

GRAPHITE FLAKE STRUCTURAL CHANGES PRODUCED
BY ANNEALING GRAY CAST IRON

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A thesis submitted to the Faculty and the Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirement for the degree of Master of Science.

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Date January 20, 1951.

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INTRODUCTION

Cast irons are essentially iron-carbon-silicon alloys containing also varying amounts of manganese, sulphur, and phosphorus as an invariable rule. For convenience or practical uses, cast irons can be considered as an iron-carbon-silicon ternary system. Under certain condition of composition and cooling, cast irons have major microstructural phases consisting of iron carbide (cementite), and a solid solution of carbon in α or γ iron. In these cases the carbon is said to be in the combined form. On the other hand, according to its composition and thermal treatment, a cast iron may have major microstructural phases consisting of graphite and a solid solution of carbon in α or γ iron. It is generally assumed that iron carbide can be considered as a metastable or thermodynamically unstable compound of considerable persistence under certain thermal treatment and with graphitizing or without carbide stabilizing alloying elements.

The mechanical properties and general behavior of a cast iron are considerably affected by the form of graphite present. The recent development of cast iron foundry practice, which produces various types of graphite in cast iron to satisfy different engineering requirements,

has made the cast irons more important than ever. Many experts have devoted their work to the investigation of the theories and mechanisms of graphite formation, cementite stabilization, graphitizing, etc., yet, no complete and satisfactory solution has been offered. In this paper, the author has devoted and restricted himself to a small problem concerning one kind of behavior of graphite flakes in ordinary gray cast iron after special heat treatment.

It is well known that graphite flakes in ordinary gray cast iron are a high temperature product; they have a structure similar to natural and synthetic graphite, which is layered hexagonal and possesses anisotropic properties. Upon any kind of heat treatment the graphite flakes in gray cast iron are supposed not to change. R. M. Brick and A. Phillips state: "Heat treatment of cast irons will not affect the graphite structure, at least not that representing carbon in excess of the amount soluble in austenite." Also, "graphite forming as flakes at high temperatures can not be changed to the nodular form."¹/ However, J. Bernstein in his experiment of annealing gray cast iron in hydrogen found that some of the graphite flakes were changed and states: "Some decarburization occurred at the surface, and the adjacent zone the flake graphite

structure had been replaced by very fine nodular graphite. The center of the section had the normal flake graphite structure. In some areas these nodules appeared to consist of remnants of graphite flakes, upon which a further precipitation of graphite had taken place during the anneal."2/ Ping-chao Chen in connection with research conducted at the Colorado School of Mines shows microphotographs of graphite spheroids instead of graphite flakes in the decarburized gray cast iron of his samples.3/ Later, S. N. Anant Narayan, also of the Colorado School of Mines, continued the research of Ping-chao Chen on the decarburization of gray cast iron for welding. He reported observing spheroidal graphite similar to that shown in Chen's pictures.4/ Chen's and Narayan's experimental results obtained under the supervision of Professor Morton C. Smith initiated the author's curiosity. Further reading brought out the discrepancy of opinions expressed by R. M. Brick, A. Phillips and J. Bernstein. Is it possible to change the structure of the graphite flakes in gray cast iron? If not, what are the sources of those fine nodular graphite particles produced in Bernstein's, Chen's and Narayan's work?

EXPERIMENTAL WORK

Part 1

PRODUCTION OF GRAPHITE FLAKE STRUCTURAL CHANGES BY ANNEALING GRAY CAST IRON

Before trying to explain anything about the structural changes of the graphite flakes in gray cast iron, we have to find out how and under what conditions we can produce this kind of change. Fig. 1 shows the graphite spheroids in gray cast iron, which were produced by J. Bernstein. Fig. 2 and Fig. 3 show individual graphite spheroids at higher magnification. J. Bernstein annealed ordinary gray cast iron in both dry and moist hydrogen for 100 hours at a temperature of $1000^{\circ}\text{C}.$, and found that either in dry or in moist hydrogen, the graphite flakes were replaced by the fine nodular graphite in the region between the decarburized surface layer and the original unchanged center portion of the sample.

In surveying Bernstein's work, the author found that there are three important and variable conditions involved in his experiment. First, $1000^{\circ}\text{C}.$ is a temperature far above the transformation range. Second, 100 hours is a rather long heating period. Third, hydrogen is a decarburizing agent. In accordance with these three conditions, the author started an experiment of heating a number of gray cast iron samples of similar composition

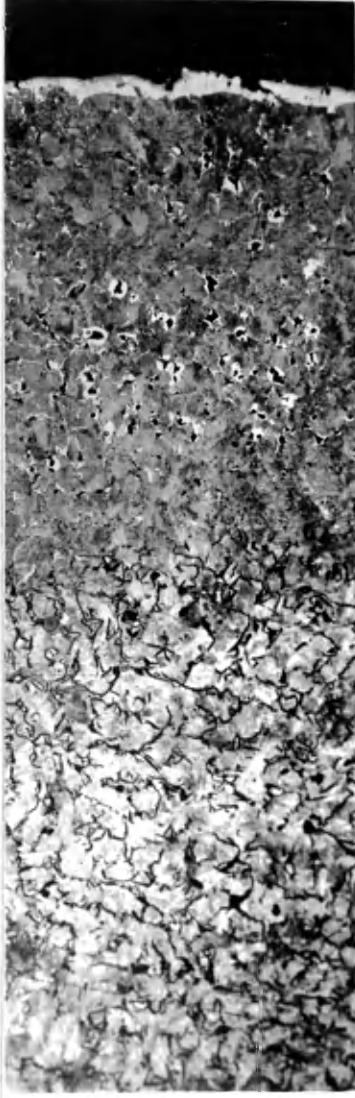


Fig. 10 Structure of grey-iron specimen annealed for 100 hr. at 1000 C. in pure dry hydrogen 60

Fig. 1. Graphite spheroids in decarburized gray cast iron.
Reproduced from *Journal of Iron and Steel Institute*,
volume 159, page 13, 1948.

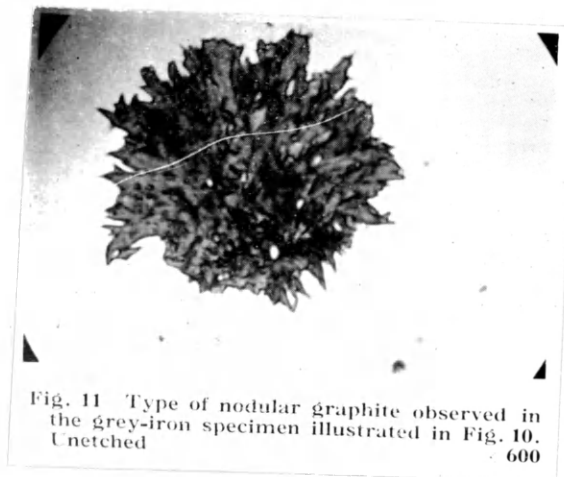


Fig. 2.

