

1926

The graphitizing behavior of iron carbide in pure iron-carbon alloys for the temperature interval 7000 C to 11000 C

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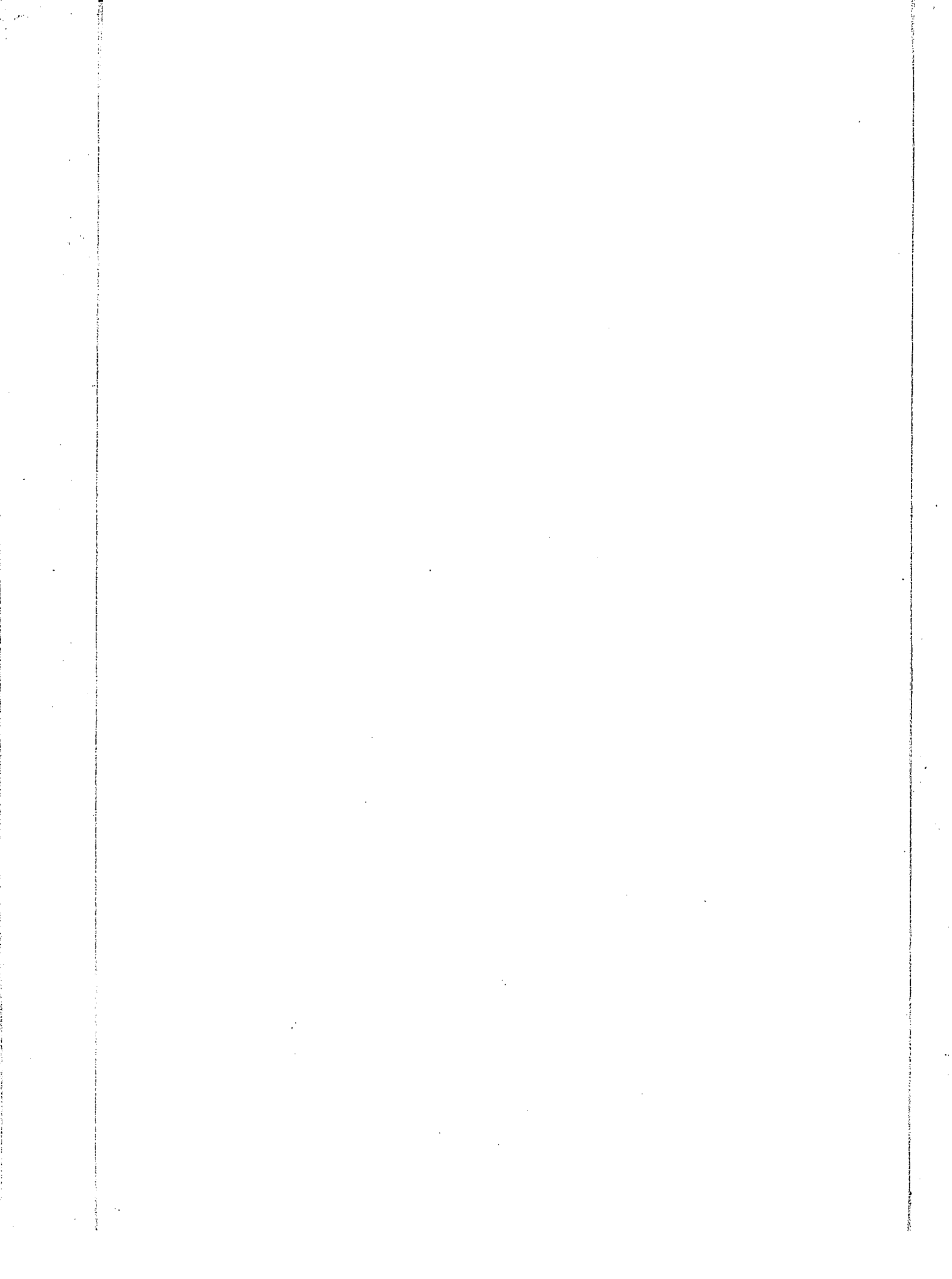
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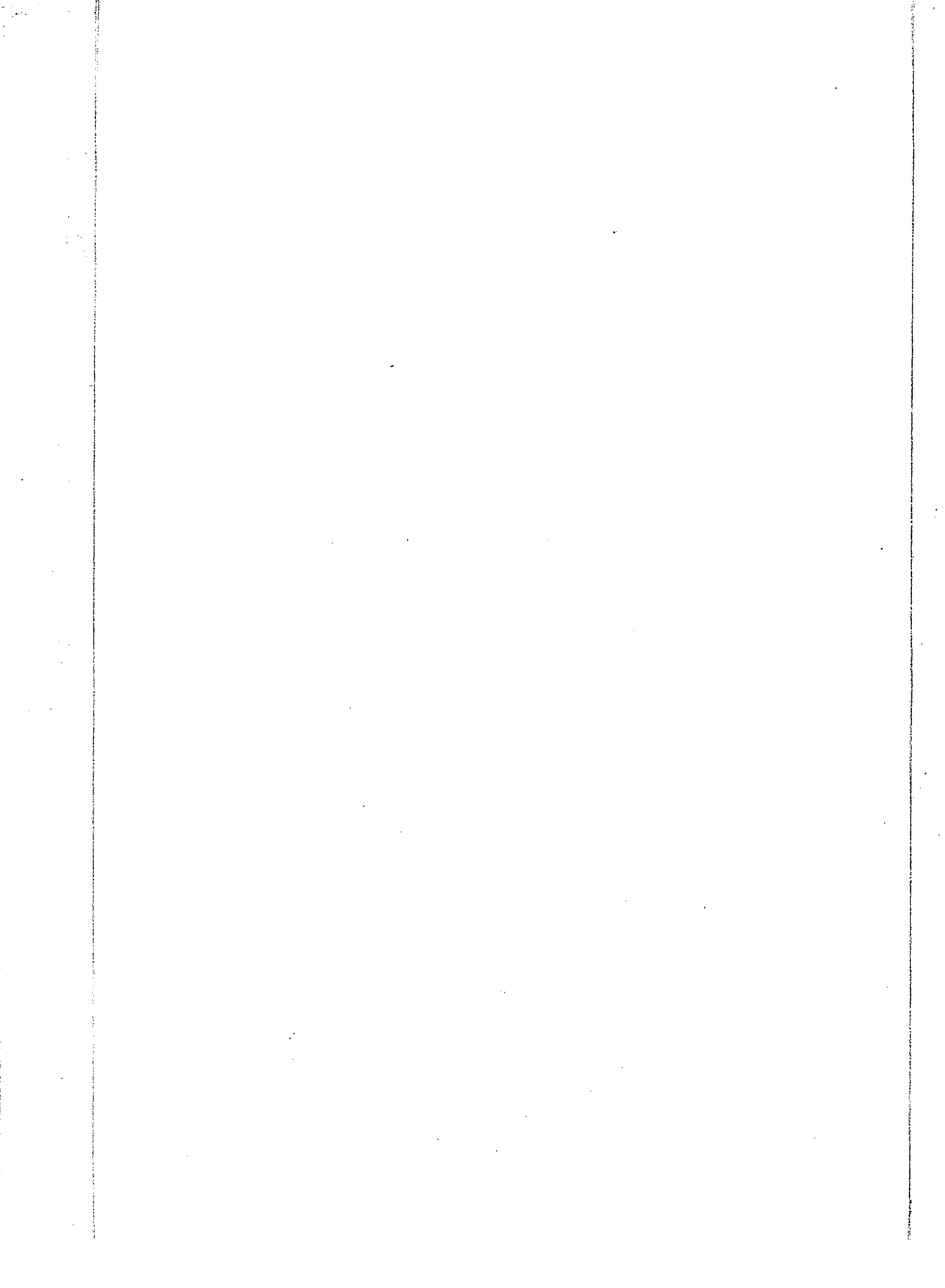
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THE GRAPHITIZING BEHAVIOR OF IRON CARBIDE IN PURE IRON-
CARBON ALLOYS FOR THE TEMPERATURE INTERVAL
700° C. to 1100° C.

