

CASE-CARBURIZATION IN PRESENCE OF
FERROSILICON.

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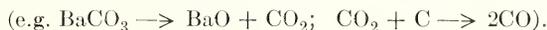
Case-carburization or case-hardening is a process of partial cementation whereby a surface layer or "case" of high-carbon steel is produced upon soft or low-carbon steel. The process involves heating the steel in contact with carbon or some substance capable of imparting carbon to the iron in such a form that it may be assimilated. When this case is hardened by quenching from elevated temperatures it is very resistant to wear or abrasion, while the soft, ductile core reduces the danger of breaking under shock or impact.

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



It seems probable that these reactions take place at the surface of the steel and that the carbon then migrates or diffuses through the austenite, which is the stable form of iron at carburizing temperatures (around 950° C.).

Many different substances may be used as carburizing materials. Solids, such as carbon, petroleum coke, charred leather; liquids, such as fused alkali cyanides and ferrocyanides; and gases, such as hydrocarbons and carbon monoxide; all of these serve particular needs. The solid carburizing materials are, perhaps, the most important, especially for the formation of deep cases. Most of these have an energizer, such as sodium or barium carbonate, mixed with them in order to give a potential source of carbon monoxide at the high temperatures



Due to the long period of heating above the critical temperature, considerable grain growth occurs. Coarse grain structure is not desirable because of the lower strength characteristics which accompany it. In order to refine the grain structure and also to produce metastable constituents which make the steel much stronger and harder, the case-carburized piece is subjected to thermal treatment. The piece may be heated and cooled as many as three times, first, heating to above the critical temperature of the core, followed by drastic quenching in order to refine the core; second, heating to above the critical temperature of the case, followed by a drastic quenching in order to harden and refine the case; and third, heating to below the critical temperatures, followed by slow cooling in order partially to relieve internal stresses.

During the time of drastic quenching enormous stresses are set up within the metal. These stresses may cause warping or cracking.

If carbon is absorbed too rapidly or if the time of carburization is prolonged the carbon content of the surface layers of the piece will rise above 0.87 of one per cent, which is the carbon content of the iron-iron carbide eutectic. Upon cooling such a carburized specimen to the upper critical temperature, cementite (iron carbide) begins to separate and continues to do so until the lower critical temperature is reached. This cementite is precipitated or thrown out of solid solution at the grain



Fig. 1—Structure of the case formed on ingot iron by heating to 950° C. for 5 hours in a commercial carburizing material.
 Specimen No.36
 Echant HNO₃
 Magnification 75
 (Reduced one-third.)

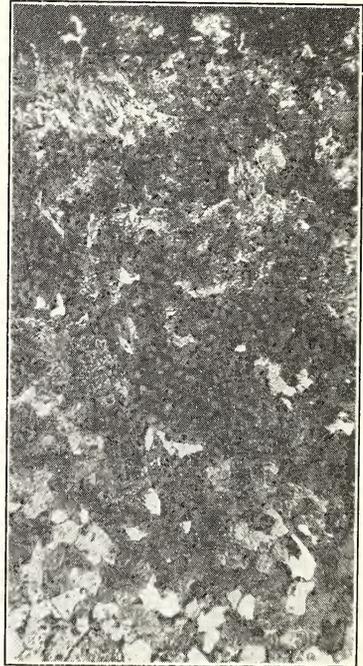


Fig. 2—Nature of case produced by a commercial carburizing material which has had 20% ferrosilicon mixed with it. Heated 5 hours at 950° C.
 Specimen No.35
 Echant HNO₃
 Magnification 75
 (Reduced one-third.)

boundaries. Consequently, a hypereutectoid zone will result, this being composed of grains of eutectic composition surrounded by iron carbide shown as a bright network in section (fig. 1). When the carbon content is high enough some of the iron carbide is precipitated also along the atom planes of the austenite grains and below the lower critical point it is found as plates or flakes in the pearlite grains (the iron-iron carbide eutectoid).

