wheel here shown no part was "protected," in order to show more clearly the homogeneity of the cementation throughout the entire surface.

The figure shows clearly how the mixed cement gives, even on pieces of complicated form, cemented zones of a uniformity equal to that of the zones obtained with the gaseous cements. Moreover, a comparison of this surface of fracture with those shown in Fig. 129 confirms very clearly the statement that the mixed cements with carbon monoxide as base permit of avoiding those sudden variations in the carburization, and therefore in the hardness, which characterize the cemented zones obtained with the ordinary mixed cements with hydrocarbons as base. Fig. 145 also shows that the harmful consequences of such sudden variations in the structure *viz.*, exfoliations, are also eliminated. In fact, the wheel shown in Fig. 145 has suffered strong deformation before breaking, but at no point has the least *exfoliation* shown itself.

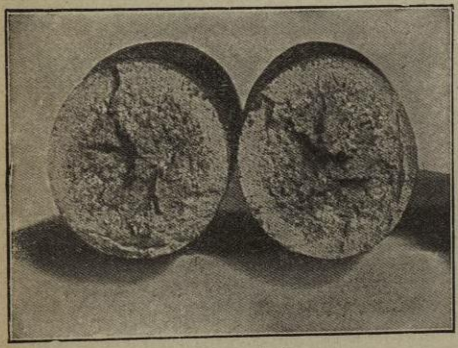

Fig. 146.

The same absence of sudden variations in structure is observed still better in the surfaces of fracture of cylinders cemented with the usual mixed cement, shown in Fig. 146, especially if these surfaces offracture are compared with those shown in Fig. 129.

As regards the "velocity" of the cementation, a simple comparison of the data already cited proves the great advantages obtained by using the mixed cement with carbon monoxide as base. Thus, for example, compare the data reported on p. 135, relative to cementation with carbon monoxide and carbon, with those cited on p. 217, carried out with a mixture of wood charcoal and bone charcoal (Bildt), and with those cited on p. 272, carried out with four solid cements in common use (Grayson), and with many other data already cited in the first part of this volume.

We will add here a somewhat more extended account of a practical character concerning the modifications in the conduct of cementation with the mixed cement for the purpose of lowering the maximum carbon content in the cemented zones and rendering its distribution more uniform. This is especially important in the cementation of certain special steels.

The result just indicated can be obtained by modifying the conduct of the cementation along two lines, either by "diluting" the carbon monoxide used with an inert gas, or one almost inert, like nitrogen, or by "isolating" during a part or all of the cementation the action of the carbon monoxide from the simultaneous action of the carbon intended to "immediately regenerate" it. Very precise results can be obtained in practice with each of these two methods.

I have already pointed out before (p. 164) that in case the reactions which take place in the use of carbon monoxide and free carbon should lead to successive states of complete chemical equilibrium, the concentration of the carbon in the cemented zones ought not to depend in any way on the partial pressure (concentration) of the carburizing gaseous mixture (carbon monoxide and carbon dioxide taken together) with respect to the inert gases added. This is because, as Schenck has shown,[1] the isothermal pressure-composition curve for the mixtures of carbon dioxide and carbon monoxide in equilibrium with free carbon coincides throughout its whole length with one of the equilibrium curves of the same gaseous mixtures with the iron-carbon mixed crystals. This last curve (forming part of a pencil of curves, each corresponding to a given concentration of carbon in the mixed crystals) is just that one which determines the maximum concentration attainable by the carbon in the cemented zones obtained at a given temperature by the process now under consideration.

But it has been already pointed out (see p. 188) that in these processes true states of complete equilibrium can be reached only in the case (never realized practically) in which the operation has been protracted so long that the whole mass of the metal subjected to cementation is uniformly carburized.

In the contrary case (the only one which ordinarily occurs in practice), when the carburized zone is limited to a portion of the mass of the steel, a new coefficient modifies the final result; *viz.*, the *velocity* with which the gases and the carbon of the mixed crystals diffuse into the solid steel. The intervention of this new "velocity" coefficient causes the *absolute* velocity of the various reactions to also exercise an effect, which they could not exercise if states of complete equilibrium were reached. This affects the final result of the cementation, and especially the concentration of the carbon in the cemented zones. But since these absolute velocities vary with variations in the partial pressure (dilution or concentration) of the active gases, it can be foreseen that the variations in this partial pressure will produce practically utilizable variations in the concentration of the carbon in the cemented zones.