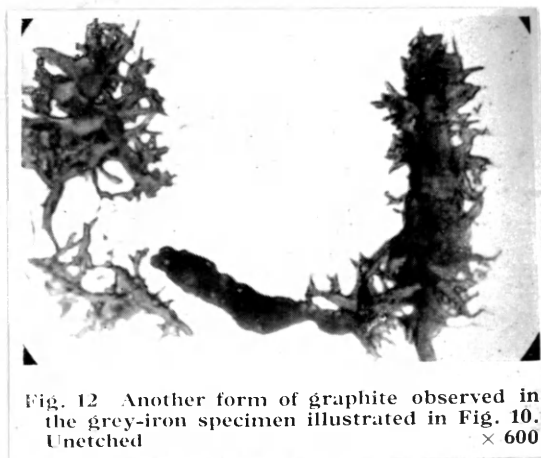


Fig. 3.

Fig. 2 and Fig. 3. Some individual graphite spheroids observed in Fig. 1, at higher magnification.

Reproduced from Journal of Iron and Steel Institute, volume 159, page 13, 1948.

and microstructure above the transformation range, in an air atmosphere.

The equipment used for this experiment included an electrical resistance pot furnace (Multiple Unit type 84); a resistance, connected in series with the heating elements of the furnace; a thermocouple, inserted from the top into the furnace in order to measure the furnace temperature.

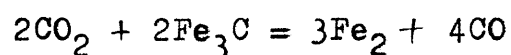
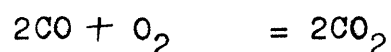
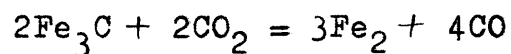
The specimens were placed in the furnace and heated in an air atmosphere. The adjusting of the resistance gradually brought the furnace temperature up to 1800°F. After a certain interval of time a sample was drawn from the furnace, and examined under the microscope to find out whether or not there was any change in microstructure of the sample.

The following table lists a series of samples obtained by the procedure as stated above.

Sample No.	Heating Time	Temperature
11	47 hours	1800°F.
12	71 "	"
13	96 "	"
14	143 "	"
15	190 "	"
16	270 "	"

Table 1.

The microstructure of the original sample, as shown in Fig. 4 and Fig. 5, essentially is the ordinary gray cast iron structure with graphite flakes in a matrix of pearlite. (Pearlite is the eutectoid of carbide and iron). Upon being heated to just above the transformation temperature (about 1330°F.), the eutectoid material becomes a solid solution of carbon in γ iron while the graphite remains unchanged. Upon further heating considerably above the transformation temperature (for instance, in this experiment, to a temperature of 1800°F.), the solvent power of austenite is greater than that of austenite at 1330°F. The heated austenite therefore begins dissolving carbon from any neighboring masses of either graphite or cementite.^{5/} The constituents existing in samples under these conditions are graphite and austenite. Since the samples were heated in air, an oxidizing atmosphere, the carbon in the combined form was first to be oxidized. (The free carbon does not oxidize unless it has first recombined with the iron).^{6/} The elimination of carbon usually occurs at the surface of the sample, according to the following equations:



It can be seen that most decarburized cast

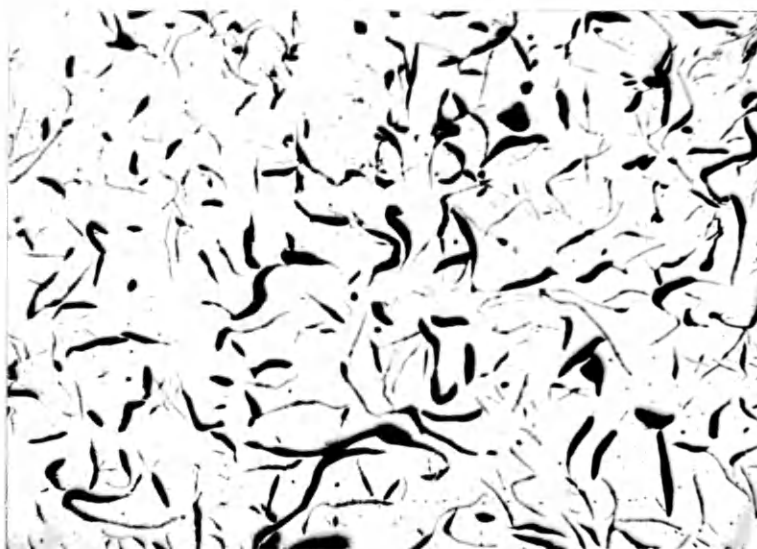


Fig. 4. Microstructure of original cast iron
sample.

Magnification: 100 diameters

Etchant: Unetched

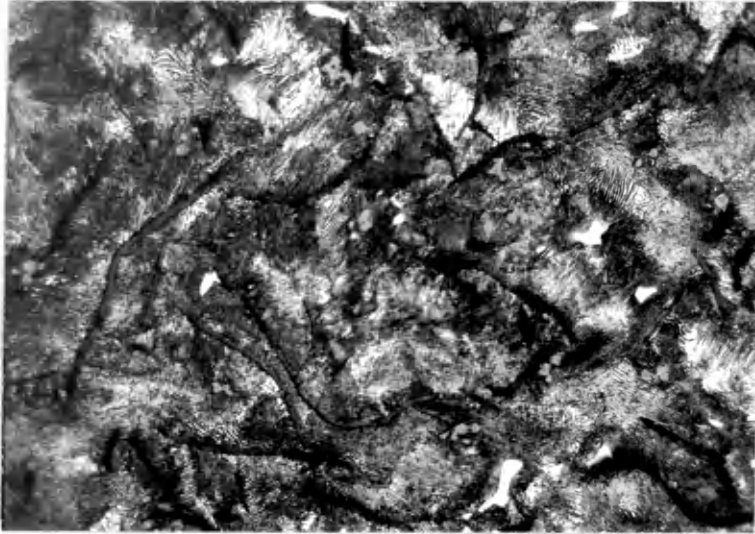


Fig. 5. Microstructure of original gray cast iron sample.

