laboratory, carried out under rigorously defined conditions, in order to learn the relations

which exist between the results of the cementation (especially as regards the *variations* in the concentration of the carbon at the various points of the cemented zones) and the conditions under which the cementation is effected,

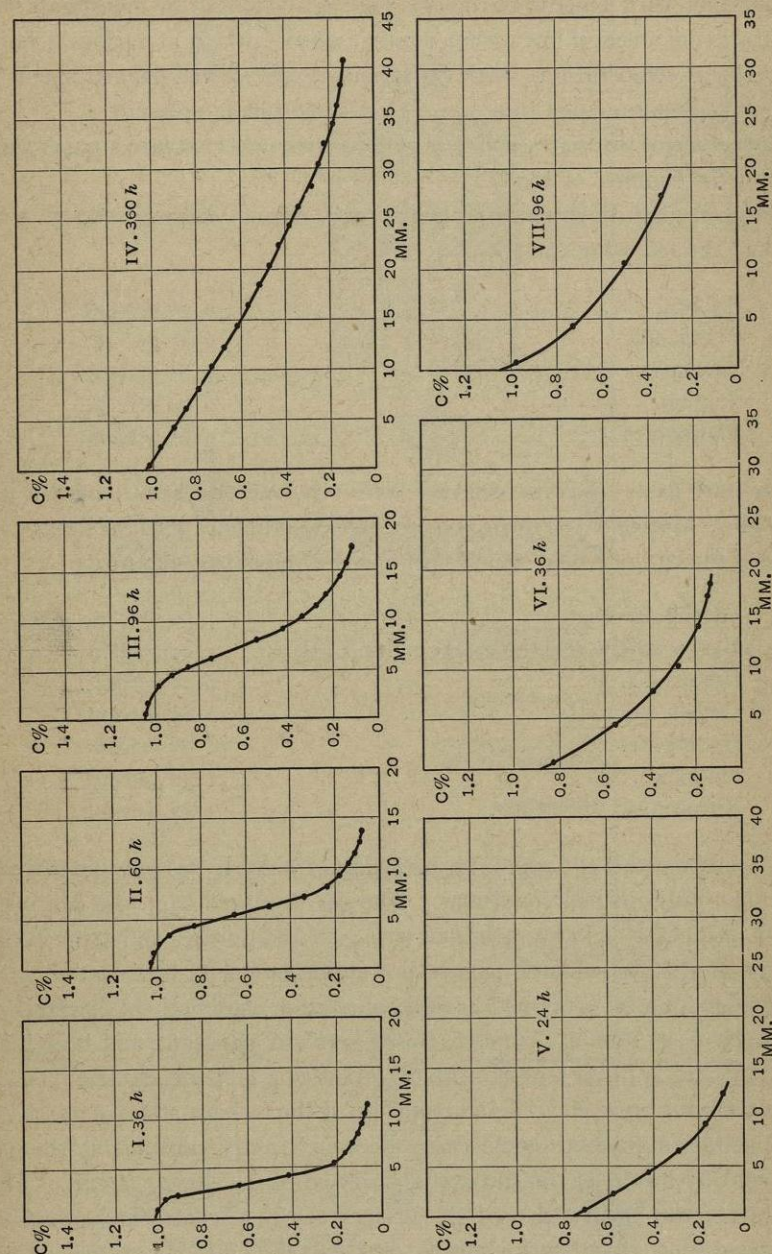


FIG. 21.

that is, the nature of the cement, the temperature, the pressure, and the thermal treatments which accompany and follow the cementation proper. I was thus able to discover the relations which exist between the distribution

of the carbon in the carburized zone and the mechanical properties of the cemented pieces, so as to improve the latter by varying the former.

A first series of laboratory experiments, carried out and published in collaboration with Doctor Carnevali, had as its object to investigate the cementation of steels of low carbon content when working at various definite and constant temperatures, with carburizing gases of well-defined chemical nature, at pressures equal to or lower than atmospheric pressure.

The results of this series of investigations were collected into a paper published in the summer of 1908.¹

The steel used, in the form of cylinders 10 mm. in diameter and 50 mm. long, had the following composition:

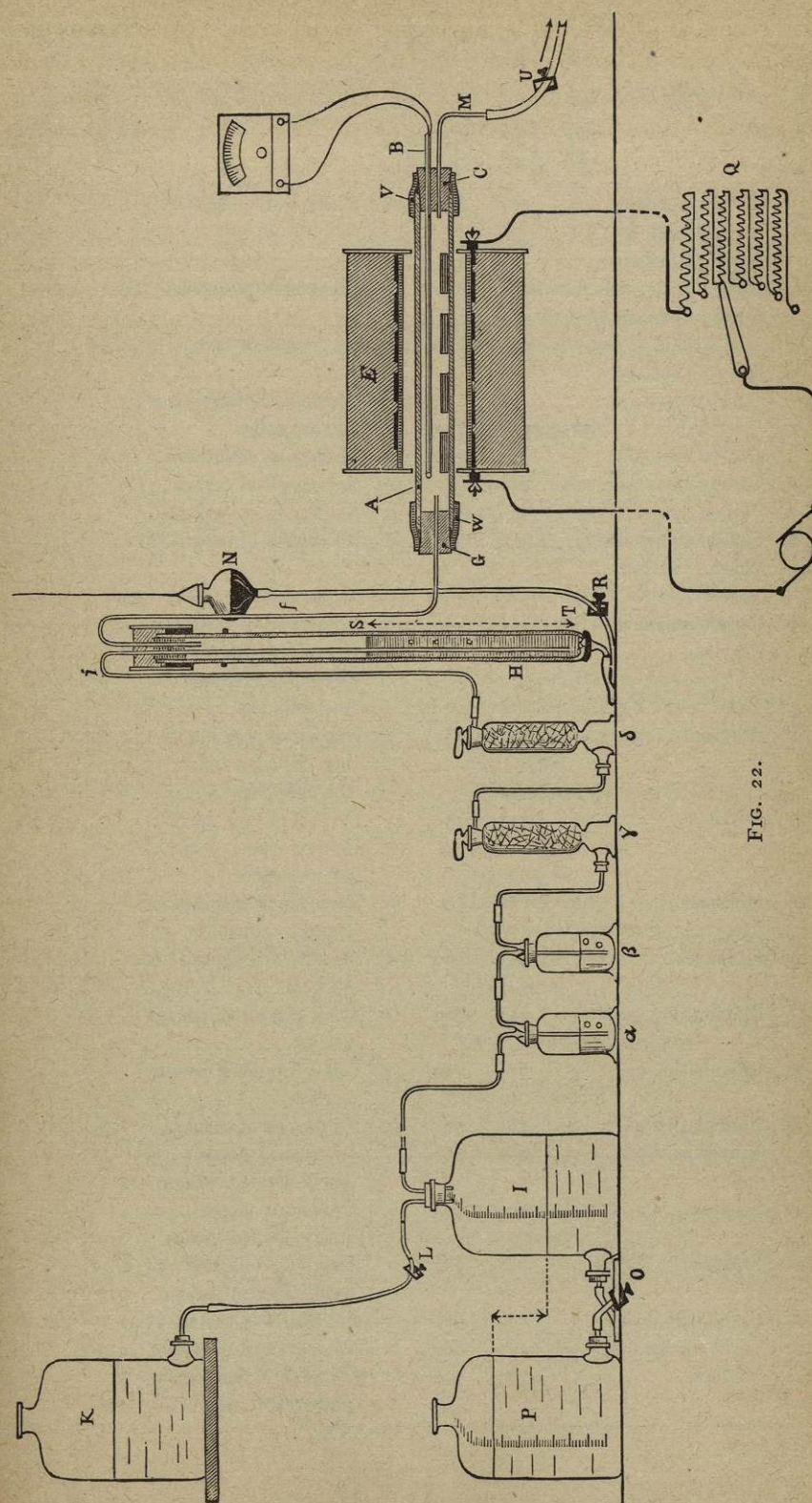
Carbon.....	0.06 percent.
Manganese.....	0.17 percent.
Silicon.....	0.01 percent.
Sulphur.....	0.04 percent.
Phosphorus.....	0.05 percent.

The pure gases used as cements were ethylene, methane, and carbon monoxide. Moreover, we made comparative experiments with the illuminating gas of the city of Rome, which then had the following composition:

Carbon dioxide.....	1.60 percent.
Hydrocarbons of the ethylene series (C_nH_{2n})...	3.40 percent.
Oxygen.....	0.20 percent.
Carbon monoxide.....	10.80 percent.
Hydrogen.....	51.95 percent.
Methane.....	31.58 percent.
Nitrogen (by difference).....	0.47 percent.

Fig. 22 represents the apparatus by means of which it was possible to work under rigorously defined conditions. The gas displaced from the Mariotte bottle *I* (by means of water saturated with gas) and purified and dried in the bottles α , β , γ , δ , passed with definite and uniform velocity into contact with the cylinders of steel contained in the cementation chamber, the glazed porcelain tube *A*, 36 mm. in diameter, closed perfectly gas-tight, and heated to a constant and uniform temperature by means of a Heraeus electric furnace with platinum ribbon *E*. The temperature of the furnace and, therefore, of the cementation chamber could easily be kept exactly constant at the desired point by means of the rheostat *Q*, inserted in the electric circuit. The temperature was then measured (to an accuracy 2° C.) at various points of the cementation chamber by means of a galvanometer connected with a

¹F. Giolitti and F. Carnevali: *Ricerche sulla fabbricazione dell'acciaio cementato*, II; Cementazione di acciai a basso tenore di carbonio, coi gas alla pressione atmosferica e a pressione ridotta, *Gazz. Chimica Italiana*, 1908, Vol. XXXVIII, Part II, pp. 309-351.