When the piece is subjected to hardening processes and high internal stresses are induced, these plates, as well as the brittle envelopes,

offer easy paths for the course of a crack or fracture. For this reason a case which has a hypereutectoid zone is usually not desirable.

Also if carbon penetration is too rapid, resulting in abrupt changes in carbon content from one layer of the case to the one immediately beneath it, peeling, flaking or chipping is likely to occur.

Consider what happens upon quenching a carburized specimen. The surface will be chilled first and it will contract. This may be relieved in part by compression of the lower layers and in part by deformation of the outer layer. As the next layer contracts the outer layer becomes too large and tensile stresses are developed between these layers. If we have carbon segregation and abrupt changes in carbon composition there will be weak points, and cracks started due to the stress may cause parts of one layer to break or peel away from the layer beneath. This takes place in the type of failure known as "exfoliation," where a surface layer breaks away in the form of a shell or coating. This method of fracture is also likely to be noticed at corners and bends.

For several years carbon migration and segregation in steel have been subjects of investigation. In some experimental work described in an earlier paper¹ it seems to have been definitely proved that elementary carbon can dissolve in and migrate through iron. Also that certain ferro-alloys, such as ferrosilicon and ferromanganese, increase the rate at which carbon migrates from cast iron drillings, used as a packing, into specimens of ingot iron. In this process ferromanganese proved to be more efficacious as an energizer than other materials used.

Naturally this suggested the possibility of using such materials in the carburizing mixture for partial cementation processes and a series of experiments with this idea in mind has recently been conducted.²

It was found that ferrosilicon, ferromanganese and ferrophosphorus did have an effect upon the rate at which carbon was absorbed when they were mixed with the carburizing material. Ferrosilicon especially had a decided effect upon the nature and depth of case produced and it was thought worth while to study in more detail the action of ferrosilicon in case-carburization processes.

From earlier experiments² we were led to the conclusion that ferrosilicon, when added to the carburizing material, has a desirable influence, first, because it gives a case that has an even gradation in carbon content from the highest carbon content at the surface to the low carbon content of the core, and, second, because for ordinary temperatures and times of carburization (5-8 hours at about 950° C.) no hypereutectoid zone is formed.

The experimental work was conducted in the following manner: Specimens about an inch and one-half in length were cut from one-half inch ingot iron rods. These were packed individually in the carburizing material in Nichrome carburizing pots, each about 5 inches in height and 3 inches in diameter. The pots were heated in a Hoskin's electric muffle furnace and the temperature was regulated by means of a Hoskin's Chromel-Alumel thermocouple and pyrometer. The commercial

¹ Mahin and Spencer: Proc. Ind. Acad. Sci., 34, 1924 (1925).

² Spencer: Master's Thesis, University of Notre Dame, August, 1926.

carburizing material was obtained from the Rodman Chemical Company and bears the trade mark "Carbo." The ferrosilicon, a solid solution of silicon and iron (this was 50 per cent silicon), was obtained from the Clark Equipment Company of Buchanan, Michigan. Both materials were ground to about 50 mesh, and when ferrosilicon was mixed with the commercial material, as homogeneous a mixture as possible was made by careful rolling on glazed paper.

This effect of the addition of ferrosilicon may be noticed by comparing figures 1 and 2. Figure 1 shows the type of case that is obtained by carburization in the commercial materials alone. The hypereutectoid zone is fairly wide and well defined. The eutectoid zone is very poorly defined and carbon gradation is decidedly uneven.

Figure 2 shows the nature of the case produced by carburization in a commercial material which contains 20 per cent of ferrosilicon. The hypereutectoid zone is absent and carbon segregation and gradation are more even.

Table I gives a comparison of the carbon penetration and thickness of different zones.

TABLE I. Comparison of depths of carbon penetration with and without addition of ferrosilicon.