Magnification: 250 diameters

Etchant: Picral

iron samples have a layer of ferrite at its surface. This structure, high carbon in the center and low carbon at the surface, results in a concentration gradient. As long as sufficient heating is carried on and the temperature is high enough, the carbon will diffuse from center toward the surface,^{6/} and decarburization will occur continuously until no carbon is left in the sample. But the air at a temperature of 1800°F. is a strong oxidizing agent; both the carbon and the iron at the surface of the sample, exposed to such a strong oxidizing agent, will be oxidized. The amount of the carbon diffusing from the center of the sample is not large and the rate is not fast enough to reduce the oxidized iron at the surface of the sample. Therefore, before the carbon in the sample has been entirely eliminated, a layer of iron oxide will form instead of ferrite. The longer the heating time, the more of the sample will be oxidized, and the more the carbon in the sample will be eliminated. Eventually, a stage of a mass of ferrite wrapped with iron oxide can be obtained. If the sample were further heated, then nothing would be left but iron oxide.

Fig. 6, a photograph, shows a series of samples after heat treatments corresponding to those listed in Table 1. The original samples were in cylindrical form about $\frac{3}{4}$ inch high, 1 inch in diameter. After annealing

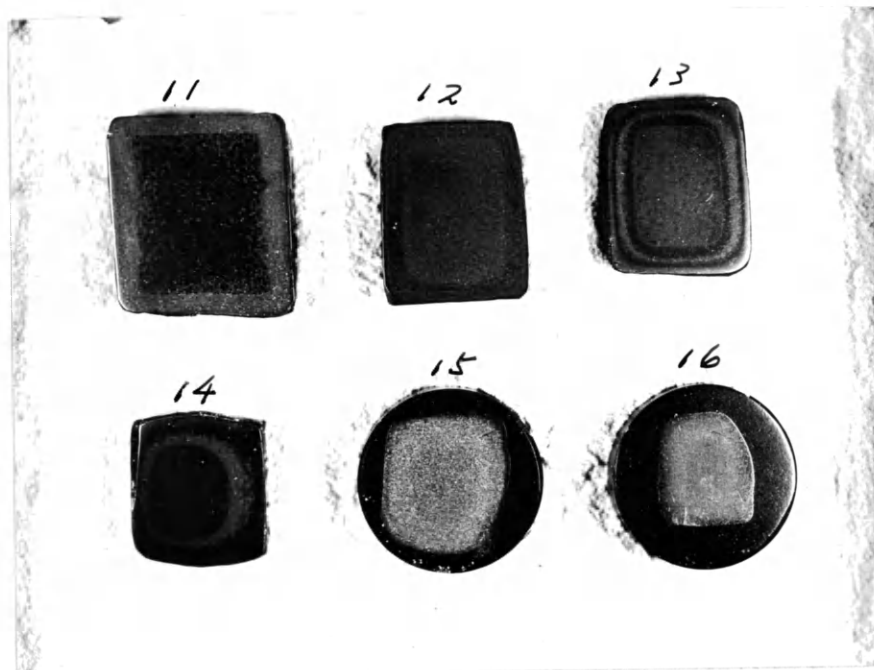


Fig. 6. Macrostructures of a series of samples after heat treatments corresponding to those listed in Table 1.

Magnification: 1 diameter

Etchant : Sample No. 11 was etched with nital.

Samples No. 12, No. 13, No. 14, No. 15,

No. 16 were etched with picral.

Samples No. 15 and No. 16 are mounted in bakelite.

in air and air cooling the samples to room temperature, each sample was bisected along the axis, then the newly cut surface was polished and examined. From this photograph it can be seen that the longer the heating period is, the more of the sample has been oxidized. The size of the sample No. 16 is about one-third of its original size (the oxidized part has been taken off).

In a decarburized cast iron sample, it is common to have layers of different microstructures. Hatfield's explanation is that the combined carbon in the center of the sample is higher than that at the surface; a concentration gradient results, causing diffusion of carbon from center toward surface. Upon cooling, the difference in concentration of combined carbon and the difference in cooling rate at different locations in the sample, will give different microstructures in the sample.^{6/} This gives a satisfactory explanation to the two rings revealed in samples No. 11 and No. 12, but for the rest of the samples, the condition seems much more complicated; no satisfactory explanation can yet be obtained.

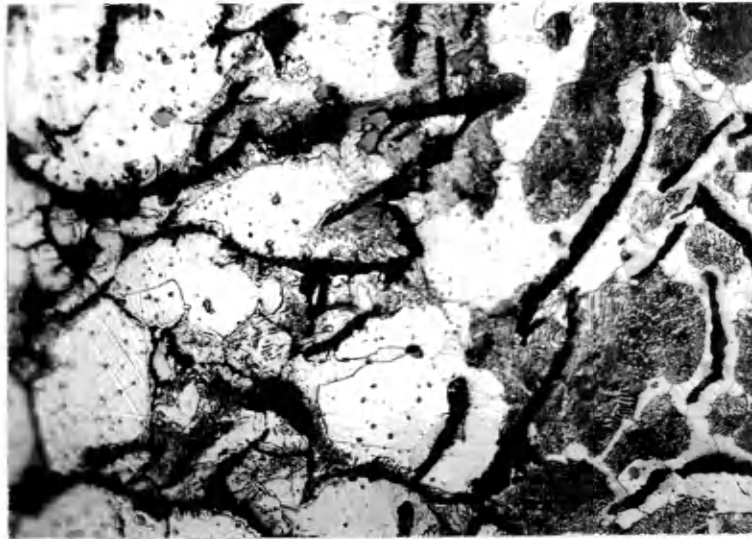


Fig. 7. Microstructure at the edge of sample
No. 11, next to the layer of ferrite.

Magnification : 250 diameters

Etchant: Nital

Heat treatment: Annealed at 1800°F. for 47 hours in an air
atmosphere and air cooled.

The graphite remains in its flaky form. Part
of the combined carbon has been eliminated. Upon cooling
the matrix has behaved as a hypoeutectoid steel.