By

Harry P. Evans

A Thesis Submitted to the Graduate Faculty
for the Degree of
DOCTOR OF PHILOSOPHY
Major Subject: Physical Chemistry

Approved:

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1926

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The writer wishes to express his sincere thanks to Professor Anson Hayes who suggested and directed this problem and gave valuable suggestions throughout the progress of the work.

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I. REVIEW OF LITERATURE.

The three double line iron carbon diagrams in most general use are those of Benedict¹, of Ruff² and of Wittorf³. The portion of these three diagrams, which is important in explaining the graphitizing properties of pure iron-carbon alloys below the solidification range, i.e., below about 1134° C., differ only in the relative slopes of the carbon solubility and of the cementite solubility lines. (The latter will be called the Acm line).

Benedict's diagram (Fig. 1) shows the slope of the Acm line to be greater than that of the carbon solubility line. Wittorf indicates that the two lines are parallel, while Ruff has drawn them with the carbon solubility line having the greater slope. Benedict's diagram would require also, as would Wittorf's as well, that pure iron carbon alloys should graphitize completely on cooling slowly, since the carbon solubility line lies to the left of the cementite solubility line. Ruff's diagram, however, offers the possibility of an intersection of these two lines. At this point of intersection, and for temperatures below it, iron carbide should be stable.

1. Metallurgie, 5, page 45 (1908).
2. Metallurgie, 8, page 457 (1911).
3. J. Russ. Physical Chem. Soc. 43, 1613 (1911). (Original article not read): Chem. Abstracts 6, page 2907 (1912).

It is well known that iron carbide in commercial white cast iron is metastable throughout the entire critical range. In the case of pure iron-carbon alloys, however, this fact has not been established. At temperatures slightly below 1134° C. iron carbide is known to be metastable. Honda states, however, that pure iron-carbon alloys will not graphitize below 900° C. Schwartz has held a sample at 900° C. for over 2000 hours with no indications of graphitization. A search of the literature yields no report of graphitization below 900° C.

Maxwell and Hayes, however, in work done in this laboratory⁴ established the fact that iron carbide is metastable at temperatures of 650° C. and 700° C. These facts would indicate either that iron carbide is stable in the temperature interval 700° C. to 900° C., or that if metastable, it exists in a very persistent metastable state.

II. THEORETICAL DISCUSSION.

The present investigations were instigated primarily in an attempt to establish the stability or metastability of iron carbide in pure iron-carbon alloys in the temperature interval 700° C. to 1100° C. If it should appear

4. Jr. of the Am. Chem. Soc., 48, page 584 (1926).

metastable in this range the fact would be established that iron carbide is metastable in the whole critical range up to 1134° C., that is, that the carbon solubility line lies to the left of the cementite solubility line.

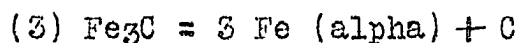
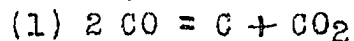
The results obtained were from iron-carbon alloys containing an extremely small amount of impurities. The analysis of the alloys accompanies the results. While no claim is made that the alloys are pure, the very low value for the impurities present should produce behaviors approaching very closely that of pure iron-carbon alloys. With these facts in mind, we resume our consideration of these alloys, calling them pure iron-carbon alloys for sake of convenience.

It was evident at the outset of the investigation that iron carbide, if metastable in this temperature range existed in a very persistent metastable condition. An attempt was made to establish the optimum conditions for the breaking down of iron carbide possibly by exposing it to the action of some catalytic agent which would hasten the rate of decomposition. Hayes and Scott⁵, in work done in this laboratory, showed that in the case of white cast iron at a temperature of 927° C., carbon monoxide carbon dioxide

5. Am. Foundrymen's Ass., Preprint No. 480.

mixtures at a pressure of 5 atmospheres increased the rate of absorption of free iron carbide nearly 100%.

The following reactions may be considered to accurately represent a possible mechanism for the graphitization of pure iron-carbon alloys below the critical range.



The fact was pointed out by Schenck that the net result of reactions (1) and (2), i.e., reaction (1) proceeding toward the right and reaction (2) toward the left, is the equivalent of reaction (3) proceeding toward the right.

Now if we let ΔF_1 , ΔF_2 , and ΔF_3 represent respectively the change in the free energy content (the change in the value of the Gibbs Zeta function, for a more complete discussion of which see "Thermodynamics" by Lewis and Randall, McGraw-Hill) accompanying each of these reactions when proceeding from left to right then the second law of thermodynamics demands that $\Delta F_1 - \Delta F_2 = \Delta F_3$. If this were not the case, a cyclical process involving reaction (3) proceeding in one direction and of reactions (1) and (2) so as to carry out the equivalent of reaction (3) in the opposite direction, could be carried out in such a manner as to accumulate an indefinite quantity of available energy.