Number	Carburizing gas used	Length of cementation (hours)	Pressure of carburizing gas (mm. mercury)	Temperature (degrees C.)	Volume of gas used (liters)	State of the surface of the steel cylinders after the cementation	Thickness of the	
							Total thickness (mm.)	Thick- Hyper-eutectic (mm.)
1	Carbon monoxide	6	761	810	10	No deposit of carbon...	0.1
2	Washed and ignited wood charcoal.....	6 $\frac{2}{3}$	761	820	..	No deposit of carbon...	0.1
3	Wood charcoal and CO.....	6	761	810	6	No deposit of carbon...	0.25
4	Wood charcoal first heated at 300° in CO.....	6	761	760	..	Deposit of brilliant hexagonal scales.....
5	Carbon monoxide	7	761	760	10	No deposit of carbon...	0.05
6	Carbon monoxide	7	657	760	10	No deposit of carbon...
7	Carbon monoxide	7	568	770	10	No deposit of carbon...
8	Carbon monoxide	7	450	770	10	No deposit of carbon...
9	Wood charcoal and CO.....	7	548	780	10	No deposit of carbon...	2
10	Carbon monoxide	7	760	780	10	No deposit of carbon...	0.2
11	Ethylene.....	7	759	780	10	Deposit of very fine carbon in some parts of the cylinders.....	0.3	0.1
12	Ethylene.....	7	454	780	7	Deposit of very fine carbon in some parts of the cylinders.....	0.3	0.1
13	Ethylene.....	7	454	780	12	Deposit of very fine carbon in some parts of the cylinders.....	0.3	0.1
14	Methane.....	7	759	780	8	Very small deposit of spongy carbon.....
15	Methane.....	7	453	780	8	Almost no deposit of carbon.....
16	Illuminating gas.	7	760	780	15	Small deposit of spongy carbon.....
17	Illuminating gas.	7	613	780	15	Small deposit of spongy carbon.....
18	Illuminating gas.	7	463	780	15	No deposit of carbon...
19	Ethylene.....	5	760	900	7	Abundant deposit of finely divided carbon..	1.3	0.3
20	Ethylene.....	5	609	900	7	Abundant deposit of finely divided carbon..	0.9	0.2
21	Ethylene.....	5	458	900	7	Abundant deposit of finely divided carbon..	0.3	0.05
22	Carbon monoxide	5	760	900	7	No deposit of carbon...	1	0
23	Carbon monoxide	5	461	900	7	No deposit of carbon...	0.6
24	Methane.....	5	760	900	7	Abundant deposit of pulverulent carbon....	0.8	0.15

cemented zone		Distribution of the carbon in the cemented zone	Maximum concentration of carbon (cem. zone) percent.	Remarks
ness of the zone				
Eutectic (mm.)	Hypo-eutectic (mm.)			
.....	0.1	According to Type I...	0.6
0.05	0.05	According to Type II..	0.9-1	Cementation takes place only at the points where the contact between the iron and the carbon is best.
0.01	0.15	According to Type II..	0.9-1
.....	No cementation.
.....	0.05	According to Type I..
.....	No cementation.
.....	No cementation.
.....	No cementation.
.....	Very faint cementation, visible only with very great enlargement.
.....	0.2	According to Type I..
0.1	0.1	According to Type II..	The cementation is very faint and intermediate between Types I and II at the points where no carbon deposit has formed.
0.1	0.1	According to Type II..	The cementation is very faint and intermediate between Types I and II at the points where no carbon deposit has formed.
0.1	0.1	According to Type II..	The cementation is very faint and intermediate between Types I and II at the points where no carbon deposit has formed.
.....	Very thin cemented zone.
.....	No cementation.
.....	Very thin cemented zone.
.....	No cementation.
.....	No cementation.
0.5	0.5	According to Type II..	1.1
0.3	0.4	According to Type II..	1.1
0.1	0.15	According to Type II..	1.1
0	1	According to Type I..	0.5
0	0.6	According to Type I..	0.3
0.25	0.4	According to Type II..	1

Number	Carburizing gas used	Length of cementation (hours)	Pressure of carburizing gas (mm. mercury)	Temperature (degrees C.)	Volume of gas used (liters)	State of the surface of the steel cylinders after the cementation	Thickness of the	
							Total thickness (mm.)	Hyper-eutectic (mm.)
25	Methane.....	5	462	900	7	Abundant deposit of pulverulent carbon....	0.6	0.1
26	Illuminating gas.	5	470	900	8	Slight deposit of carbon	0.8
27	Illuminating gas.	5	463	900	8	Very slight deposit of carbon.....	0.5
28	Ethylene.....	5	760	1000	7	Abundant deposit of carbon.....	2.0	0.6
29	Ethylene.....	5	462	1000	7	Abundant deposit of carbon.....	1.8	0.5
30	Carbon monoxide	5	760	1000	7	No deposit of carbon...	2.0
31	Carbon monoxide	5	462	1000	7	No deposit of carbon...	1.4
32	Methane.....	5	760	1000	7	Not very abundant deposit of powdery carbon.....	2.0	0.7
33	Methane.....	5	466	1000	7	Not very abundant deposit of powdery carbon.....	2.0	0.7
34	Illuminating gas.	5	760	1000	10	Slight deposit of carbon.	1.5
35	Illuminating gas.	5	460	1000	10	Very slight deposit of carbon.....	1.2
36	Ethylene.....	3	760	1100	5	Very abundant deposit of pulverulent carbon.	2.9	1.6
37	Ethylene.....	3	458	1100	5	Very abundant deposit of pulverulent carbon.	2.0	0.9
38	Carbon monoxide	3	760	1100	5	No deposit of carbon...	3.0
39	Carbon monoxide	3	461	1100	5	No deposit of carbon...	3.0
40	Methane.....	3	760	1100	5	Deposit of compact carbon.....	2.6	1.2
41	Methane.....	3	463	1100	5	Deposit of compact carbon.....	2.5	1.3
42	Illuminating gas.	3	760	1100	7	Very slight layer of pulverulent carbon.....	2.1
43	Illuminating gas.	3	459	1100	7	Very slight layer of pulverulent carbon.....	2.1
44	Carbon monoxide	3	760	1100	9	No deposit of carbon...	4.0
45	Carbon monoxide	10	760	1100	9	No deposit of carbon...	4.0
46	Ethylene.....	3	760	1100	1	Slight deposit of carbon.
47	Ethylene.....	3	760	1100	15	Very abundant deposit of pulverulent carbon.	4.5	2.5
48	Ethylene.....	10	760	1100	11	Very abundant deposit of pulverulent carbon