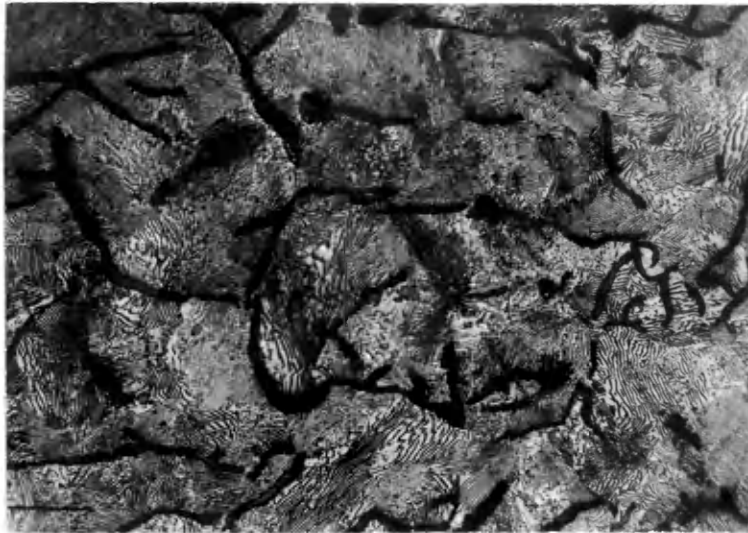


Fig. 8. Microstructure on the pearlite ring of
sample No. 11.

Magnification : 250 diameters

Etchant: Nital

Heat treatment: Same as in Fig. 7

As in Fig. 7, the graphite flakes here remain unchanged, but the combined carbon is higher than that in Fig. 7--approximately the eutectoid composition. Upon cooling the matrix has become entirely pearlitic.

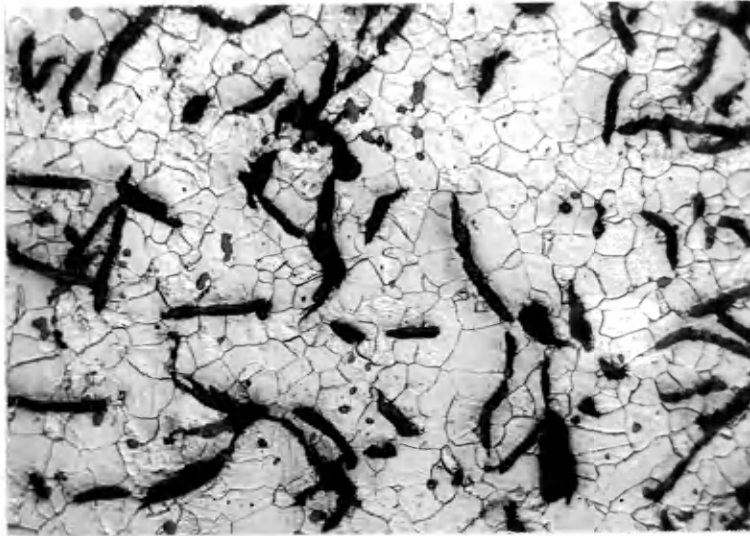


Fig. 9. Microstructure at the center of sample
No. 11.

Magnification : 250 diameters

Etchant: Nital

Heat treatment: Same as in Fig. 7

At the austenitizing temperature, the austenite in this part of the sample became saturated with carbon; also the rate of subsequent cooling was slower than that at the edges. Upon cooling, both the proeutectoid and eutectoid cementite were decomposed into ferrite and carbon; the former remained as matrix while the latter combined with the masses of graphite, which originally were present as graphite flakes.^{5/} As shown in this picture, the graphite flakes are considerably thickened.

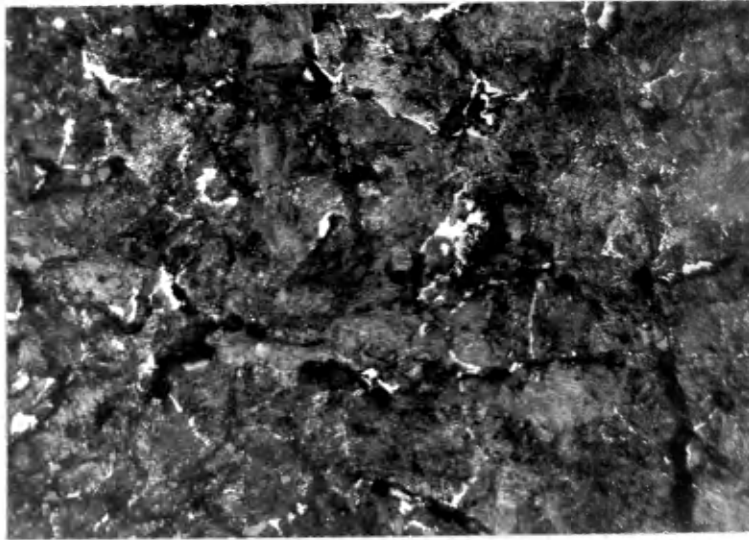


Fig. 10. Microstructure on the pearlite ring of
sample No. 12.

Magnification : 250 diameters Etchant: Picral

Heat treatment: Annealed at 1800°F. for 71 hours in an air
atmosphere and air cooled. The annealing
time was 23 hours longer than for sample
No. 11.

The graphite still remains in its flaky form.
The matrix is pearlite with a slight amount of proeutectoid
ferrite outlining the original austenite grain boundaries.

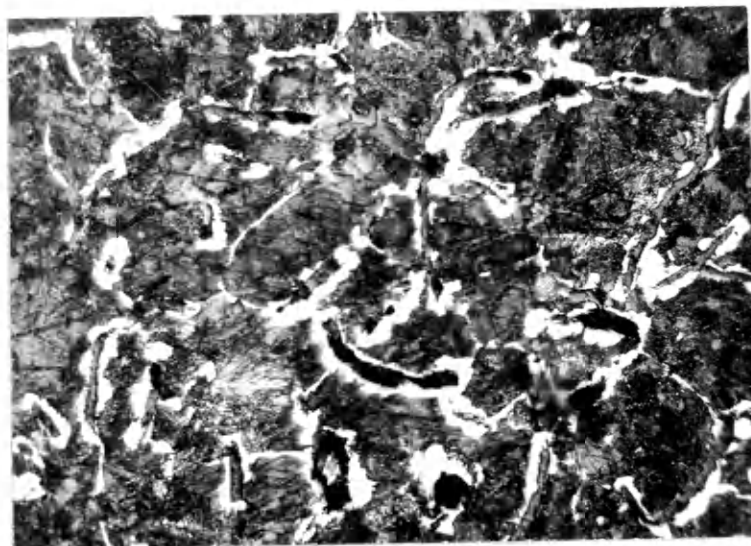


Fig. 11. Microstructure at the center of sample
No. 12.

Magnification : 250 diameters

Etchant: Picral

Heat treatment: Same as in Fig. 10.

As the annealing process is carried on, more of the combined carbon is eliminated. According to the iron-carbon equilibrium diagram, the solubility of carbon in austenite is definite at certain temperature. In order to reach the equilibrium condition, some of the carbon from adjacent graphite masses has to be redissolved into the austenite. As shown in this picture, the graphite still remains in its flaky form, but the flakes are not so thick as those shown in Fig. 9. Upon cooling, austenite transforms into pearlite. Austenite may give an entirely graphitized matrix or partly graphitized matrix according to the cooling rate and the silicon content in the sample.

