EFFECT OF OTHER ELEMENTS UPON MIGRATION OF CARBON IN STEEL.

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In the course of an investigation which has been conducted in this laboratory during the past six years, designed to throw light upon the effect of non-metallic inclusions upon the problem of carbon migration and segregation, both ingot iron and low-carbon steel were heated in intimate contact with gray and malleable cast iron, respectively. A striking difference in the ability of carbon to migrate into the steel was observed, penetration occurring much more readily from the gray iron than from the malleable casting.

The fundamental differences in the nature of gray and malleable iron are principally with regard to silicon, manganese and carbon. Gray iron contains most of its carbon in the form of graphite flakes, as shown in figure 1. In this photomicrograph the bright portion represents iron, the dark portion sections of curved flakes (often grouped) of free car-

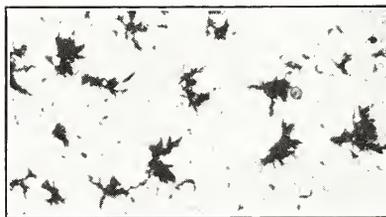Fig. 1. Gray cast iron. Graphite flakes in matrix of ferrite. x 100. (Reduced one-third.)

Fig. 2. Malleable cast iron. "Temper carbon" in matrix of ferrite. x 100. (Reduced one-third.)

bon. It is this structural peculiarity that gives ordinary castings their apparent brittleness, the graphite flakes interrupting the continuity of the otherwise ductile ferrite (carbon-free iron.)

In malleable iron castings also, the carbon is chiefly in the free state but the graphite is here in more compact masses; this results in an appreciable increase in the ductility and malleability of the mass. Such iron is shown in figure 2.

This difference in the state of carbon is largely due to the presence of other elements. Silicon has an important influence in the direction of increasing the instability of iron carbide, so that carbon separates as the casting is cooled, but while in the higher temperature ranges. Carbon thus takes its characteristic flaky form. Manganese has an effect opposite to that of silicon, as it increases the tendency for carbon to remain combined, as iron carbide.

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"Malleable" castings are produced by reheating "white" cast iron. This material contains most of its carbon in the combined state, which is made possible by the use of less silicon and more manganese in the original melt, so that moderately rapid cooling will almost entirely avoid the formation of free carbon. If, however, this material is reheated for prolonged periods to temperatures between 700° and 900° C., even this carbide is mostly dissociated, the free carbon thus produced assuming the form characteristic of malleable castings (fig. 2).

Gray iron is thus characterized by high carbon and silicon and low manganese, while malleable iron contains high carbon and moderate amounts of both silicon and manganese. Commercial practice varies rather widely but the following table gives an approximate idea of average compositions.

TABLE I. Composition of cast iron

	Carbon	Silicon	Manganese
Gray	2.5—4	1—3.5	0.1—0.5
Malleable	2.5—3	0.5—1	0.4—0.6

Case-carburization. All case-carburizing (cementation) processes involve the formation of a high-carbon steel skin or "case" on a low-carbon body. The ductile mass is then proof against breaking by shock, while the very hard case resists wear or abrasion. This condition is brought about by heating a mild steel for periods of 1 to 10 hours in contact with some material capable of yielding carbon in a form from which it may be assimilated as iron carbide by the iron of the piece.

A great variety of mixtures have been exploited and used commercially for carburizing such pieces. In many cases the superior merits claimed for a given material or mixture are largely imaginary, although admixture of the carbonaceous material with other elements or compounds does sometimes affect the rate of carbon absorption. Roughly speaking, carburizers may be classified as (a) solid mixtures of carbon or easily carbonized materials, with or without "accelerators" of inorganic nature; (b) cyanides or ferrocyanides, approximately pure or mixed with diluents; (c) gases, which may be hydrocarbons, carbon monoxide or mixtures of these with each other or with other gases. Such a mixture is ordinary coal gas, such as is served for fuel in most cities.

Cementation is usually understood to be a reaction of iron with either carbon monoxide or cyanogen, somewhat as follows:

$$3Fe + 2CO = Fe, C + CO_2,$$
$$CO_2 + C = 2CO, \text{ etc.}$$
$$3Fe + CN = Fe_3C + N.$$
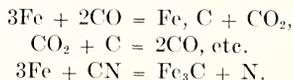
It seems not likely that undecomposed carbon monoxide or cyanogen can penetrate to any appreciable depth and the inward migration of carbon is probably of carbon in solid solution in iron, as austenite, although the opposite view has been supported by Giolitti. Also it has generally been assumed that solid carbon, as such, cannot be absorbed

appreciably by iron within the ordinary carburizing temperature ranges (800° to 900° C.), the intermediate formation of a carbon-containing gas being necessary. We shall refer to this point later in this paper.