cemented zone		Distribution of the carbon in the cemented zone	Maximum concentration of carbon (cem. zone), percent.	Remarks
ness of zone				
Eutectic (mm.)	Hypo-eutectic (mm.)			
0.2	0.3	According to Type II..	1
.....	0.8	According to Type II..	0.8	The cemented zone has a structure already approaching Type I.
.....	0.5	According to Type II..	0.6	The cemented zone has a structure already approaching Type I.
0.4	1.0	According to Type II..	1.3	The "concentration-depth" diagram and a micrograph are reproduced further on.
0.4	0.9	According to Type II..	1.3
.....	2.0	According to Type I...	0.35	A micrograph of this zone is reproduced further on.
.....	1.4	According to Type I...	0.24
0.3	1.0	According to Type II..	1.3
0.3	1.0	According to Type II..	1.3
0.2	1.3	Intermediate between Types I and II.....	0.9
.....	1.2	Intermediate between Types I and II.....	0.85	Approaches Type I more nearly than the preceding, lacking the eutectic zone.
0.4	0.9	According to Type II..	1.3
0.4	0.7	According to Type II..	1.3
.....	3.0	According to Type I...	0.18
.....	3.0	According to Type I...	0.12
0.4	1.0	According to Type II..	1.3	The "concentration-depth" diagram for this zone is reproduced further on.
0.4	0.8	According to Type II..	1.3
0.3	1.8	Intermediate between Types I and II.....	0.9
0.3	1.8	Intermediate between Types I and II.....	0.9
.....	4.0	According to Type I...	0.3
.....	4.0	According to Type I...	0.27	The "concentration-depth" diagram for this zone is reproduced further on.
.....	According to Type II..	0.9
0.4	1.5	According to Type II..	1.5
.....	Hyper-eutectic steel to the axis of the cylinder.	1.5	Hyper-eutectic cementation to the axis of the cylinder.

thermo-electric couple, the joint of which was introduced into the porcelain tube *B*, closed at the extremity projecting into the interior of the tube *A*.

The apparatus *H, R, N* . . . served to lower the pressure of the gas in the cementation chamber *A* to a definite and constant value. Its manner of operation is quite obvious.

The cemented specimens of steel were allowed to cool slowly in the furnace, then cut normally to the axis, polished, etched with a 4% solution of nitric acid in amyl alcohol, and observed under the microscope. In the cases in which the cemented zone was deep enough, we also made gravimetric carbon determinations on the material obtained on the lathe from successive layers of the cylinders, half a millimeter thick, in the manner already described.

The results of the forty-eight experiments are collected in the foregoing tables.

In order to explain clearly the designations "Type I" and "Type II" in the twelfth column of the tables, relative to the distribution of the carbon in the cemented zones, I must refer to the micrographs and "concentration-depth" diagrams of some of the more characteristic zones.

In the following table are collected the results of the gravimetric determinations of carbon made on successive layers, 0.5 and 0.75 mm. thick, obtained in the manner already indicated from the cylinders of steel cemented in Experiments 28, 40 and 45:

Experiment 28 Cementation with 7 liters of ethylene at 1000° for 5 hours		Experiment 40 Cementation with 5 liters of methane at 1100° for 3 hours		Experiment 45 Cementation with 9 liters of carbon monoxide at 1100° for 10 hours	
Depth, mm.	Carbon, percent.	Depth, mm.	Carbon, percent.	Depth, mm.	Carbon, percent.
0.25	1.30	0.25	1.28	0.75	0.27
0.75	0.86	0.75	1.30	1.50	0.21
1.25	0.52	1.25	1.02	2.25	0.16
1.75	0.26	1.75	0.82	3.00	0.11
2.25	0.08	2.25	0.58
.....	2.75	0.21

The same data are represented graphically in the accompanying "concentration-depth" diagrams of Figs. 23, 24 and 25.

From the numerical data, and still more from the curves of the three diagrams, the characteristics which distinguish clearly the cemented zone obtained with carbon monoxide in Experiment 45 from the other two, obtained by cementing the same steel under analogous conditions with ethylene and methane respectively, are evident. These differences come out still more clearly in the comparison of the two photograms of Figs. 26 and 27, the first of which reproduces, with an enlargement of 75 diameters, the

microstructure of the cemented zone obtained with ethylene at 1000° C. in Experiment 28.

The second photogram (Fig. 27) refers to the cemented zone obtained with carbon monoxide at 1000° C. in Experiment 30, a zone for which the

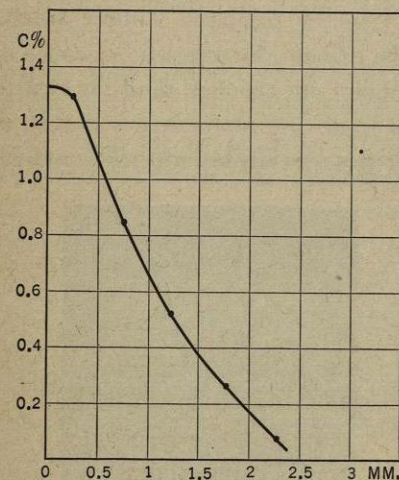


FIG. 23.