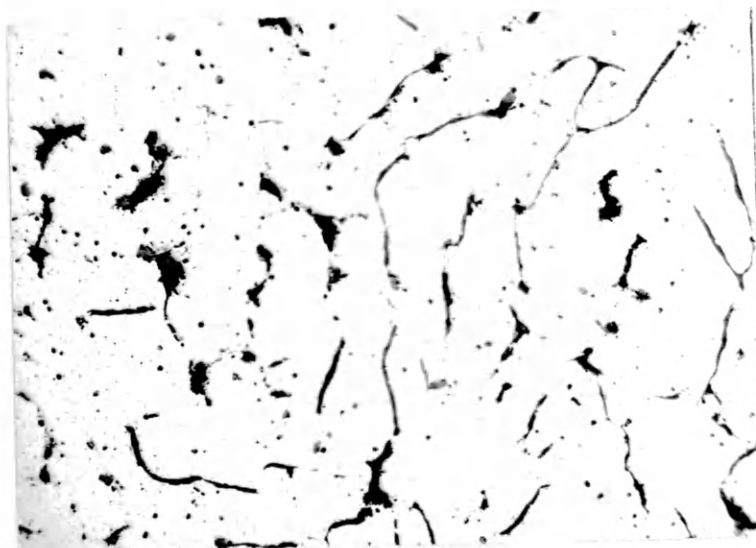


Fig. 12. Graphite in sample No. 13.

Magnification : 250 diameters

Etchant: Unetched

Heat treatment: Annealed at 1800°F. for 96 hours in an air atmosphere and air cooled. Annealing time was 25 hours longer than sample No. 12, and 48 hours longer than sample No. 11.

As the annealing process proceeds, the combined carbon in the sample is continuously eliminated, and the graphitic carbon continuously goes into solution. As shown in this picture, the graphite flakes are much thinner than in sample No. 11, and the flake form remains unchanged.

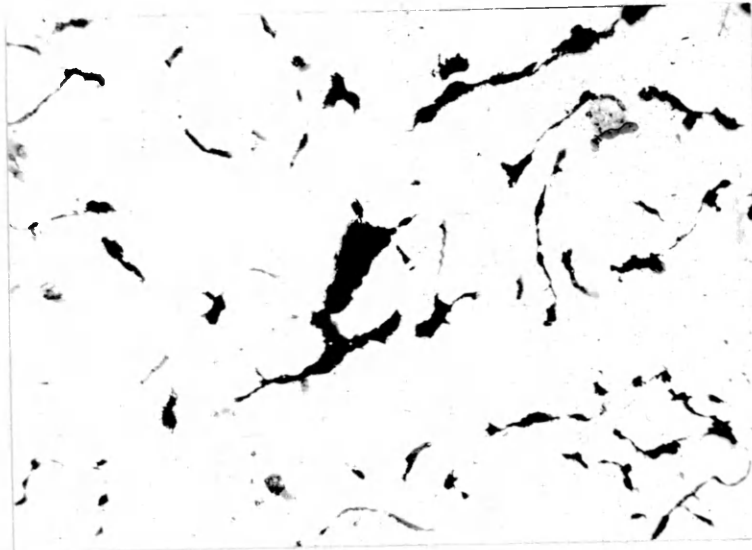


Fig. 13. Graphite in sample No. 14.

Magnification : 250 diameters

Etchant: Unetched

Heat treatment: Annealed at 1800^oF. for 143 hours in an
air atmosphere and air cooled.

The continuous elimination of carbon decreases
the amount and size of graphite flakes.

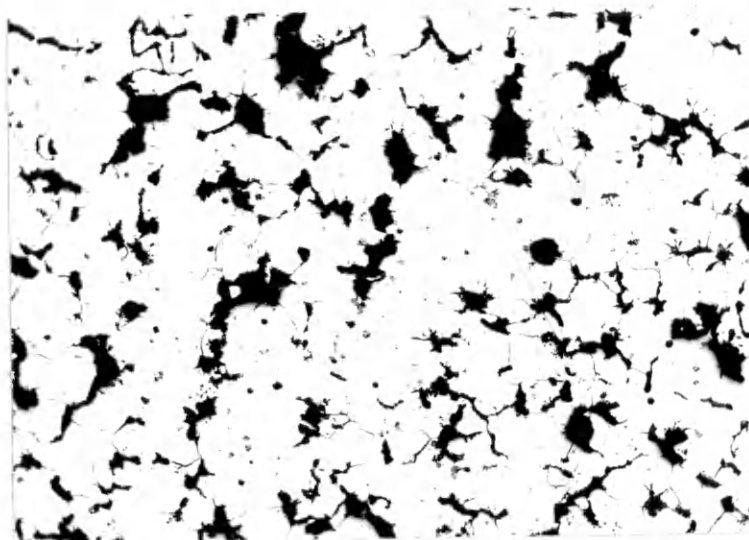


Fig. 15. Graphite masses in sample No. 15.

Magnification : 100 diameters

Etchant: Unetched

Heat treatment: Annealed at 1800°F. for 190 hours in an
air atmosphere and air cooled.

A very strange change of the graphite structure occurs in this sample. As shown in Fig. 6, the appearance of the structure of this sample is quite uniform, and so is the microstructure. Most of the graphite flakes are changed to the form shown in the picture above, except in the extreme center portion of the sample, where the graphite still remains in its flaky form.

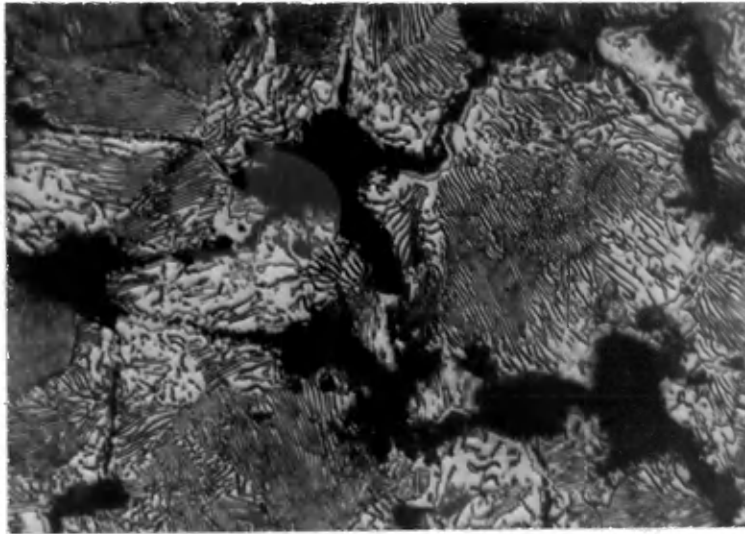


Fig. 16. Microstructure of sample No. 15.