Thus, to be more specific, assume that reaction (3) represents a spontaneous process when proceeding from left to right and that during the breakdown of one formula weight of the carbide, a quantity of available energy ΔF_3 is stored up and that this quantity of energy is greater than $\Delta F_1 - \Delta F_2$, which latter quantity represents the available energy stored up when the same change is carried out by means of reactions (1) and (2).

Under such a set of conditions, it would be possible to use a portion of the energy ΔF_3 to produce a formula weight of the carbide Fe_3C from carbon and alpha iron by means of the two reactions (1) and (2) carried out in the reverse direction. When this is accomplished, all of the various substances are in the original condition and as a net result we have gained a quantity of available energy represented by the quantity $\Delta F_3 - (\Delta F_1 - \Delta F_2)$. The conclusion thus reached is that $\Delta F_3 = (\Delta F_1 - \Delta F_2)$.

The mass law equilibrium constants for reactions (1) and (2) may be represented by the following expressions:

$$K_1 = \frac{P_{1-CO_2}}{P_1^2} \quad \text{and} \quad K_2 = \frac{P_{1-CO_2}}{P_2^2 - CO}$$

where p represents the partial pressures of the carbon monoxide and carbon dioxide at equilibrium with the solid phases for reactions (1) and (2) respectively.

Now $\Delta F_1 = -RT \ln K_1$ and $\Delta F_2 = -RT \ln K_2$ where the reactants are brought into the reaction at unit pressure and where the products of the reaction are removed at unit pressure (See Lewis and Randall, "Thermodynamics", McGraw-Hill), and where R is the molal gas constant and T is the absolute temperature.

From these relations it follows that

$$\Delta F_3 = \Delta F_1 - \Delta F_2 = RT(\ln K_2 - \ln K_1).$$

If reaction (3) is a spontaneous process ΔF_3 must be negative, i.e., the free energy content of Fe_3C must be greater than that of $3 Fe (\alpha) + C$. This in turn requires that

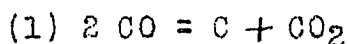
$$K_2 < K_1 \quad \text{or that} \quad \frac{P_{2-CO_2}}{P_2^{2-CO}} \quad \frac{P_{1-CO_2}}{P_1^{2-CO}} \quad \text{or}$$

if the total pressure is constant at one atmosphere, this requires that $P_{2-CO_2} < P_{1-CO_2}$ and that $P_{2-CO} > P_{1-CO}$.

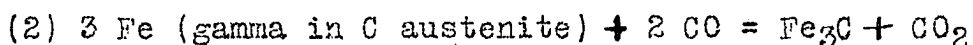
Above the critical range figure 2, which is taken from Schenck and which represents the results of equilibrium studies of Matsubara, requires that the carbide in pure iron-carbide alloys be stable. Attention should be called to the fact that at these temperatures, the partial pressure of carbon monoxide is higher in equilibrium with carbon than it is in contact with saturated austenite and free iron carbide. Also, the partial pressure of carbon dioxide is

greater in contact with iron carbide and austenite than with carbon.

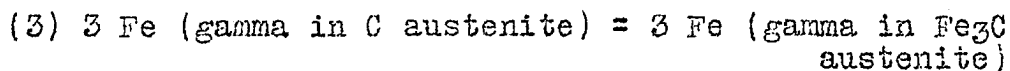
That this condition of pressure gradient exists when iron carbide is the stable phase in pure iron-carbon alloys may be shown from a consideration of the changes of state necessary for the formation of one formula weight of Fe_3C from the gamma iron of austenite and carbon as follows:



$$\text{Free energy change} = \Delta F_1 = -RT \ln K_1$$

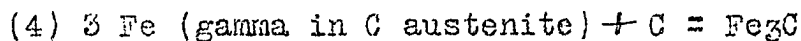


$$\text{Free energy change} = \Delta F_2 = -RT \ln K_2$$



$$\text{Free energy change} = \Delta F_3$$

Addition of (2) and (3) minus (1) gives



$$\text{Free energy of formation of iron carbide} = \Delta F_4$$

$$\text{or, } \Delta F_4 = \Delta F_2 - \Delta F_1 + \Delta F_3 = RT(\ln K_1 - \ln K_2) + \Delta F_3.$$

Now if Fe_3C is the stable phase, the free energy content of the (C austenite) and of the carbon from which Fe_3C is formed is greater than the free energy content of the Fe_3C , i.e., ΔF_4 is negative. Furthermore, ΔF_3 must be positive. This latter conclusion may be reached as follows.

Note: The expressions "(C austenite)" and "(Fe C austenite)" are used to represent austenite saturated with carbon from carbon and from Fe_3C respectively.

The solubility of a constituent from a metastable system is always higher than from a stable phase. If Fe_3C is the stable phase, austenite saturated with carbon from carbon contains more carbon than does austenite saturated with carbon from Fe_3C . This being the case, the concentration of gamma iron in (C austenite) would be less than it is in (Fe_3C austenite). Since energy is required to transfer a constituent from a lower to a higher concentration ΔF_3 is positive if Fe_3C is the stable phase. Going back to a consideration of the relation

$$\Delta F_4 = \Delta F_2 - \Delta F_1 + \Delta F_3 = RT(\ln K_1 - \ln K_2) + \Delta F_3$$

the following conclusion may be reached.

ΔF_4 is negative since Fe_3C is assumed to be the stable phase and ΔF_3 is positive, therefore ΔF_1 must exceed the sum of

$$\Delta F_2 + \Delta F_3 \quad \text{or}$$

$$F_1 > F_2 \quad \text{and}$$

$$K_1 < K_2 \quad \text{or}$$

$$\frac{P_1\text{-CO}_2}{P_1\text{-CO}} < \frac{P_2\text{-CO}_2}{P_2\text{-CO}}$$

from which it will be seen that a pressure gradient of CO_2 should exist from carbon to Fe_3C and of CO in the opposite direction.

Considerations exactly similar to these will show that if Fe_3C is assumed to be the metastable phase, $K_2 < K_1$ or the direction of the pressure gradients are reversed.

From the above treatment it is to be expected that if iron containing carbon near the saturated value is readily permeable to a gas mixture of carbon monoxide and carbon dioxide, these gases should assist in the graphitizing process. Figure 3 shows the gas mixture acting as a carrier of carbon from cementite to carbon spot, and in short, shows the significance of the metastability of cementite at this temperature.