Many experimental results confirm the correctness of these remarks, and constitute concrete examples of the practical results which can be obtained by applying the principles to which I have referred.

To work with "diluted" active gases, it is sufficient to simply substitute air for the carbon dioxide, working otherwise in the same manner as indicated for cementation with carbon monoxide. It is clear that the mixture of active gas resulting from the action of oxygen of the air on the carbon will in this way be diluted with a volume of nitrogen about double its own volume,

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[1] See Schenck, *Chimie physique des métaux*, 1911, pp. 200–201 (translated by Lallement), Paris, Dunod et Pinat, 1911.

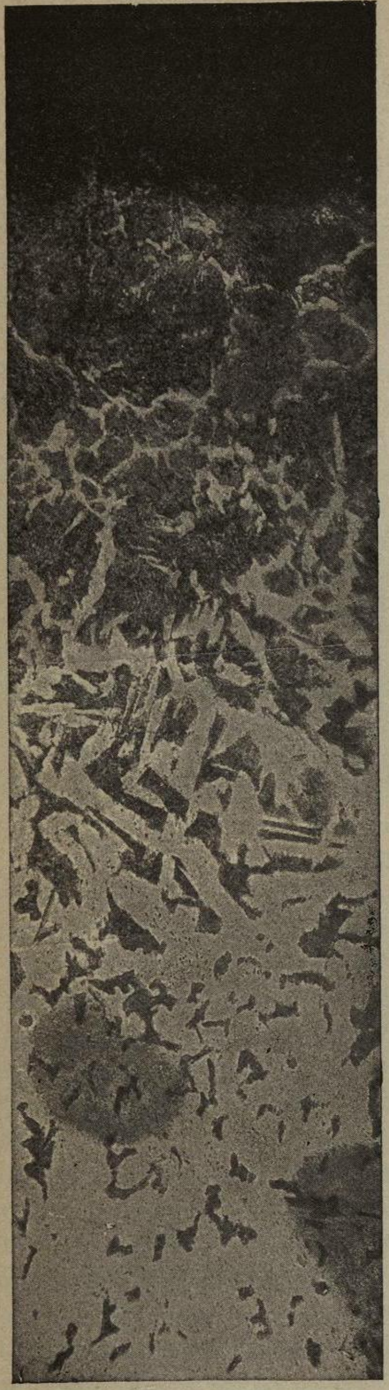

Fig. 147.

since, at the temperature of the cementation, the active mixture is composed almost wholly of carbon monoxide, containing but 1% or 2% of carbon dioxide.

Figs. 147, 148 and 149 show, magnified 50 diameters, sections etched with a 5% alcoholic solution of picric acid. They are three cemented zones obtained by making the carbon act in a slow current of air on an ordinary soft steel under conditions identical to those described in the preceding pages, and at the temperatures and during the times indicated.

Fig. 147.—Six hours at 1000° C.
Fig. 148.—Six hours at 1100° C.
Fig. 149.—Twelve hours at 1100° C.

A simple comparison with the micrographs shown in the first part of this volume, and also with Fig. 142, shows clearly that the dilution of the mixture of active gas ($CO + CO_2$) with an inert gas or one almost inert, such as nitrogen,[1] results in a marked decrease in the maximum concentration of the carbon in the cemented zones,[2] although there is preserved therein the characteristic uniform distribution of the carbon which constitutes the principal advantage of the process.

The practical advantages which can be obtained in many cases by the application of this last modification of the process with which we are dealing are

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[1] See F. Giolitti and L. Astorri, *Ricerche sulla fabbricazione dell'acciaio cementato*, IV (*Gazz. Chim. Ital.*, 1910, XL, I).

[2] From all the data reported previously we see that by working under the conditions giving the zones reproduced in Figs. 147, 148 and 149, there would have been obtained a maximum concentration of the carbon of at least 0.9% extending to a layer of a thickness equal to at least one-third the total thickness of the cemented zone.

Fig. 148.