Magnification : 500 diameters Etchant: Nital

Heat treatment: Same as in Fig. 15.

With higher magnification the picture shows some individual graphite masses (represented by blackened areas) in a matrix of pearlite.

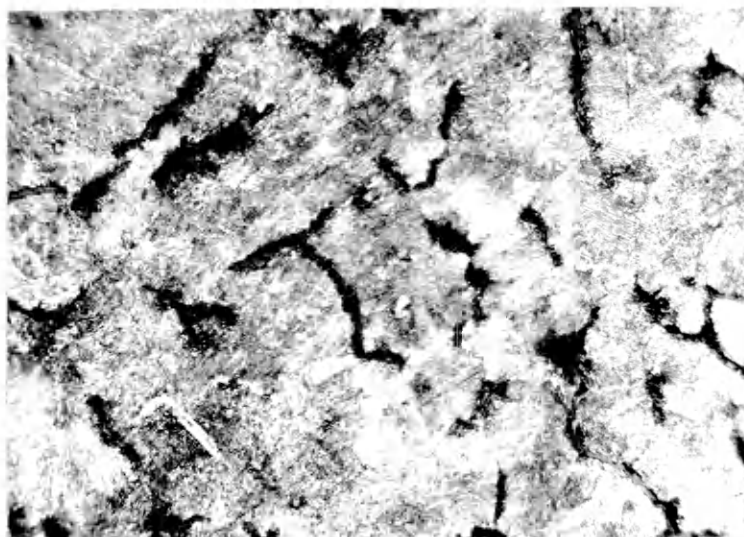


Fig. 17. Microstructure at the center of sample
No. 15.

Magnification : 250 diameters

Etchant: Picral

Heat treatment: Same as in Fig. 15.

The pearlitic ground mass is unchanged throughout the sample, but some of the graphite still persists in its flaky form.



Fig. 18. Microstructure of sample No. 16.

Magnification : 250 diameters

Etchant: Unetched

Heat treatment: Annealed at 1800°F. for 270 hours in an air atmosphere and air cooled. The annealing time was 80 hours longer than sample No. 15.

In sample No. 15, the voids revealed at the polished surface (represented by the blackened areas in Fig. 15) are supposed to have been occupied previously by graphite. But the oxidizing atmosphere may penetrate into the sample to a certain depth during the annealing period, and the oxidation may also result in some oxidized voids.^{6/} In order to make sure that those voids in sample No. 15 are not oxidized voids, further annealing and more oxidation were given to sample No. 16. As shown in this picture, no apparent voids nor discontinuities can be seen under microscope.

The graphitic carbon in this sample has been almost entirely eliminated.

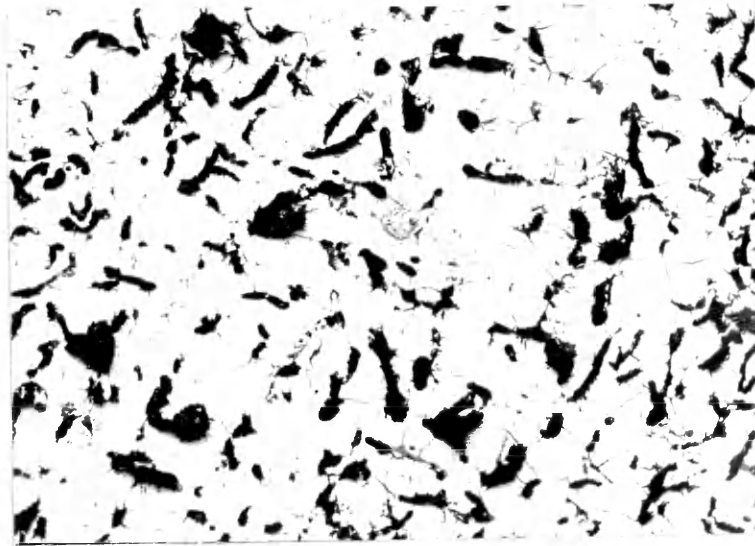


Fig. 19. Microstructure of sample No. 15Q.

Magnification : 100 diameters Etchant: Unetched
Heat treatment: Annealed at 1800°F. for 190 hours in an
air atmosphere and quenched in water.

(Refer to sample No. 15). According to the equilibrium diagram the solubility of carbon in austenite is higher at higher temperature. Upon cooling, following the A_{cm} line, the excess carbon will separate from the austenite as cementite. And subsequently, if cooling rate is low, the separated cementite will decompose into graphite and ferrite. Although no evidence of decomposed cementite (i.e. no free ferrite) can be seen in Fig. 16 and Fig. 17, this experiment was made to ensure that there is no possibility that the graphite in sample No. 15 was separated from austenite during cooling. When a sample similar to Nom 15 was quenched from 1800°F., as shown in picture above, the graphite remains the same as in Fig. 15.

Part 2
ANNEALING OF GRAY CAST IRON BELOW THE
TRANSFORMATION TEMPERATURE

In the previous experimental work we have seen that the graphite flakes can be changed under certain special conditions to a certain extent. Now we come to the question of whether or not the change can be produced at lower temperature.

The equipment and procedures used for this experimental work are the same as those used in part 1, except that the temperature was kept at 1300°F., just below the transformation temperature.

The gray cast iron samples, which were used for this experiment, have the same composition and micro-structure as those used in part 1. The results are shown in the following pictures.



Fig. 20. Microstructure of sample No. 01.

Magnification : 250 diameters

Etchant: Nital

Heat treatment: Annealed at 1300^oF. for 48 hours in an
air atmosphere and air cooled.

The eutectoid cementite in the sample was decomposed into carbon and ferrite; the ferrite remains as matrix, and the carbon combined itself with the graphite which was originally present as flakes. As shown in this picture, the structure is simply thickened graphite flakes in a matrix of ferrite. Neither decarburization nor oxidation occurred.



Fig. 21. Microstructure of sample No. 07.

Magnification : 250 diameters

Etchant: Nital

Heat treatment: Annealed at 1300^oF. for 21 days in an
air atmosphere and air cooled.

The microstructure remains same as in Fig. 20.