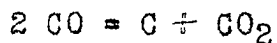
A consideration of the mechanism by which a gas mixture acts will show definitely that a gas mixture richer in carbon monoxide than that corresponding to the equilibrium value for carbon will introduce carbon into austenite saturated with carbon from carbon. See figure 4. It also indicates that a still higher value of carbon monoxide would convert iron into free iron carbide and that a carbon monoxide content less than that corresponding to equilibrium with carbon would oxidize carbon from a sample saturated with carbon either from cementite or carbon.

If then a pure iron-carbon alloy be subjected to a gaseous mixture, keeping on the carbon dioxide side of equili-

brium values, it is to be expected that at some depth in the piece the gas mixture will reach an equilibrium value with carbon. In the exterior of the piece the excess carbon dioxide will act as an oxidizing agent, oxidizing iron carbide to iron and carbon monoxide. As the gas mixture diffuses into the piece, the carbon dioxide in contact with iron carbide will continue to pick up carbon, by forming carbon monoxide, until at a certain depth the gas mixture reaches an equilibrium value with carbon. Immediately beyond this point the gas mixture should catalyse the breakdown of cementite and the formation of carbon according to figure 3.

It was with these facts in mind that the present piece of work was undertaken. In figure 5 is shown the carbon monoxide content of the carbon monoxide and carbon dioxide mixtures in equilibrium with carbon over the temperature range 650° C. to 1000° C. and at pressures of one and five atmospheres as given in data from work of Rhead and Wheeler⁶.

The values for temperatures below 800° C. were obtained by extrapolation from the higher temperatures where experimental determinations were obtained by Rhead and Wheeler. In this extrapolation the change in the heat content ΔH of the reaction



6. Jr. Chem. Soc., 99, page 1140 (1911).

was taken as -41950 calories and the equation

$$2303 \log \frac{K_2}{K_1} = \frac{\Delta H}{R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

was used.

III. APPARATUS AND METHOD OF PROCEDURE.

The apparatus shown in figure 6 was developed in which gas mixtures of varying ratios of carbon monoxide and carbon dioxide contents could be obtained and in which those mixtures could be applied to the sample at pressures up to 100 pounds per square inch and at temperatures up to 1000° C. A description of this apparatus and the manner of operating it follows.

A is a carbon dioxide tank, B is a pressure gauge and C a control valve. D and H are drying chambers made from two inch black pipe eighteen inches long, threaded at both ends and fitted with caps. These chambers are filled with calcium chloride and phosphorus pentoxide. The carbon chamber E is made from three inch black pipe, three feet long threaded at both ends and fitted with caps. This chamber is filled with carbon. The lower end is filled with loose gas carbon and the part exposed inside the muffle furnace F is packed with powdered wood charcoal or graphite. A thin layer of gas carbon is packed on top of this. This

tube is filled only to the point at which it emerges from the furnace at the top. G is a chamber, similar in size and construction to D and H and is filled with a 35 per cent solution of potassium hydroxide to absorb any great excess of carbon dioxide. I is the pressure furnace. It is made from a piece of ten inch steam main, eighteen inches long, threaded at both ends and fitted with companion flanges. The ends are closed by bolting copper plates between the flanges at each end. A rubber gasket between the plate and the inside flange serves to make the chamber hold pressure up to 100 pounds. In the center of this chamber is placed a twelve inch heating element J. This is held in place by a silocel packing and heat insulator. The gas mixture is led in through the rear plate directly to the end of this element. The end of the element is closed with transite board washers. The element is heated by 110 volt alternating current and the temperature controlled by placing rheostats in the circuit. K is a nickel receptacle with an iron lining on its upper surface. The sample is placed in this and packed with finely divided carbon, graphite or wood charcoal, leaving only the end next to the observation tube P exposed. The temperature is recorded by means of an optical pyrometer focused through P on the sample. The stopcock L is left partially open during the anneal and the gas mix-

ture burned at this point. At frequent intervals samples of the gas are withdrawn here, collected over mercury, and analyzed for carbon monoxide and carbon dioxide by use of an Orsat gas analysis apparatus.

The sample to be annealed is placed in K and packed with carbon as described. The receptacle is placed approximately in the center of the heating element and the front plate and flange bolted on. Transite board washers with a one-fourth inch hole may be used to fill the end of the heating element. They prevent considerable radiation and are specially necessary in annealing long samples.

The tube G is filled about two-thirds full of the potassium hydroxide solution and is assembled in the line. This and the carbon chamber should be refilled after each anneal but the drying tubes need not be filled more than once in three or four runs.

After the muffle furnace has reached the desired temperature the control valve C is opened slightly and the carbon dioxide is allowed to pass slowly into the apparatus. The stopcock L is left open and as soon as the gas will burn here a sample is collected and analyzed. When the proper mixture is obtained, the stopcock is nearly closed and the gas pressure is slowly built up. To reach a total pressure of five atmospheres and a composition of about 95 per

cent carbon monoxide, required about thirty minutes to build up the pressure.

As soon as the proper pressure has been reached the current is turned on in the pressure furnace without any resistance in the circuit. It required about fifteen minutes for the sample to come to dull red heat at this rate, and about twenty minutes longer to reach 927° C. By adjustment of the rheostats this temperature can be accurately maintained for any given length of time. On cooling it requires twenty-five to thirty minutes to cool from 927° C. down to dull red heat again.

IV. PREPARATION OF ALLOYS.

Pure iron-carbon alloys were made by melting pure Armco iron and pure Acheson graphite. The iron was cut into discs from rods, and the graphite was finely divided. Weighed quantities of the iron discs and graphite were placed alternately in a magnesia lined graphite crucible and melted in an induction furnace. The magnesia linings were made from Bakers Analysed highest purity magnesium oxide. The alloy was held in the molten state for one-half hour to insure uniform composition. The alloys prepared weighed approximately 100 grams and on microscopic examina-

tion proved to be free from graphitic carbon. A representative analysis of the alloys gave the following composition:

<u>S</u>	<u>Si</u>	<u>P</u>	<u>Mn</u>	<u>C</u>
0.025%	0.022%	0.0045%	0.045%	2.34%

V. EXPERIMENTAL DATA AND DISCUSSION.

Sample I: The original sample on which treatments below were made is shown in Figure 7. It consists of free cementite and pearlite. In Figure 8 and Figure 9 are shown the results of a five hour anneal at 927° C. under a pressure of 5 atmospheres in a carbon monoxide, carbon dioxide mixture whose composition varied during the run from 80% to 85% carbon monoxide. The samples were etched in 5% nitric acid in alcohol. There was complete absorption of free cementite almost to the center of the piece. In Figure 8 is shown the structure at a depth of approximately 3/16 inches. Absorption of free cementite is complete and considerable bull's eye structure is evident. In Figure 11 is shown the structure at the center of the piece. A comparison of this figure with the original shown in Figure 8 shows a marked absorption of cementite and deposition of temper carbon.