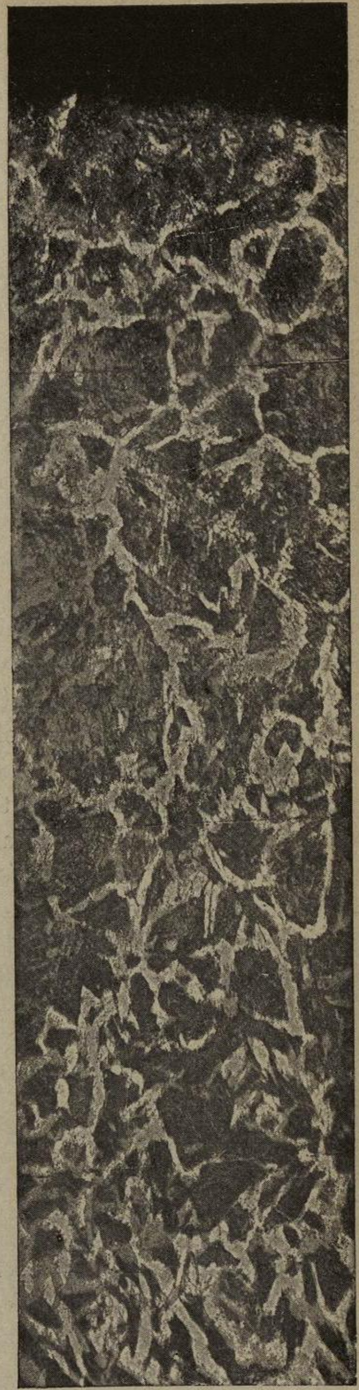

Fig. 149.

evident, especially in the cementation of those special steels for which the particular curve of equilibrium of the mixture of carbon dioxide and carbon monoxide with its mixed crystals coinciding with the curve of equilibrium of the same mixture with carbon corresponds to a rather high concentration of carbon in the mixed crystals.

Let us see, now, some practical examples of the results which can be obtained by the second method, consisting in isolating, during a part of the cementation, the action of the carbon monoxide from that of the free carbon, which we have already seen can easily be obtained with the vertical furnace by expelling at the suitable moment from the cementation chamber that portion of the granular carbon which in the first part of the operation was in direct contact with the surface of the objects to be cemented, and leaving in the lower part of the retort a layer of this carbon of sufficient thickness to establish the chemical equilibrium of the gaseous mixture which passes through it.

The effects of the isolated action of the carbon monoxide on the cemented zones obtained by the mixed cement acting in a first phase of the operation have already been referred to, especially on pages 135 to 137. But, while I dealt then with the effects to which such a procedure gives rise when it is applied to thin cemented zones, the data which I now wish to present refer to cementations of medium depth (from 5 to 10 mm.), for which (as also for the deeper ones) the application of the procedure in question presents the greater technical interest.

The tables which follow give the data (gravimetric carbon determinations in layers 0.5 mm. thick) of some cementations carried out with the mixed cement and followed by the action of the carbon monoxide, "isolated" in the way which I have indicated above. The same results are represented graphically in the diagrams which follow the tables of each series. The precise conditions under which the operation was conducted in its two distinct phases are also given.

SERIES I

Material used: ordinary soft steel of the following composition:

Carbon	0.12 percent.
Silicon	0.06 percent.
Manganese	0.47 percent.
Sulphur	0.02 percent.
Phosphorus	0.03 percent.

Results after each of the individual phases of the treatment:[1]

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[1] Both in this first series of experiments as also in the following series, several pieces of steel were subjected simultaneously to each of the various treatments, and under identical conditions, one of them being then used, after each operation, for the gravimetric determinations of the carbon in the successive layers.

(*a*) Cementation of ten hours at 1100° C. with mixed cement:

No. of individual layer analyzed	Distance of surface of the piece from the median zone of the layer analyzed (mm.)	Concentration of the carbon in the individual layers		
		1st determination	2nd determination	Mean
1	0.5	1.16	1.18	1.17
5	2.5	0.80	0.82	0.81
10	5.0	0.33	0.35	0.34

(*b*) Heating of the preceding zone for five hours at 1100° in "isolated" carbon monoxide:

No. of individual layer analyzed	Distance of surface of the piece from the median zone of the layer analyzed (mm.)	Concentration of the carbon in the individual layers		
		1st determination	2nd determination	Mean
1	0.5	0.84	0.86	0.85
5	2.5	0.76	0.80	0.78
10	5.0	0.46	0.46	0.46
15	7.5	0.23	0.27	0.25

(*c*) Heating of the preceding zone for another five hours (in all, ten hours of heating) at 1100° in "isolated" carbon monoxide:

No. of individual layer analyzed	Distance of surface of the piece from the median zone of the layer analyzed (mm.)	Concentration of the carbon in the individual layers		
		1st determination	2nd determination	Mean
1	0.5	0.69	0.71	0.70
5	2.5	0.66	0.68	0.67
10	5.0	0.52	0.54	0.53
15	7.5	0.38	0.40	0.39

The numerical data contained in the three tables constituting the first series are represented graphically in the following diagram (Fig. 150).

