

THE ACTION OF ENERGIZERS DURING CASE-CARBURIZATION

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The process of imparting carbon to iron or mild steel by heating the ferrous part, packed in solid carbon, is an old one. Cementation of wrought iron in this way for the production of steel was the only extensive commercial process of steel manufacture until the introduction of the Bessemer process, about 1855, and the low-carbon—and, therefore, ductile—steels are commonly case-hardened by surface cementation, followed by thermal treatment. Gases containing compounds of carbon are employed, in certain instances, as substitutes for solid carbon.

It is now clear that cementation by solid carburizers takes place to only an insignificant extent unless oxygen is available in some form. Ordinarily enough oxygen is contained in the air enclosed with the solid carburizer in the pot to start the necessary reactions but this does not provide for sufficiently rapid carburization and all commercial carburizers contain one or more compounds included in the general class of "energizers."

The only important direct carburizing agent is carbon monoxide. In certain cases hydrocarbon gases are to be considered but the solid carburizers generate only negligible quantities of such compounds. Carbon monoxide is formed as a result of interaction between oxygen and carbon. As the temperature of the carburizing pot rises, carbon dioxide is largely formed, but with further rising temperature the reduction



proceeds, the equilibrium mixture of the two oxides, in presence of carbon, containing nearly 94 per cent of carbon monoxide at 850° C., a common carburizing temperature. At 1000° C. the per cent of carbon monoxide has increased to 99.4, as reported by Rhead and Wheeler.¹

Carbon monoxide dissolves in the surface layers of iron or steel, reacting then as follows:



Carbon so liberated forms a solid solution (austenite), which gives hardening characteristics. Carbon dioxide diffuses to the surface, where it reacts with more carbon to form carbon monoxide, so that a continuous cycle of reactions may take place, involving a given quantity of oxygen. However, in order to carry on the carburization more rapidly, some other agent must be added as an energizer.

If we may suppose that, in a given carburizing pot, approximately one liter of air is enclosed in the interstitial spaces, approximately 200

¹ J. Chem. Soc., 97:2179 (1910).

"Proc. Ind. Acad. Sci., vol. 42, 1932 (1933)."

milliliters of oxygen will be so enclosed. Excluding, for the moment, all chemical reactions, thermal expansion due to a rise of temperature from 20° to 850° will have reduced this oxygen content to 52 milliliters, as measured at the initial temperature. There is no change in gas volume due to formation of carbon dioxide but formation of carbon monoxide doubles the volume and, as the pot is never hermetically sealed, expansion from both causes expels gas mixture from the pot so that approximately atmospheric pressure prevails. Assuming the conversion of 94 per cent of the original carbon dioxide to monoxide at 850° (this is slightly altered by the presence of atmospheric nitrogen), the 52 milliliters of oxygen (represented by oxides of carbon) will now have become about 28 milliliters—again, as measured at 20° .

It is easy to see why the rate of carburization may be quite low, with so little oxygen available for these reactions, and energizers which will liberate carbon dioxide when heated will noticeably increase this rate. Energizers commonly used include carbonates of barium, calcium and sodium. The explanation for their action, as commonly accepted, is that they slowly evolve carbon dioxide at carburizing temperatures, and that this reacts with solid carbon to maintain the equilibrium mixture of oxides.

This role of energizers has recently been called into question. Enos² carried out a series of experiments, using wood charcoal and pitch coke as bases and a considerable number of carbonates, oxides and miscellaneous substances as energizers. While a detailed analysis of his results would be out of place here, his general conclusions were to the effect that carbonates, as such, are not needed as energizers, but that the oxides corresponding to these carbonates are equally good. He considers it a satisfactory explanation of energizing action to state that added substances act as catalyzers—some good, others not so good and still others as negative catalyzers.

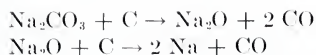
Ragatz and Kowalke^{3,4} similarly performed carburizing experiments, using wood charcoal as a base and a considerably larger list of both promising and apparently absurd compounds as possible energizers. They also concluded that the accepted explanation of energizing action is incorrect, with the conclusion that in all such compounds, the activity is a function of the metal itself, the rest of the compound being relatively unimportant. As one proof of this, they cited the case of calcium carbonate, often added to energize commercial carburizing mixtures, but found by them to be practically inert, although it decomposes readily to yield carbon dioxide when heated. (It may be remarked that others disagree with these authors concerning the relative value of calcium carbonate. See the discussion of Enos' paper, already cited.)

Ragatz and Kowalke, in their second paper, offer an ingenious explanation of the action of energizers, involving the discussion of gas concentration gradients and the use of differential equations. They suppose that, at carburizing temperatures, sodium carbonate reacts with carbon as follows:

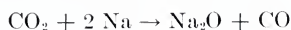
² Trans. Am. Soc. Steel Treating, 20:27 (1932).

³ Metals and Alloys, 2:290 (1931).

⁴ Ibid., 2:343 (1931).



The sodium so formed is projected as vapor into the gaseous phase, where it reduces carbon dioxide:



These reactions are thought to be responsible for the excellent properties of sodium carbonate as an energizer.

Barium carbonate also is a very much used energizer but the above explanation does not apply so well to it, on account of the fact that barium does not vaporize.