Sample 2: The original sample on which treatments below were made is shown in Figure 9. This sample is similar in structure to that of Sample 1. In Figure 10 are shown the results of a 27 hour anneal at 800° C. under a pressure of 5 atmospheres in contact with a carbon monoxide carbon dioxide gas mixture containing 55% carbon monoxide. From Figure 4 it will be observed that at 800° C. the equilibrium value for CO in a CO - CO₂ gas mixture in contact with carbon under a pressure of 5 atmospheres is slightly above 60%. This experiment, therefore, was carried out on the CO₂ side of equilibrium values, i.e., in a slightly oxidizing atmosphere. This sample, which was in the form of a short rod, was polished on the side rather than on the end. By repeated removal of narrow sections the course of graphitization could be traced into the interior of the sample.

In Figure 10 is shown the structure toward the exterior of the piece. As is to be expected, the matrix shows hypoeutectoid structure. There is very little evidence of bull's eye structure. Carbon had been thrown out and has not been completely removed by oxidation. As the examination proceeds toward the interior of the sample, the structure approaches that of a eutectoid matrix. At a depth of approximately 3/16 inch the bull's eye structure, as shown

in Figure 11 has developed. The structure of the matrix at this depth is very slightly hypo-eutectoid. The composition is therefore very close to that one would expect for pure iron-carbon alloy of iron-carbon eutectoid composition.

The work of Hayes and Flanders⁷ on white cast iron compositions indicates that bull's eye structure is produced during the operation of the iron-carbon eutectoid. The fact that similar structures were obtained in the present work may be considered evidence of the operation of an iron-carbon eutectoid in pure iron-carbon alloys, if the temperature at which this point should occur is very near 800° C. Since the method of treatment is such as to make certain that at some point in the alloy compositions of austenite corresponding to that of the iron-carbon eutectoid must be produced, it is also possible that some of this bull's eye structure may have been formed while cooling the sample. In this case the conclusion would be reached that the temperature of the iron-carbon eutectoid in pure iron-carbon alloys is somewhere between 720° C. and 800° C.

In Figure 13 is shown the structure of the unetched sample at the same depth as Figure 12. Abundant carbon spots are in evidence. Iron carbide is not encountered till a

7. Trans. of Am. Soc. for Steel Treating, Feb. (1924), page 183.

considerably greater depth is reached. In Figure 14 is shown the structure in this region. Considerable unabsorbed free cementite is evident, as is also temper carbon. In Figure 15, which is unetched, is shown the structure at a still greater depth. Carbon spots are still very numerous in the pearlite areas. The structure shown in Figure 14 and Figure 15 continues to the center of the piece with slightly increasing free cementite areas.

VI. CONCLUSION.

The experimental data presented in this thesis indicates that under the conditions of the experiment iron carbide is metastable at 800° C. and 927° C. It is a well known fact that commercial white cast irons undergo an expansion when graphitized. We would expect the same order of expansion for pure iron-carbon white cast irons. We should also expect, from pressure considerations alone, that since graphitization occurs at a pressure of five atmospheres it should occur even more readily at a pressure of one atmosphere since the decrease in pressure allows more readily the expansion due to graphitization.

There remains the possibility that the decrease in pressure of the gas mixture from five atmospheres to one atmosphere may decrease the solubility of CO and CO₂ in

iron and iron carbide in such a manner as to change the activities of iron and iron carbide to values that will make carbon stable as iron carbide rather than as carbon, i.e., iron carbide might be stable in contact with these gas mixtures at one atmosphere pressure. In order for such a condition as this to exist, however, it can be shown that considerable quantities of CO and CO₂ must be absorbed by the metal. Measurements of the quantities of these gases absorbed at five atmospheres pressure have not been made. Consequently, it is only possible to state that at 800° C. and 927° C. pure iron-carbon alloys of approximately 2.34% C content graphitize when in contact with suitable gas mixtures of CO and CO₂ at a pressure of five atmospheres.

In other words, iron carbide in pure iron-carbon alloys is a metastable phase in the presence of CO and CO₂ mixtures applied at a pressure of five atmospheres.

VII. SUMMARY.

Pure iron-carbon alloys have been graphitized for the first time in the temperature interval 700° C. to 900° C. Evidences are presented which suggest the operation of an iron-carbon eutectoid in pure iron-carbon alloys.

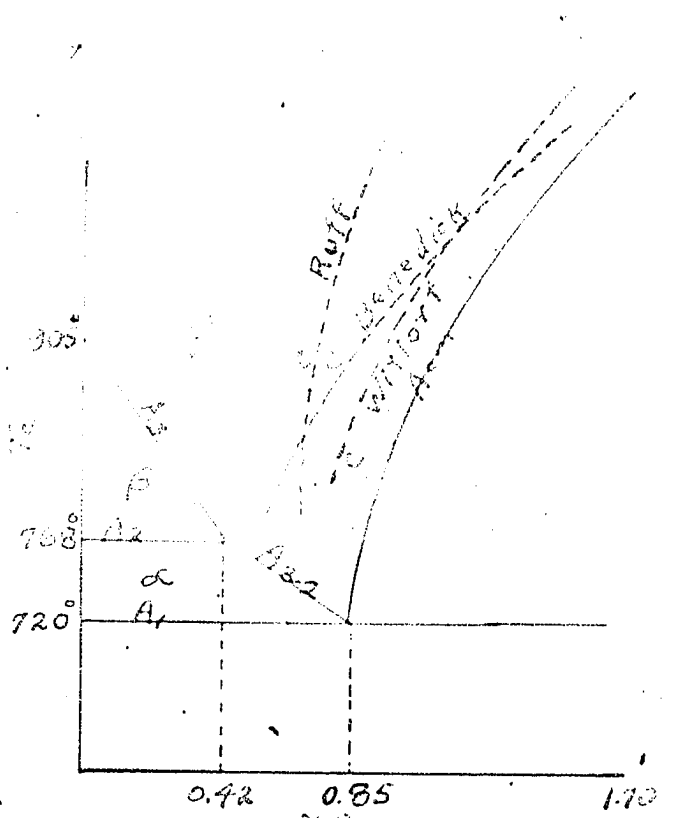


Fig. 1

Fig.1. Iron Carbon Equilibrium Diagram.