SERIES II

Material used: chromium-nickel steel of the following composition:[1]

Carbon	0.33 percent.	Phosphorus	0.015 percent.
Silicon	0.06 percent.	Chromium	1.50 percent.
Manganese	1.15 percent.	Nickel	3.17 percent.
Sulphur	0.02 percent.		

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[1] As is seen, this is a steel of the type of the ordinary steel for Krupp armor. For it the data here reported, relative to cementations of slight depth, are certainly of interest. A greater interest, however, will be presented by the data (given later) of very deep cementations carried out on this steel with the process just described.

Results after each of the individual phases of the treatment:

(*a*) Cementation of ten hours at 1100° C. with the mixed cement:

No. of individual layer analyzed	Distance of surface of the piece from the median zone of the layer analyzed (mm.)	Concentration of the carbon in the individual layers		
		1st determination	2nd determination	Mean
1	0.5	1.18	1.14	1.16
5	2.5	0.79	0.82	0.81
10	5.0	0.49	0.51	0.50

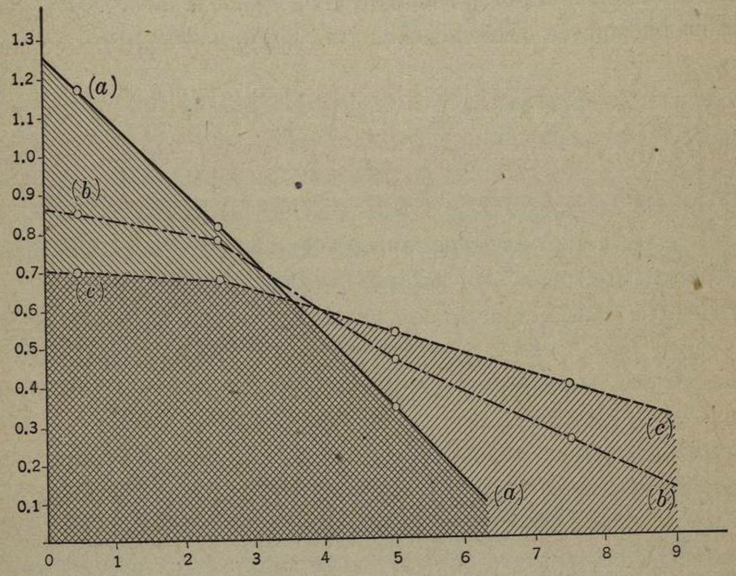

FIG. 150.

(*b*) Heating of the preceding zone for five hours at 1100° C. in "isolated" carbon monoxide:

No. of individual layer analyzed	Distance of surface of the piece from the median zone of the layer analyzed (mm.)	Concentration of the carbon in the individual layers		
		1st determination	2nd determination	Mean
1	0.5	0.80	0.81	0.80
5	2.5	0.76	0.78	0.77
10	5.0	0.58	0.58	0.58
15	7.5	0.45	0.44	0.45

(*c*) Heating of the preceding zone for another five hours (in all, ten hours of heating) at 1100° C. in "isolated" carbon monoxide:

No. of individual layer analyzed	Distance of surface of the piece from the median zone of the layer analyzed (mm.)	Concentration of the carbon in the individual layers		
		1st determination	2nd determination	Mean
1	0.5	0.87	0.85	0.86
5	2.5	0.85	0.88	0.87
10	5.0	0.75	0.75	0.75
15	7.5	0.60	0.58	0.59

The numerical data contained in the last three tables constituting the second series are represented graphically in the following diagram (Fig. 151).