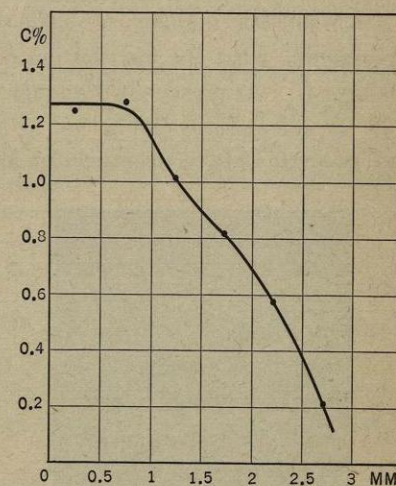


FIG. 24.

"concentration-depth" curve has a form perfectly similar to that of Fig. 25 (cementation with carbon monoxide at 1100° C.).

From the examination of the diagrams and of the micrographs we see that we can distinguish two types of cemented zones, characterized by a different distribution of the carbon in their successive layers:

1. The cemented zones belonging to the first type, corresponding to the diagram of Fig. 25 and to the micrograph of Fig. 27, are characterized by the fact that in them the concentration of the carbon does not reach at any point (and not even at the periphery) its value in the eutectic (0.9%), and diminishes progressively and in a uniform and slow manner as we pass from the surface toward the interior of the cemented pieces.

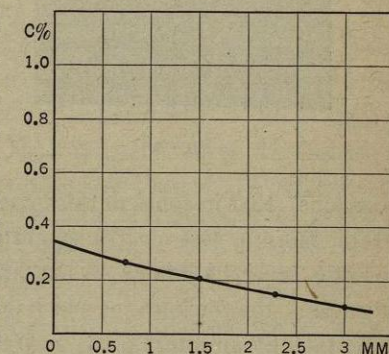


FIG. 25.

In the experiments summarized in the two tables of pages 78-81, the zones of this first type correspond always and only to cementation carried out with pure carbon monoxide, in which the formation of any deposit of free carbon on the surface of the steel cylinders does not manifest itself.

2. The cemented zones belonging to the *second type*, corresponding to the diagrams of Figs. 23 and 24 and to the micrograph of Fig. 26, are characterized by a highly carburized external layer in which the concentration of the carbon surpasses its value in the eutectic (0.9%).

Below this first external layer the concentration of the carbon diminishes in a *non-uniform* manner; we shall see later, on the basis of more precise experiments, what the distribution of the carbon characteristic of zones of this type is. At present it is enough to point out the fact, resulting clearly from the micrograph of Fig. 26, as also from that reproduced some pages back from the work of Bruch (which also refers to cementation carried out with

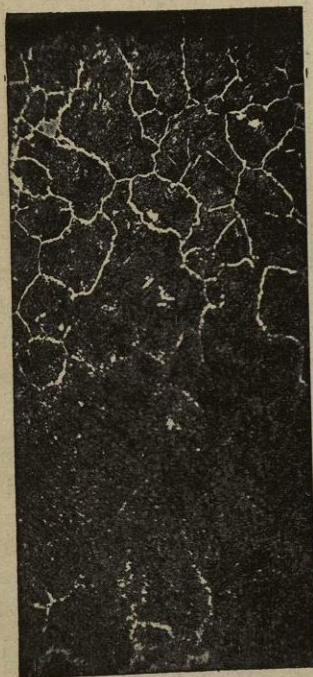


FIG. 26.

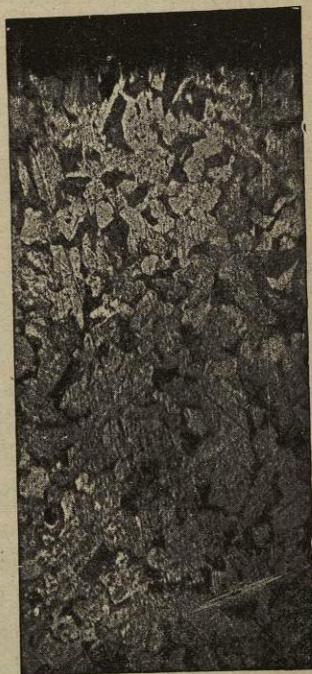


FIG. 27.

acetylene), that in zones of this type there are always observed three distinct strata, more or less clearly separated from each other; an external hyper-eutectic layer, followed by an intermediate eutectic layer (with 0.9% of carbon), the thickness of which does not exceed half a millimeter, followed in its turn by an internal hypo-eutectic layer.

In the experiments (1 to 48) summarized in the two large tables, the zones of the second type (more or less deep, according to the temperature used) are always found in cementations carried out with ethylene and with methane, and are always accompanied by a deposit of free carbon on the surface of the steel specimens. Thus, in Experiments 11, 12 and 13 (carried out by cementing with ethylene at 780°), in which the deposit of free carbon was

formed only in some regions of the steel cylinders, the cemented zones assume clearly the characteristics of the second type only in the parts on which the carbon has deposited, while in the other parts they assume an aspect intermediate between the first and the second type.

In Experiments 34, 35, 42, and 43, carried out by cementing with the illuminating gas whose composition was given, there are obtained (as is indicated in the twelfth column of the table) cemented zones in which the distribution of the carbon is intermediate between the first and the second types. This intermediate type of cemented zone, the practical importance of which we shall see later, is characterized by the lack of the external hyper-eutectic zone, which always characterizes the second type, but it differs from the first type in the fact that the carbon reaches in it a higher concentration, which remains equal (or quite close) to 0.9% in a more or less thick external layer formed of pearlite alone, and then gradually diminishes in the layers lying beneath. We shall see later how this intermediate type of cemented zone can be always obtained by carrying out the cementation with carbon monoxide in the presence of solid cements or in the presence of definite quantities of hydrocarbons.