The graphite still remains in its flaky form. No
decarburation and no oxidation occurred.

(The microstructures of the samples between sample No. 01
and sample No. 07 are exactly the same as in both Fig. 20
and Fig. 21).

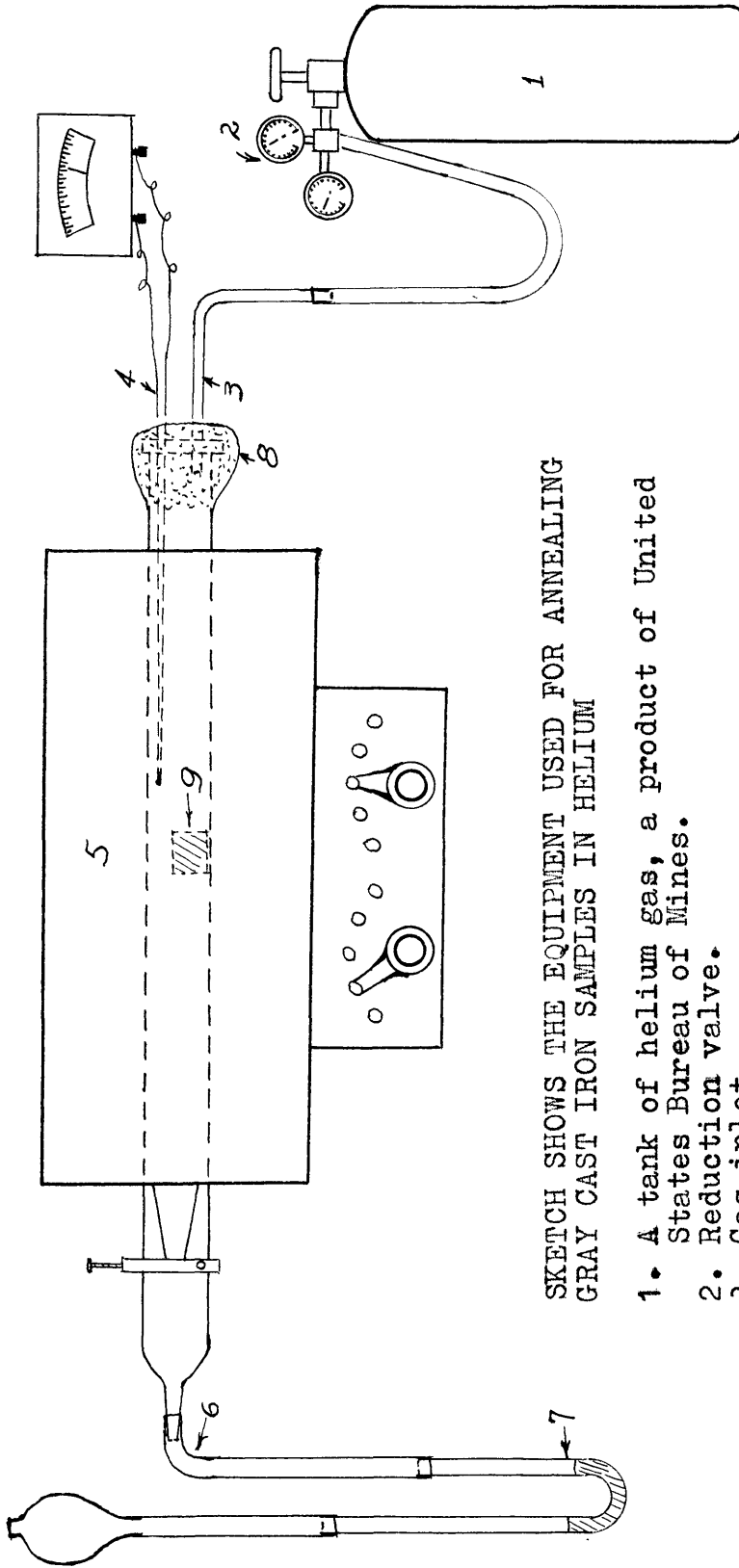
Part 3

ANNEALING OF GRAY CAST IRON IN HELIUM

As stated in part 2, if the annealing temperature is below the transformation range and the sample is in an ordinary atmosphere, no matter how long the annealing time is, the graphite in gray cast iron will remain in its flaky form. But the graphite flakes will change if heated above the transformation range and in an oxidizing or decarburizing atmosphere. So, the next question is: Is it possible to change the graphite flake structure without oxidation or decarburization?

In part 1 sample No. 15, a sample was heated for 190 hours in an air atmosphere at 1800°F.; the sample was severely oxidized. In this experiment, the main purpose was to prevent the oxidation or decarburization while the rest of the conditions were kept the same as for sample No. 15.

An inert gas (helium) atmosphere for annealing the sample was suggested by Professor Morton C. Smith, and the author arranged the set-up of equipment as shown in the sketch on the next page.



SKETCH SHOWS THE EQUIPMENT USED FOR ANNEALING GRAY CAST IRON SAMPLES IN HELIUM

1. A tank of helium gas, a product of United States Bureau of Mines.
2. Reduction valve.
3. Gas inlet.
4. Thermocouple.
5. Burrell high temperature tube furnace, with adjustable transformer.
6. Gas outlet.
7. Manometer to measure the gas pressure inside the tube.
8. Sealing plaster.
9. Position of sample.

The procedure of annealing can be briefly described as follows: First, insert the sample through the opening into the middle of the tube. Then put on the steel stopper, which is connected with gas inlet and thermocouple, and then seal off with plaster. After the plaster is dry, turn on the gas, drive out the air from the tube, then connect the gas outlet with the tapered end of the tube. Adjust the reduction valve to maintain a pressure in the tube slightly higher than the atmospheric. Adjust the transformer to bring the temperature around the sample gradually up to 1800°F. At the end of 190 hours, turn off the furnace, cool down the tube to room temperature, then cut off the gas supply, take out the sample, and examine the sample under the microscope.



Fig. 22. Microstructure of sample No. 21.

Magnification : 250 diameters Etchant: Unetched

Heat treatment: Annealed at 1800^oF. for 190 hours in
helium and furnace cooled.

Careful polishing reveals the graphite in the sample. Original graphite flake structure disappeared; instead is the graphite as shown in picture above.