Experimental. The work described in this paper is intended to be the beginning of an extensive investigation covering the influence of other elements upon the iron-carbon system, as regards the ability of carbon to enter iron and to migrate from regions of high concentration to those of low concentration, both of which processes are fundamental to the cementation of iron. The following experiments were conducted:

Specimens of gray and malleable cast iron were drilled with one-quarter-inch holes and smoothed rods of ingot iron were carefully driven into them. The rods fitted the holes tightly and air and foreign matter were completely excluded.

Pairs of these prepared specimens were placed in closed crucibles (to minimize oxidation) and heated in electric muffle furnaces for periods of five hours, one set at each of the following temperatures: 750°, 800°, 850°, 900° and 950°. They were cooled in the furnace and then removed and sectioned transversely to the axis of the rod insert. A freshly cut section of each piece was polished in the usual way, then etched with nitric acid and examined under the microscope and photographed. The results are shown in Table II and in the photomicrographs, figures 3 and 4, for the heating at 950°.
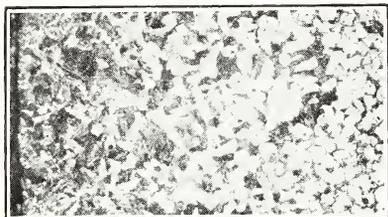

Fig. 3. Penetration of carbon from gray iron (at left) into ingot iron (main portion). Dark grains of pearlite in light ferrite. x 75. (Reduced one-third.)
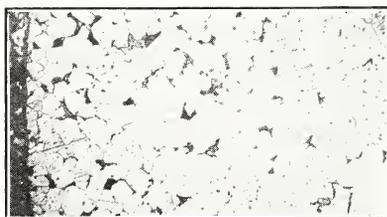
Fig. 4. Penetration of carbon from malleable iron (at left) into ingot iron (main portion). Pearlite in ferrite. x 75. (Reduced one-third.)

TABLE II.   Depth of penetration (in millimeters) of carbon from gray and malleable cast iron.

Temp. °C.	Gray	Malleable
800	Irregular, 0—0.25	0
850	0.60	0.20
900	1.00	0.45
950	1.20	0.8

No appreciable cementation occurred below 800°, which is about the lower temperature limit for ordinary commercial case-carburization, or cementation.

Carbon seems to enter iron from malleable cast iron slowly and to migrate slowly, while from gray iron the cementation is more rapid. With malleable iron, even when the temperature is high enough to carry carbon well into the interior, the steel layer thus formed is relatively low in carbon, as shown by the scattering pearlite grains in the outer layers of the ingot iron insert. At 950°, while penetration has occurred to a depth of about 0.8 millimeter, the pearlite grains indicate at no point a carbon content greater than about 0.3 per cent.

With gray iron the case is quite different. Carbon enters the ingot iron readily and penetrates more rapidly. The outer layer of the carburized piece, as shown in figure 3, is practically eutectoid in composition (carbon=0.9 per cent), which is about what is desired in a commercially carburized piece.

These experiments prove conclusively that solid carbon can dissolve in and migrate through iron, forming carbide upon cooling, as is the case with the gases carbon monoxide and cyanogen. The explanation of the difference in rate of migration remains. This latter may be due to (a) difference in carbon content of the carburizing piece, (b) difference in the concentration of silicon in this piece, (c) difference in the concentration of manganese or (d) any combination of these factors. These points are being studied at greater length.

Polished pieces of ingot iron were next packed in (a) gray iron drillings, (b) gray iron with 10 per cent of ferrosilicon, (c) gray iron with 10 per cent of ferromanganese, (d) a commercial brand of case-carburizing compound and (e) mixtures of this material with varying amounts of ferrosilicon or ferromanganese. The iron with its packing was placed in large porcelain crucibles, the covers sealed on with fire clay and the entire assembly heated in the muffle furnace at about 950° for five hours.

Transverse sections of the pieces treated as just described, followed by furnace cooling, showed that gray iron alone, used as packing, yielded practically no carbon to the ingot iron, only a trace of pearlite appearing at the extreme outer surface of the piece. The ingot iron packed in gray iron with 10 per cent of ferrosilicon showed a carburized case, 1¼ millimeter in depth, while the piece packed in gray iron with 10 per cent of ferromanganese showed a case two millimeters in depth, with the outer skin nearly eutectoid in composition.

Conclusions. As has already been stated, this is merely the beginning of what is hoped will be an extensive investigation into the influence of foreign elements upon the rate of carburization and carbon migration. The results here reported indicate rather decidedly that increasing the per cent of silicon or manganese in the carburizing mixture increases the tendency of iron to absorb carbon. This, of course, refers only to silicides and manganese alloys, and not to salts, such as silicates or manganese salts as such. Detailed experiments are now in progress, covering a wide range of mixtures and of heating conditions.