After the detailed study in the first part of this volume on the causes of the various phenomena of brittleness and of exfoliation which may manifest themselves in cemented steels, any explanatory comment on the data contained in the preceding tables and represented in the two diagrams would be superfluous. In fact, when we remember the conclusions from those studies, a simple examination of the gradual variations in form and in position which the concentration-depth curves undergo as the result of the more and more prolonged treatment with the "isolated" carbon monoxide is sufficient to show clearly how the rational application of the process of cementation with which we are now dealing permits of obtaining cemented zones in which the principal causes of the phenomena of brittleness and of exfoliation which always manifest themselves to a more or less marked degree in steels cemented

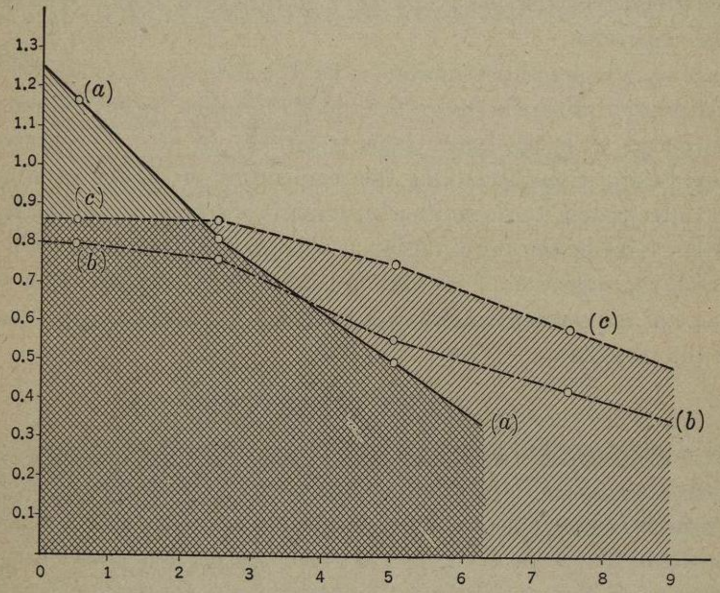

FIG. 151.

by the ordinary processes are eliminated. As a simple reminder of the considerations developed before, I recall here that the principal of these causes are the high concentration of the carbon in the surface zones of the cemented pieces and its rapid decrease as we pass to deeper and deeper layers. Also that this rapid decrease contributes to a very great extent to intensifying the phenomena of liquation of the cementite (or of the corresponding complex carbides of the various special steels) and of the ferrite. These phenomena are the cause, in their turn, of the sudden local variations in the concentration of the carbon which are produced during the cooling of the cemented pieces, to which are due the phenomena of exfoliation of the cemented and hardened zones.

Finally, the possibility of making the form of the cementation curves vary in the manner I have demonstrated indicates the way for successfully cementing also those special steels which by the ordinary processes of cementation furnish excessively brittle cemented zones. The interesting technical results derived from this possibility have already been amply confirmed by practical experience.

It is of marked practical importance that the use of the mixed cement with carbon monoxide as base in the vertical muffle furnaces, permitting (contrary to what occurs when the cementation is carried out with solid cements in the usual boxes) of easily varying the temperature of the cementation and even of interrupting the operation by rapidly discharging and recharging the retorts, furnishes means of raising at pleasure and up to very high limits the *normal* concentration of the carbon in the cemented zones, thus taking advantage of the phenomena which accompany oscillations in the temperature of the cementation. (See p. 160 *et seq.*)

§ 6. SPECIAL CEMENTATION

This section refers to those processes of cementation which, either owing to their purpose or to the special conditions under which they must be put into operation in practice, can not be included in any of the preceding groups.

Leaving aside the processes of electrical cementation, because thus far they have never been applied on an industrial scale, and some others of still less practical importance, there remain the special application to the manufacture of ship armor, and the so-called processes of "metallic cementation," the object of which is to produce the diffusion of elements other than carbon into solid steel.

The chemical laws which are applied in the cementation of armor are the same as those which we have already studied for other cases, so that the rules to be followed are the same. However, the cements which we have called too "sudden" are at a serious disadvantage, for the necessity of extending the cementation to great depths (in general, from 20 to 30 mm.) forces us to protract the operation for a very long time or to carry it out at a very high temperature; and then, in either one case or the other, we know that if the cement which is used is not very "mild" the concentration which the carbon attains in the peripheral part of the cemented pieces assumes very high values, giving rise, especially after the hardening, to dangerous brittleness.

This is the reason which has led many manufacturers to abandon rapid and more economical cements (such as the well known mixture of carbon and barium carbonate) for others considerably slower but "milder," such as simple wood charcoal or the mixtures of wood charcoal and animal charcoal.