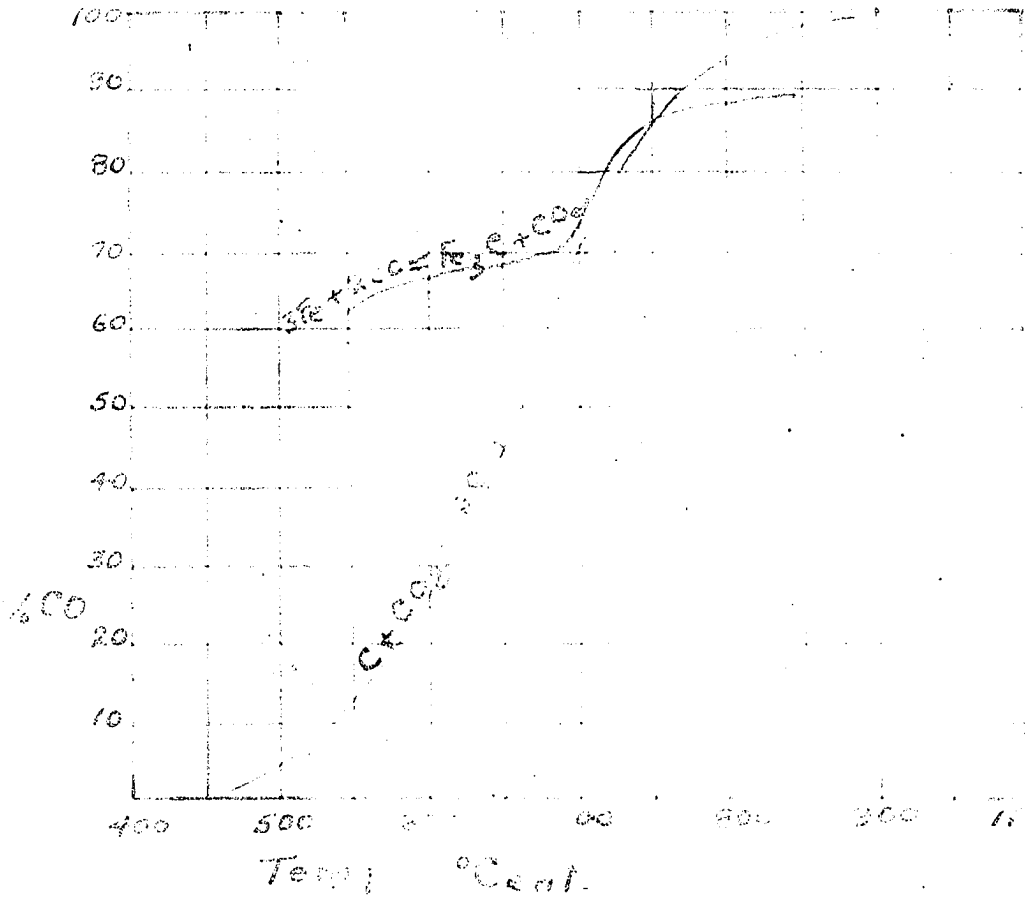


Fig. 2.

Fig. 2. Gas Equilibrium Diagram.

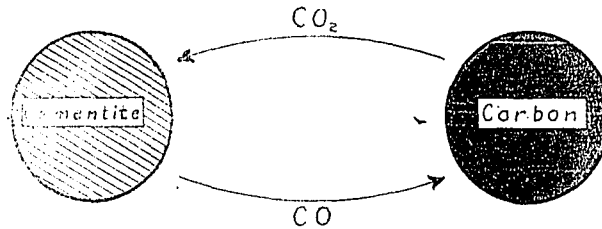


Fig. 2.

Fig. 3.

Gas Mixture Acting as a Carrier of Carbon in Graphitizing Process.

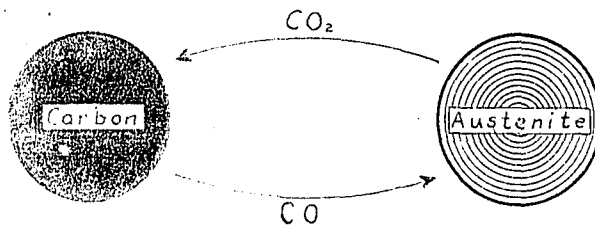


Fig. 1.

Fig. 4.

Gas Mixture Acting as a Carrier of Carbon in Carbonizing Process.

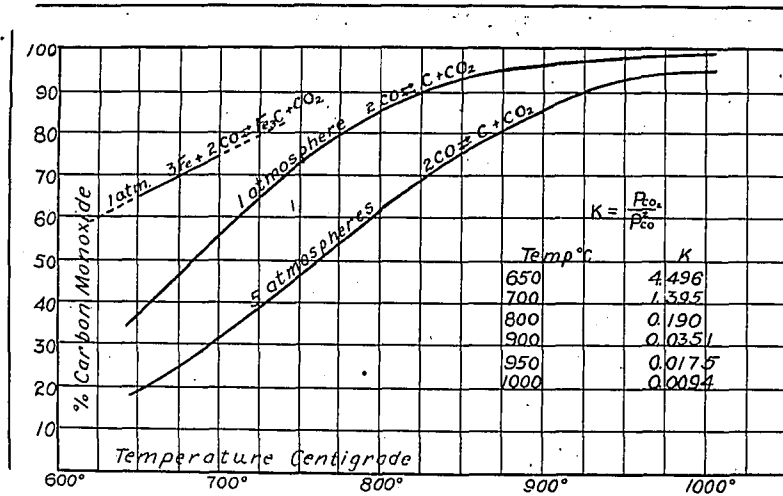


Fig. 12.

Fig. 5.

Compositions of gases in equilibrium with carbon and in equilibrium with alpha iron and iron carbide.