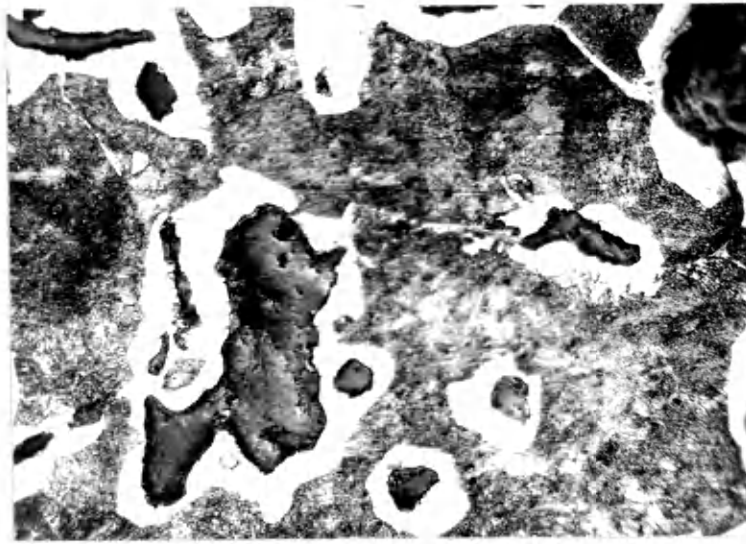


Fig. 23. Microstructure of sample No. 21.

Magnification : 250 diameters

Etchant: Picral

Heat treatment: Same as in Fig. 22.

Etched sample shows the pearlitic matrix. The eutectoid cementite around the graphite has been graphitized (due to slow cooling from the annealing temperature), and it leaves ferrite around the graphite. This microstructure, compared with malleable cast iron, is quite similar to the Bull's-eye type.



Fig. 24. Microstructure of sample No. 21.

Magnification : 500 diameters

Etchant: Unetched

Heat treatment: Same as in Fig. 22.

At the higher magnification, some individual graphite spheroids are revealed in the sample.



Fig. 25. Microstructure at one part of sample
No. 21.

Magnification : 100 diameters

Etchant: Unetched

Heat treatment: Same as in Fig. 22.

It is very curious and interesting to note that at one part of the sample some of the graphite still remains in its long flaky form, but arranged in a certain order, probably outlining the previous austenite grains.

From the results of this experiment, it can be said that the flaky form of graphite in gray cast iron can be changed under certain conditions, but the mechanism of change is still questionable. According to the author's opinion, the graphite flakes can not be changed by themselves in the same way that eutectoid cementite can be spheroidized by annealing. Possibly it is changed by the solution and precipitation of carbon in and out of austenite. If this possibility is true, then we can hasten the change by alternate heating and cooling.

The following two pictures show the author's attempt to hasten the process of change in the graphite flake structure.

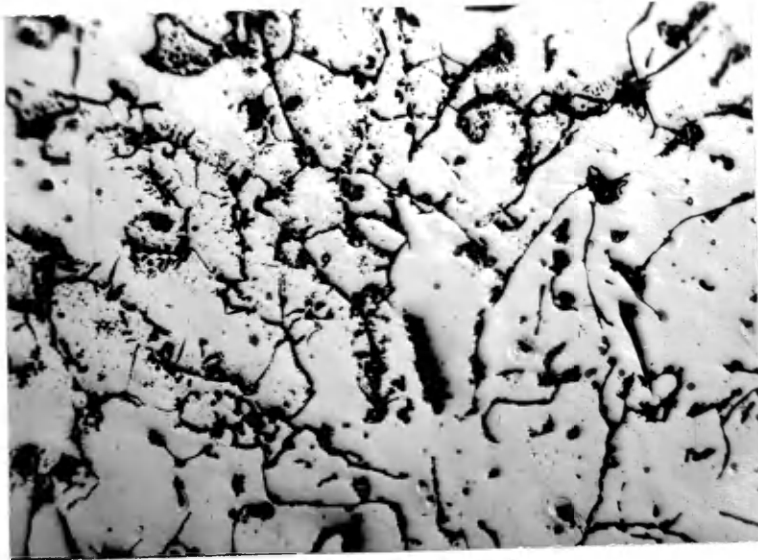


Fig. 26. Microstructure of sample No. 31.

Magnification : 250 diameters

Etchant: Unetched

Heat treatment: Original gray cast iron sample was heat-treated by heating and cooling alternately between 1800°F. and 800°F. for five times (in a period of approximately 20 hours) in Burrell high temperature tube furnace in an atmosphere of helium, and furnace cooled.

The author's attempt is not completely satisfactory, but the graphite shows a tendency to spheroidize.

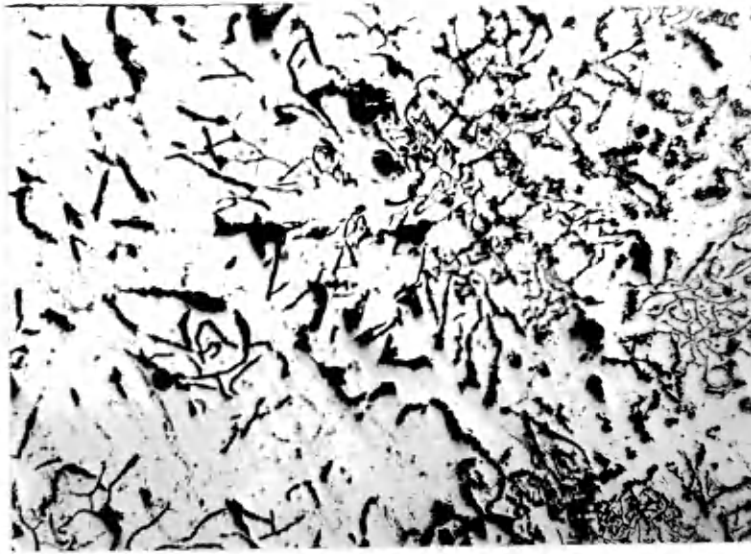


Fig. 27. Microstructure of sample No. 41.

Magnification : 250 diameters

Etchant: Unetched

Heat treatment: Original gray cast iron sample was heat-treated by heating and cooling alternately between 1800°F . and 1600°F . for ten times (in a period of approximately 10 hours) in Burrell high temperature tube furnace in an atmosphere of helium, and furnace cooled.

Again the author's attempt is not successful. The flaky graphite shows a tendency to change, but to a less extent compared with that in the previous sample.

CONCLUSIONS

1. Graphite flakes in gray cast iron can be spheroidized at a temperature above the transformation range and with a sufficiently long heating time.
2. The possible mechanism of spheroidizing the flaky form of graphite is the solution and precipitation of carbon by austenite.
3. To produce the change in a shorter time than 190 hours has not been successful.
4. The metallurgical and industrial significance of such a treatment has not been investigated. This research is only a beginning.

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