Great advantages are presented, for this special purpose, by the mixed cements with carbon monoxide as base, already amply described, and especially when use is made of the expedient of "isolating" the action of the carbon monoxide in the second phase of the cementation.

Some numerical data will serve to show the variations in the concentration of the carbon in the successive layers of the cemented zones which are ordinarily obtained in armor.

1. Plate of Krupp steel (Cr-Ni) 280 mm. thick, cemented with illuminating gas:

Distance of the analyzed layer from the external surface of the cemented zone (mm.)	Concentration of the carbon, percent.
1	1.75
6	1.50
11	1.03
16	0.88
21	0.66
26	0.42

2. Plate of chromium-nickel steel of higher nickel content than the Krupp metal. Thickness of the plate, 250 mm. Cementation carried out with the mixed cement, the action of the carbon monoxide being isolated at the end of the operation:

Distance of the analyzed layer from the external surface of the cemented zone (mm.)	Concentration of the carbon, percent.
1	1.02
6	1.04
11	0.97
16	0.92
21	0.72
26	0.64
31	0.57

While the laws which govern the cementation up to such considerable depths are the same as hold for shallower cementations, their practical application must, however, be carried out with special precautions in the case with which we are now dealing, owing to the large masses of the substances which take part in the operation, and require special apparatus and arrangements. These technical details constitute, as a whole, special processes concerning which the manufacturers desire to keep the greatest secrecy, and although I have had occasion to deal with them personally in various establishments, I think it my duty not to publish anything which may have any real practical value. Not wishing, on the other hand, to summarize here the data of no practical value already published by others in various journals, I think it desirable not to develop this purely technical subject at all, but again insist on the fact that, as far as regards the laws which govern the course of the cementation, the considerations which are developed in the first part of this volume hold completely even for these cementations extended to great depths.

We must repeat the same observations as regards the technical applications of "metallic cementation."

We have already referred briefly in the preceding chapters to the results of some scientific investigations on the diffusion of elements other than carbon into solid steel.[1] Later we shall refer also to some patents which claim processes of this kind. I may add here that in the last few years there have been obtained interesting practical results (already protected by patents

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[1] Among others, the works of Boussingault on the diffusion of sulphur (see p. 23); those of Arnold and MacWilliam on the diffusion of various elements (see p. 35); those of Campbell . . . . and several others. The question of the diffusion of sulphur into solid steel has again recently been taken under examination by Grayson (see *The Journ. of the Iron and Steel Institute*, 1910, Vol. I, pp. 287–303). As to the addition of sulphur compounds to the carburizing substances for the purpose of increasing the velocity of penetration of the carbon, it is well to recall the correct observations made by Le Chatelier (see the abstract of the *Revue de Métallurgie*, 1905, p. 120) in connection with a patent of the "Feuerfeste Industrie Gesellschaft" of Dusseldorf, claiming the use of a cement formed of a mixture of carborundum and sodium sulphate. Le Chatelier observes that the fact, proved with certainty, that iron sulphide penetrates with great ease through all the spaces between crystals of ferrite makes it not improbable that the sulphur added to the carburizing mixtures may serve as "vehicle" for the carbon which diffuses into the iron. Account must be taken in practice, however, of the very harmful effects which the presence of sulphur exercises on the qualities of iron.

Considering the phenomena of the diffusion of the various elements into steel from a general point of view, and taking into account, by analogy, the facts observed in the diffusion of carbon, it may be considered that these phenomena must be due either to the intervention of gaseous compounds or to the formation of solid solutions of the elements which diffuse (or of their compounds, such as the carbides) in the iron. The formation of the solid solutions of the metallic carbides in the iron must be considered as the most important factor in the diffusion of the metals into the solid iron in the processes of "metallic cementation" proper.

all over the world) on the diffusion into solid steel of a certain number of elements other than carbon, such as nickel, chromium, manganese, boron, tungsten, etc. Personal reasons prevent me from furnishing here detailed accounts of these results, already successfully applied at the present time on an industrial scale.[1]

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[1] In this connection it may be well to point out here how, for some time, industrial practice has showed that several of the elements which Arnold and MacWilliam (see p. 35) had classified among the "fixed" elements (that is, those incapable of diffusing into solid iron) can in reality diffuse into steel in the solid state. Among such elements are manganese and tungsten.