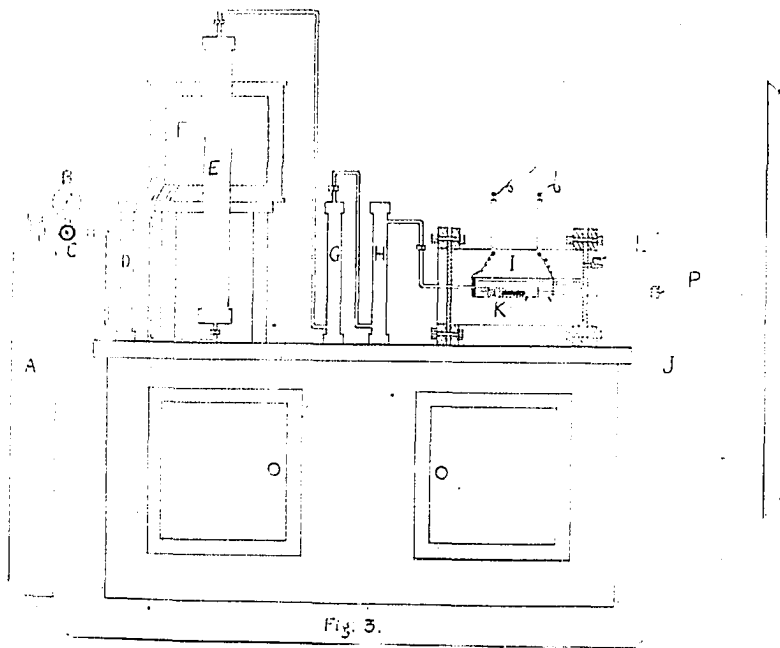


Fig. 3.

Fig. 6.

Apparatus for Annealing under Various Pressures of Carbon Monoxide, Carbon Dioxide Mixtures.

A--Carbon Dioxide Tank, B and C--Pressure Regulator, D and H--Calcium Chloride Drying Towers, F--Hoskins Muffle Furnace, Set on End, E--Iron Pipe, Packed with Carbon, G--Potassium Hydroxide Tower, I--Silocel, K--Sample, Packed in Graphite, J--Heating Element, L--Gas Cock, P--Observation Tube.

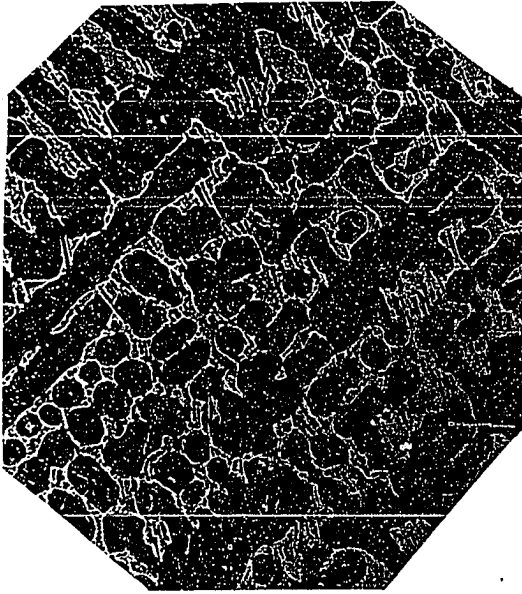


Fig. 7. Sample 1, original.
Etched in nitric acid. x 90.

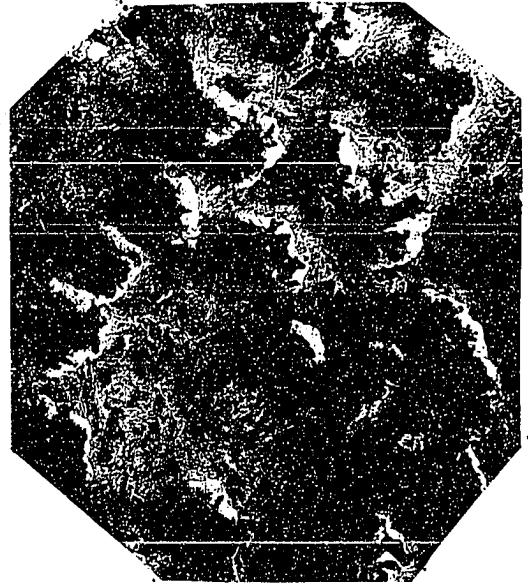


Fig. 8. Sample 1, Depth $3/16$ in.
Etched in nitric acid. x 90.

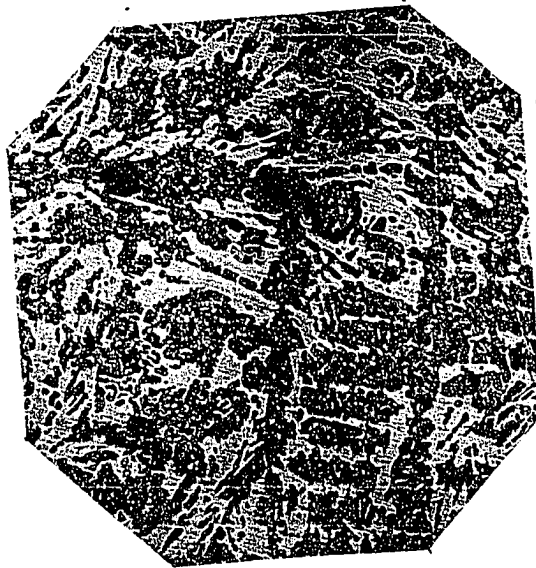


Fig. 9. Sample 1. Center of piece.
Etched in nitric acid. x 90.

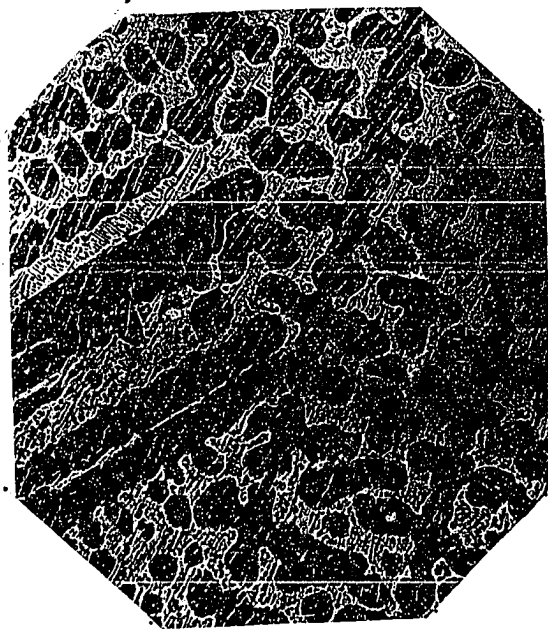


Fig. 10. Sample 2, original.
Etched in nitric acid. x 90.