It is evidently this second case which manifests itself in cementations carried out with the illuminating gas whose composition was given.

Returning to the cementation carried out with pure carbon monoxide, we can at once draw some conclusions:

The concentration of carbon in the cemented zone depends on various elements, and especially on the temperature, on the pressure of the gas, and on the velocity of the current of gas.

This follows very clearly from the experiments which I have summarized in the tables, as is seen from the following considerations:

1. All other conditions being equal, the concentration of the carbon in the cemented zone is *smaller* the *higher* the temperature. To become convinced of this, compare with each other the results of Experiments 22, 30, 38 and 45.

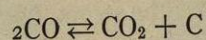
2. All other conditions being equal, the concentration of the carbon in the cemented zone is *smaller* the *lower* the pressure of the gas. To become convinced of this, compare the results of Experiment 22 with those of 23, those of 30 with those of 31 and those of 38 with those of 39.

3. All other conditions being equal, the concentration of the carbon in the cemented zone increases when the quantity of pure carbon monoxide which comes in contact with unit of surface of the steel during the cementation increases. A comparison of the results of the three experiments, 38, 44 and 45, proves this, it being noted that in all three the total surface of the steel subjected to cementation was the same (60 sq. cm.).

These phenomena are easily explained when we take into account first of all the fact that in all the cementations carried out with carbon monoxide at a temperature higher than 850° C., and passing the gas over the pieces of

steel with the velocity used by us, no deposit whatever of free carbon is formed, and the surface of the pieces of cemented steel remains perfectly clear and shiny. This shows that the free carbon which is formed in the transformation of the carbon monoxide into carbon dioxide dissolves entirely in the γ -iron with which it comes in contact. In other words, under the conditions above indicated the velocity with which the free carbon is formed is lower than that with which this carbon passes into solution in the γ -iron as austenite or martensite (according to the temperature).

Granted this, it is evident that, under these conditions, a new variable will enter into the equilibrium of the reaction



to which the carburizing action of carbon monoxide is due. This new element is the concentration of the carbon (appearing in the second member) in its solution in the γ -iron, for *all* of the carbon which is liberated passes into the state of solution.

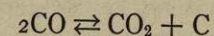
The carbon which is liberated by the catalytic action of the iron on the carbon monoxide, according to the reaction written above, therefore dissolves completely in the external layers of iron (which, at the temperature worked with, is in the state of γ -iron) until it reaches the concentration which corresponds to the state of equilibrium of the system $\text{CO}:\text{CO}_2:\text{C}$ in solution in γ -iron at the temperature and pressure experimented with.

The fresh carbon monoxide which comes into contact with the steel should then undergo the same decomposition, but to a lesser degree, for, by yielding fresh carbon to the external layers of steel, the concentration of this element is increased so that under the new conditions the equilibrium will exist for a smaller quantity of carbon dioxide and hence for a less extensive decomposition of the carbon monoxide. In this case, the concentration of the carbon in the external layers of the steel should increase rapidly and the carbon itself should diffuse into the layers lying beneath by simple difference in concentration, necessarily following the same laws which govern the diffusion of the carbon in the cementation with solid carbon. But we have seen that the distribution of the carbon in the carburized zones obtained by cementing steel with solid carbon¹ differs profoundly from that which is found in the zones obtained by cementing with carbon monoxide. In the first the concentration of the carbon decreases rapidly as we pass from the external layers to those which are deeper and deeper, following exactly the course which corresponds to the diffusion of a dissolved substance by "difference of concentration," but in the steels obtained by cementing with carbon monoxide the concentration of the carbon varies so little from the external layers of the carburized zone to the deeper ones (see Experiment 45 and the diagram of Fig. 25) that it is not possible to admit that the carbon

¹ See, for example, the experiments on a large scale previously cited, p. 74.]

has diffused into the mass of γ -iron by a simple phenomenon of solution due to the difference in concentration of the various layers, and we cannot but recognize that another cause has co-operated in producing the diffusion. This cause is evidently the penetration of the carbon monoxide into the steel.

When the gaseous mixture of CO and CO_2 which is in equilibrium at a given temperature with the carbon dissolved in the exterior carburized layer of the steel comes in contact with the steel of the internal layers, in which the concentration of the carbon is smaller and with which it is, therefore, no longer in equilibrium, it yields to their γ -iron a little carbon, increasing its content in carbon dioxide; this causes it to oxidize anew a part of the more highly concentrated carbon contained in the exterior layers—and so on. It therefore results that carbon monoxide, mixed with varying quantities of carbon dioxide, diffusing into the mass of γ -iron, merely equalizes in it the concentration of the carbon, and this within certain limits depending on the relative velocities of the various reactions and on the various phenomena of solution of the carbon and of diffusion of the gases. It is therefore to be foreseen that all causes which tend to shift toward the right the reaction



must necessarily increase in the γ -iron of the cemented zone the concentration of carbon, to correspond to the new conditions of equilibrium.

Among such causes, as is well known, must be numbered especially the lowering of the temperature and the raising of the pressure, and this because of the fact that the reaction is (in the direction indicated) *exothermic* and takes place with a decrease in volume. As we saw a short time back, these predictions are fully confirmed by experiment.