It seems to the present authors that in the attempt to find a complex explanation of the mechanism of the action of energizers, the authors already cited have overlooked a comparatively simple one. Enos dismisses the whole matter by supposing that added energizers act as "catalysts," the rate of catalysis and the sign, positive or negative, being a specific function of the substance employed. He concludes that a good energizer must be one containing oxygen but offers no explanation for the action of this oxygen. But few chemists are satisfied with a simple statement that a compound is a catalyst, if it is possible to determine what cycle of reactions is involved in the catalysis.

In making a detailed examination of the results reported in all of these papers one is impressed with the fact that generalizations may be made, as follows:

1. The positive energizers are either carbonates or compounds which may form carbonates in presence of carbon dioxide.

2. Of such compounds, the better energizers are those whose carbonates are decomposed—but *decomposed slowly*—at carburizing temperatures. Thus, sodium and barium carbonates or oxides are good energizers, calcium carbonate is a relatively poor one.

3. Certain compounds have no positive action, or they even have a negative one. In the lengthy list of Ragatz and Kowalke, such compounds as thiosulphates, borates and tungstates were found to be ineffective, as might well have been predicted.

4. It may be remarked that where wood charcoal is employed as a carburizer base, the presence of considerable quantities of potassium and sodium carbonates in the ash cannot be ignored. These are themselves excellent energizers.

In the discussion of the earlier portion of the present paper, we attempted to show that if we rely upon pure carbon and the air normally enclosed in the carburizing pot, carburizing action is very slow, largely because by the time carburizing temperatures are attained the available oxygen is relatively small in quantity, thermal expansion and increase in volume due to formation of carbon monoxide having expelled gases from the pot. Since carburization may be effected only by means of carbon monoxide, the concentration of this gas is brought to too low a value for rapid action to take place.

Consider, first, the effect of a slowly decomposable carbonate. As the temperature approaches that at which carburization may take place,

carbon dioxide begins to be evolved from the carbonate. This causes the expulsion of some gas from the pot but the gas mixture so expelled is chiefly atmospheric air, thus replacing a mixture approximately one-fifth oxygen by pure carbon dioxide, each molecule of the latter being equivalent, in potential carburizing power, to one molecule of oxygen. The essential carburizing gas thus rises in concentration, since carbon dioxide is converted, at higher temperatures, into carbon monoxide. However, if the carbonate decomposes too easily and in the lower temperature ranges, its enriching power is too soon spent. Later backward diffusion of air continuously dilutes the carbon monoxide with nitrogen, so that in protracted carburizations the concentration of carbon monoxide drops back continuously toward that which would have prevailed if pure carbon had been employed.

In order that a carbonate may serve as a practical energizer, it should yield its carbon dioxide slowly and over a period extending to several hours. In this manner it will continuously oppose normal dilution by backward diffusing nitrogen.

Consider next the case of the oxide of the metal, corresponding to a given carbonate. At the lowest temperature recorded by Rhead and Wheeler (*loc. cit.*) the equilibrium mixture of the two oxides of carbon, in contact with solid carbon, contains 62.4 per cent of carbon dioxide. This is for a temperature of 650° and there is undoubtedly some oxidation of carbon at still lower temperatures. Such carbon dioxide will partially combine with the metallic oxide, thus disturbing equilibrium between the two gases and resulting in the formation of more carbon dioxide. At the same time absorption of the gas will prevent, to a considerable extent, expulsion of gases from the pot. If the resulting carbonate is one that decomposes at relatively low temperatures, correspondingly small quantities of carbon dioxide will combine with the metallic oxide to form carbonate, while if the carbonate is one which would decompose slowly and only at higher temperatures, it is easily seen that the carbonate formed will act as a reservoir for carbon dioxide (potential carbon monoxide) thus acting exactly as would have been the case if the carbonate, instead of the oxide, had been employed in the first place. In other words, whether we start with carbonate or oxide, we shall have, at a given higher temperature, about the same compound present in either case.

In order to test this hypothesis, two carburizing mixtures were prepared. The carbon base of both was of sugar carbon and this was mixed with 15 per cent of energizer. In one mixture calcium oxide, made by heating calcium carbonate, was the energizer, in the other barium oxide.

These mixtures were heated to various temperatures, enclosed in quartz tubes having one end closed and the other connected with a water seal, to prevent backward diffusion of air. The tubes were heated, in turn, at temperature intervals of 100°, from 400° to 900°. At the end of ten minutes at the stated temperature the contents of the tubes were removed and carbon dioxide determined.

Allowing for the small amount of carbonate found in the original oxides, by a previous analysis, it was found that the carburizer containing calcium oxide increased in carbonate content up to 800°, where

its carbon dioxide content indicated that it was approximately one-fourth converted into carbonate. At 900° carbon dioxide had fallen to about 4 per cent of that corresponding to pure carbonate.

The sample energized with barium oxide contained 6.1 per cent of carbon dioxide at 400° and this steadily increased up to 800°, where conversion was practically complete. At higher temperatures the carbon dioxide content fell somewhat, indicating the gradual decomposition of the carbonate.

So far as these experiments have progressed, the results would seem to confirm the general hypothesis, and to render unnecessary either an accounting for all energizing effects upon the vague assumption of "catalysis," or the setting up of complicated mechanisms, based upon assumed and highly hypothetical reactions.