		5 hrs. at 950° C.	7 hrs. at 950° C.	9 hrs. at 950° C.
Specimen carburized in commercial material.	Total penetration	1.6 mm.	2.30 mm.	2.94 mm.
	Eutectoid zone	0.67 mm.	1.10 mm.	1.52 mm.
	Hypereutectoid zone...	0.2 mm.	0.66 mm.	0.90 mm.
Specimen carburized in mixture with 20% of ferrosilicon.	Total penetration	1.13 mm.	1.74 mm.	2.50 mm.
	Eutectoid zone	0.40 mm.	0.69 mm.	0.84 mm.
	Hypereutectoid zone...	0.00 mm.	0.00 mm.	(0.30)* mm.

*The hypereutectoid zone occurred only locally, over about one-third of the case.

Whatever may be the mechanism of the action of ferrosilicon in causing these differences, it seemed reasonable to suppose that it was only the ferrosilicon immediately surrounding the specimen that was affecting the nature of the case. Consequently, a number of pastes or paints containing ferrosilicon were made and tried on different specimens. A paste made of one part by volume of water-glass to one part by weight of ferrosilicon gave approximately the same type of case as did the original 80-20 mixture. The paste was applied by simply dipping the specimen into the water-glass-ferrosilicon mixture. This was allowed to dry on the specimen and the whole was packed in ordinary unground commercial carburizing material.

In one experiment where only one side of the specimen was dipped into the paste, the exact point at which the influence of the ferrosilicon stopped could be determined from the nature of the case when the specimen was prepared and observed over the microscope.

Since, for ordinary temperatures and times of carburization, the case produced when ferrosilicon is used in the carburizing material has no hypereutectoid zone, and also since the carbon content decreases

gradually from the eutectoid zone towards the core, the use of ferrosilicon in a carburizing material should prove desirable in this respect at least. Cases having only eutectoid composition at the surface and a relatively deep penetration of carbon may be prepared by heating for shorter periods of time at higher temperatures than are ordinarily used for the production of such a case.

The work presented here represents a part of more comprehensive experiments which are in progress at the present time, this investigation forming the basis for a thesis by one of the authors (Spencer) for the Doctorate.

COLLOIDAL ARSENIC TRIOXIDE IN THE ARSENIC DETERMINATION.

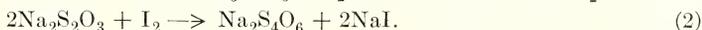
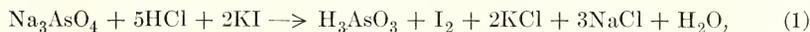
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Arsenic is an essential constituent of various commonly used insecticides. In such materials it may occur in either state of oxidation (trivalent or pentavalent) and as either free acid or combined as salts—arsenites or arsenates. Paris green is a double copper salt of acetic acid and arsenous acid, of variable composition, but the commercial article may contain also cupric arsenate or free arsenous or arsenic acid. As these compounds vary in solubility, insecticidal efficiency and effect upon foliage, methods for their determination are necessary; but one determination that is always of first importance is that of total arsenic.

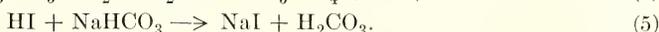
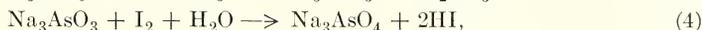
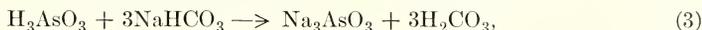
For this determination two methods have at various times been made official by the Association of Official Agricultural Chemists. Until the publication of the revision of 1919, the official method for total arsenic¹ was, in outline, as follows:

The weighed sample is heated with a solution of sodium hydroxide until decomposition is complete. Cuprous oxide is precipitated, the solution then containing sodium acetate, sodium arsenite and sodium arsenate. The last named salt is from oxidized arsenic already existing in the sample, as well as from arsenite which has been oxidized during the process of digestion with the basic solution.

The pentavalent arsenic is then brought to the trivalent form by the addition of hydrochloric acid and potassium iodide, followed by careful removal of liberated iodine by sodium thiosulphate:



An excess of sodium bicarbonate is then added to maintain the solution in a weakly basic condition, after which the arsenic is titrated by standard iodine solution, by the aid of starch as an indicator:



¹ Bur. Chem., Bull. 107, 25 (1908).