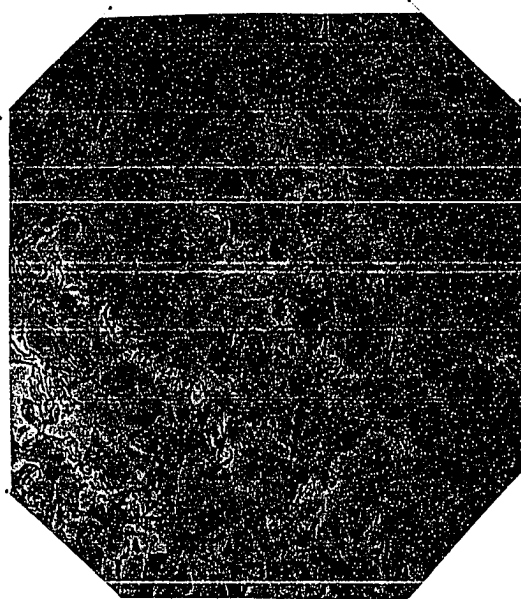


Fig. 11. Sample 2, close to
surface. Etched in nitric
acid. x 90.

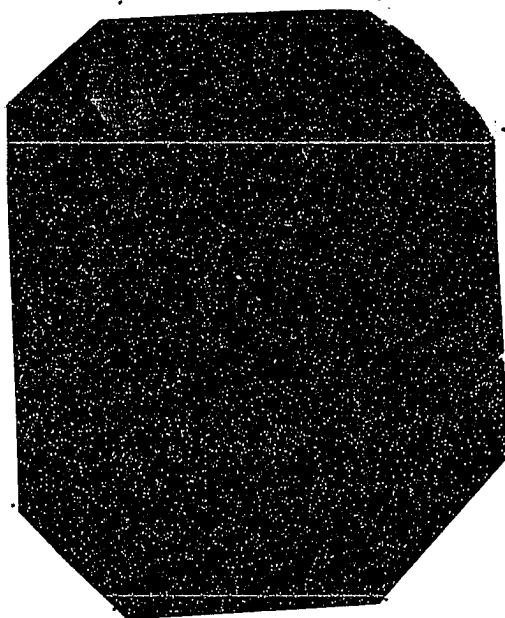


Fig. 12. Sample 2, depth 3/16
in. Etched in nitric acid.
x 90.

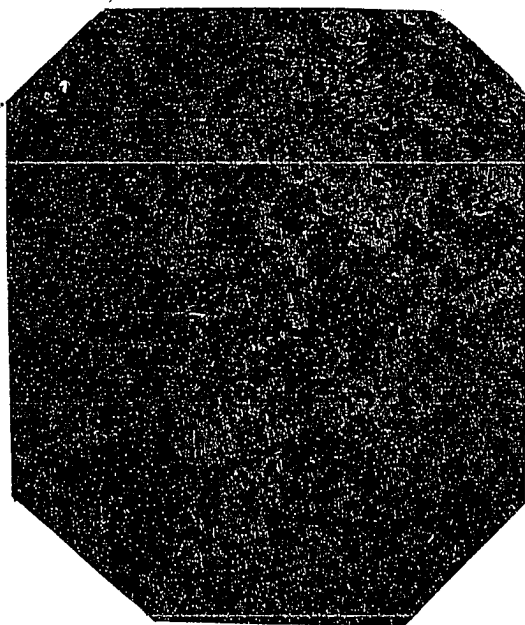


Fig. 13. Sample 2 (deeper
than Fig. 12). Etched in
nitric acid. x 90.

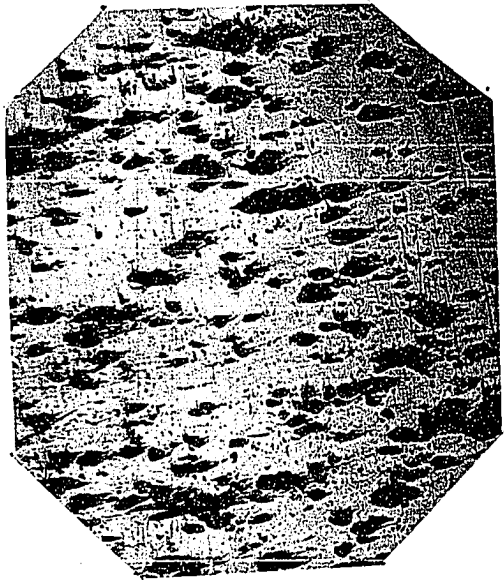


Fig. 14. Same depth as Fig. 13. Unetched. x 90.

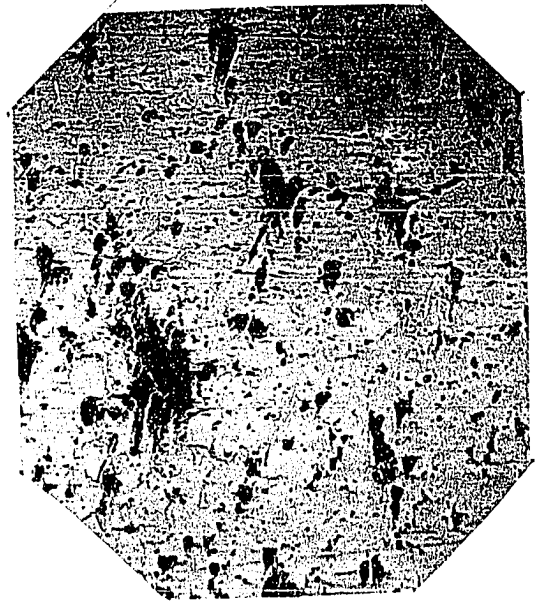


Fig. 15. Still greater depth. Unetched. x 90.

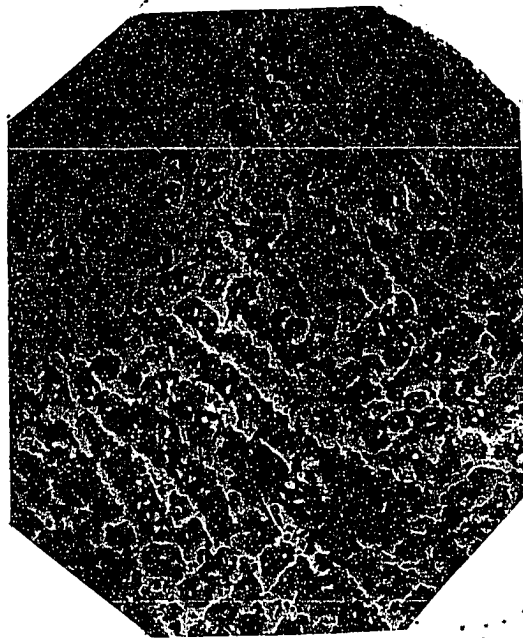


Fig. 16. Near center. Etched in nitric acid. x 90.