It is therefore easy to explain, on the basis of what we have just said, the experimental fact that the concentration of the carbon in the cemented zone increases, all the other conditions remaining the same, when the quantity of carbon monoxide coming in contact with a given surface of steel in the unit of time is increased. In fact, while both the velocity of penetration of the carbon by solution into the γ -iron and that of the diffusion of the carbon monoxide into the metallic mass remain constant in this case, on account of the constancy of the temperature and of the pressure, the concentration of the carbon monoxide (which is more rapidly renewed) is higher and hence the quantity of carbon which is deposited in the cemented zone of a given thickness is greater.¹

¹ I would remark that the gaseous mixtures of carbon monoxide and carbon dioxide which are, above 1000°C ., in equilibrium with free carbon (wood charcoal) are richer in carbon monoxide than those which are in equilibrium with solid solutions of cementite in iron containing less than 0.9% of carbon. This results not only from the indirect proofs which I adduce in what follows, but from many direct determinations which I have thus far but briefly made public (see *Rendiconti della Società Chimica di Roma*, 1908, Vol. VI, No. 16).

Besides establishing these important facts, the experiments summarized in the tables on pages 78-81 enable us to make some other quite interesting observations. They not only confirm the well-known influence of temperature on the velocity of cementation, but enable us to show that this influence manifests itself just as well in cementations carried out with ethylene or methane as in those carried out with carbon monoxide; but, while in the latter the increase in depth of the cementation due to rise in temperature is accompanied by a decrease in the concentration of the carbon in the cemented zone, in the cementations with ethylene or methane the cemented zone obtained in a given time, although also increasing markedly in thickness with rise in temperature, other conditions remaining constant, maintains about the same concentration and the same distribution of the carbon in the three characteristic layers of which I have already spoken.

As to the influence of pressure on the velocity of cementation I shall have occasion to give later more complete data.

If we compare the results of Experiments 36 and 47, carried out by cementing with ethylene at constant temperature (1100°) under constant pressure (760 mm.) during the same length of time (three hours), but varying the *quantity* of carburizing gas used (from five to fifteen liters), we see that the *depth* of the cementation, all other conditions being equal, increases greatly with increase in the *volume* of gas used. In all cases an abundant deposit of free pulverulent carbon is formed; it is therefore evident that the penetration of the carbon can not be due solely to the carbon deposited diffusing into the iron, by difference in concentration, since in this case the diffusion should take place in an identical manner in the two experiments. It is therefore evident that in the cementation carried out with gaseous hydrocarbons, diffusion of the gas "as such" into the iron also comes into play.

Finally, the experiments with which I am now dealing show also how a true process of cementation of steels of low carbon content cannot take place at temperatures below 780°, a result which is in apparent contradiction with those of many earlier experiments.¹

The explanation of this apparent contradiction is better developed in a communication which I presented shortly afterward,² in collaboration with Doctor Carnevali, before the Chemical Society of Rome. The cause of the apparent disagreement is to be found in the different methods of observation used to establish and measure the cementation, and to the consequent varying significance attributed to the word "cementation." In fact,

¹ See especially Charpy, *Comptes Rendus de l'Académie des Sciences*, Vol. CXXXVII, pp. 120-122; Giolitti, *Gazz. Chimica Italiana*, September, 1908.

² F. Giolitti and F. Carnevali, *Sul limite inferiore dell'intervallo di temperatura entro il quale si compie il processo della cementazione* (*Rend. della Società Chimica di Roma*, 1908, Vol. VI, No. 17).

Charpy and all the other experimenters who have affirmed the possibility of the cementation of iron at temperatures below 700° have based this assertion on the results of simple *gravimetric determinations* (direct or indirect) of the carbon which has penetrated by diffusion into the iron, without taking care to learn in what state this carbon is present in the iron and what effects it produces on the nature and on the structure of the metal into which it has penetrated; in other words, they have meant by "cementation" any process whatever of "carburization" of iron.

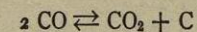
We, on the other hand, making use essentially of microscopic examination to determine and measure the cementation (although often accompanying it with chemical analyses) spoke of the existence of a cemented zone only in the cases in which we could establish the formation of a layer, more or less thick, of a *true steel proper, more highly carburized* than the steel subjected to the cementation; therefore we have meant to indicate by the words "cemented zone" a zone not only of higher carbon content but also possessed of the structure characteristic of a true proper steel having a higher carbon content.

Now, since it is known that this structure results from the segregation in the iron, during cooling, of the solid *solution* of the carbon to the state of cementite, and since this solution can not be formed at a temperature lower than 780° (α -iron), it is evident that it is impossible to observe any true *cementation* proper (in the sense meant by us) at a temperature below 780° C.

It is easy to explain the superficial carburization observed at relatively low temperatures (500°-600°-700°), by other experimenters, by two well-known phenomena:

1. All the experimenters who have affirmed the possibility of cementing iron at temperatures below 700° used as cementing agent either carbon monoxide or substances capable of evolving this gas, such as mixtures of carbon and barium carbonete. Now, by a mechanism analogous to that which I have already explained (see p. 87), the carbon monoxide diffusing into the iron deposits carbon there, even in the case when this carbon can not dissolve in the iron, such as when the iron is in the state of α -iron.¹ This carbon, however, whether it remains in the free state or forms a carbide of iron, does not impart to the metal the properties of a *more highly carburized true steel*, for the essential constituents of the latter (pearlite

¹ It is well to point out that the quantity of carbon which a given weight of carbon monoxide can liberate is greater (within limits) the lower the temperature, being dependent upon the equilibrium of the reversible reaction.



The carbon concentration is proportional to the concentration of the carbon dioxide at the equilibrium of the system $\text{CO}:\text{CO}_2:\text{C}$. And this concentration, according to the results of the investigations of Boudouard (*Ann. de Chim. et de Phys.* [7], XXIV, pp. 5-85), while it is only 0.7% at 1100° C., is equal to 42% at 700°, 77% at 600° and 89% at 550°.

together with the remainder of the pre-existing ferrite, or pearlite and cementite) can come only from the segregation of iron-carbon solid solutions. There is in this case, therefore, no true cementation.

2. The carbon pre-existing in the cementing material or resulting from the decomposition of carburizing compounds (such as carbon monoxide, hydrocarbons, etc.), coming in contact with the surface of the steel can form there a fine layer of free cementite; this, however, does not diffuse into the soft steel lying below, which preserves its primitive structure. This fact we were able to establish conclusively, as is shown by the micrographs reproduced in the paper which I have already cited.¹ In this case also, therefore, the process of carburization which manifests itself at a relatively low temperature is not a true cementation.

Having recognized the "discontinuity" of the distribution of the carbon in the cemented zones of high carbon content which are obtained with the cements commonly used, and which all give strong carburizations, I very quickly came to recognize an interesting relation between this discontinuity and a phenomenon well known and important for the practice of the cementation of machine parts; I refer to the phenomenon of "exfoliation" of pieces of soft steel superficially cemented and hardened.

Having had occasion to examine the "distribution" of the carbon in a very large number of pieces cemented and quenched under various conditions under my direction (especially drills, bits, toothed wheels, rings and cups for ball bearings, axles, etc.), many of which subsequently exfoliated in service, I was able to establish the causes of the discontinuities observed and, therefore, of the phenomena referred to, and this allowed me to establish some useful rules to avoid both the one and the other.

The first of these observations were communicated briefly to the Chemical Society of Rome in 1908.² These phenomena, studied with greater experimental accuracy, in collaboration with Doctor Tavanti, form the subject of a more extensive paper published in the following year.³

The phenomenon of the "exfoliation" or "splitting" of cemented steels is well known to all who have had occasion to examine machine pieces of "case-hardened" soft steel fractured in service. While in hard, homogeneous, quenched steels the surfaces of fracture always have a characteristic conchoidal form, soft steels carburized by cementation only in a surface layer more or less deep and subjected to a homogeneous hardening present surfaces of fracture with totally different characteristics. In fact, in this second case

¹ *Rend. Soc. Chim. di Roma*, 1908, No. 17.

² F. Giolitti, *Sul fenomeno della sfaldatura negli acciai cementati, e sui mezzi per evitarlo* (*Rend. della Soc. Chim. di Roma*, 1908, No. 17).

³ F. Giolitti and G. Tavanti, *Ricerche sulla fabbricazione dell'acciaio cementato*, III: Sui fenomeni di liquazione che si verificano negli acciai cementati (*Gazz. Chim. Ital.*, 1909, Vol. XXXIX, Part II).

the steel breaks along a surface almost parallel to the external surface of the cemented piece, so that, instead of metallic lenticular masses detaching themselves from it as in the case of homogeneous steel, whole surface "leaves," more or less thick according to the depth to which the cementation has extended, detach themselves. Of this phenomenon, which experts know well and characterize by saying that a cemented piece "exfoliates," a very clear example is furnished by an automobile part of cemented soft steel re-

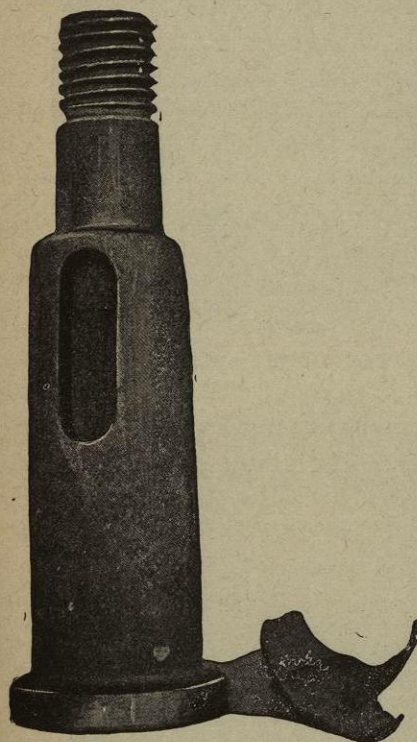


FIG. 28

produced in Fig. 28, taken from a work of Portevin.

Another very clear example of the phenomenon with which I am dealing is that reproduced in Fig. 29, which represents a fragment of a large drill of cemented soft steel. There appears very clearly, at *a*, on the fractured tooth of the section, the superficial "fold" of fine structure, sharply separated from the mass of coarser structure lying beneath.

Every expert knows that the surface along which a piece of steel "exfoliates" corresponds to a sharp surface of separation between two zones of

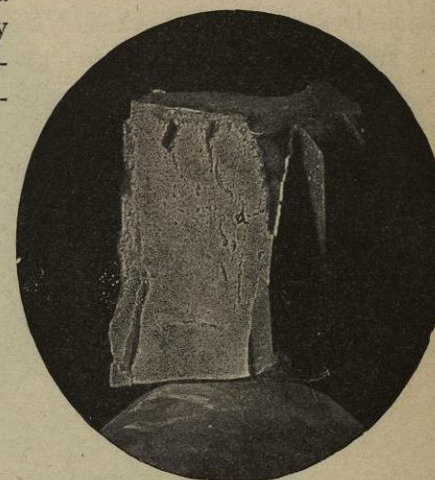


FIG. 29.



FIG. 30.