

1930

The effect of chromium on white cast iron

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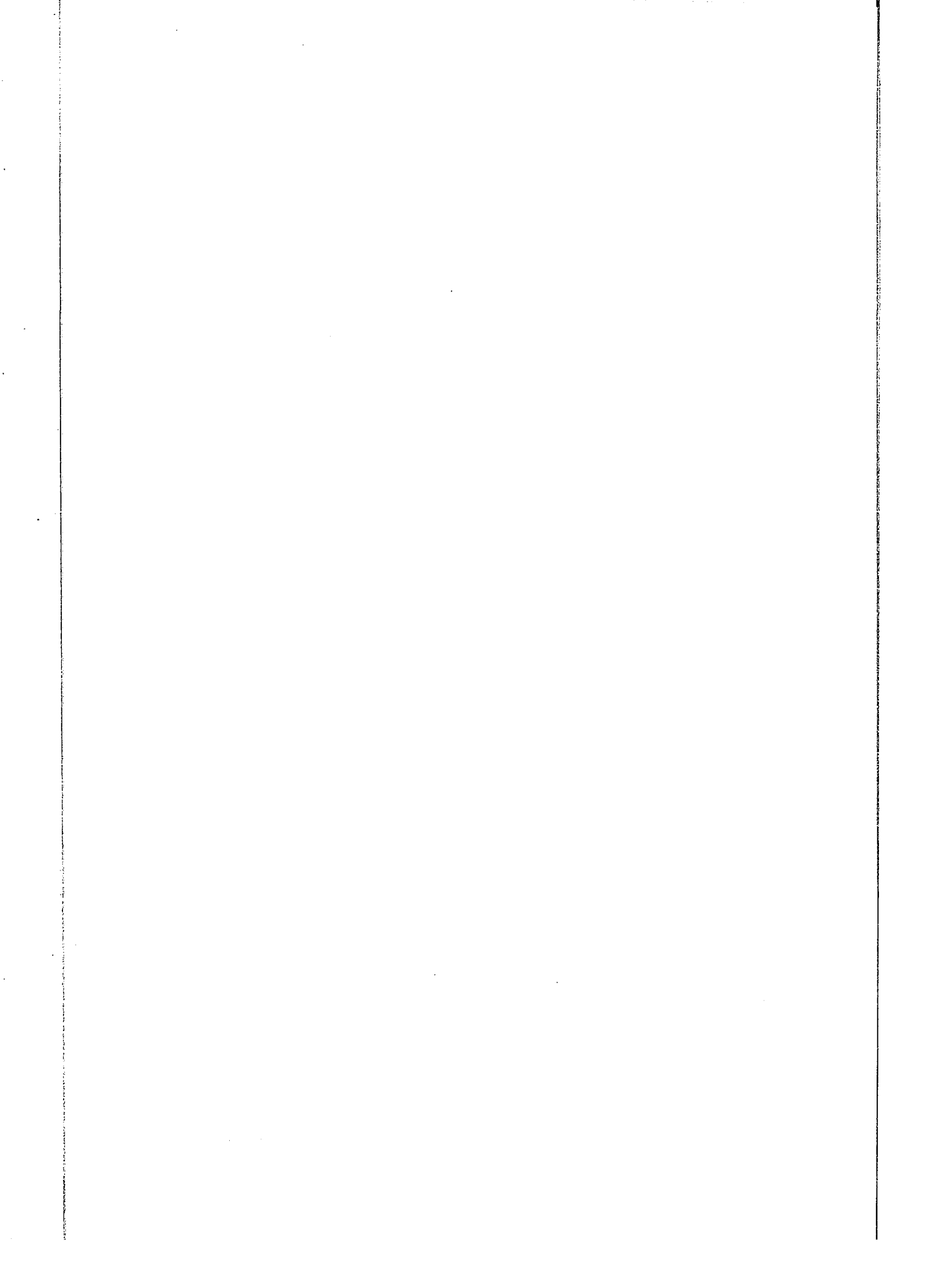
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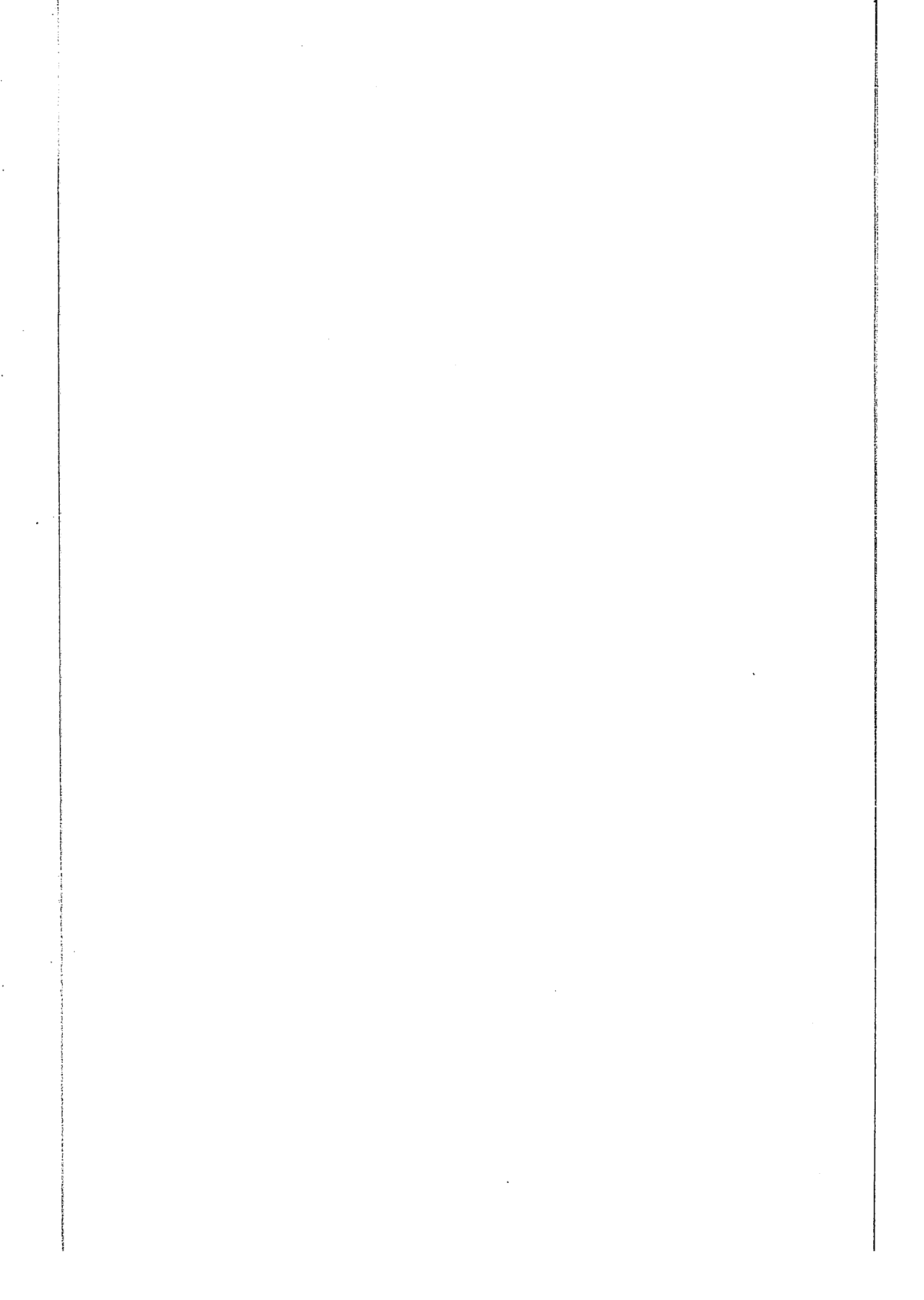
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THE EFFECT OF CHROMIUM ON WHITE CAST IRON

By

Clarence D. Foulke

A Thesis Submitted to the Graduate Faculty
for the Degree of

DOCTOR OF PHILOSOPHY

Major Subject Physical Chemistry

Approved:

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1930

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THE EFFECT OF CHROMIUM ON WHITE CAST IRON

I. INTRODUCTION

White cast iron is essentially an alloy of iron with more than 1.7% carbon and varying but rather limited amounts of silicon, manganese, sulphur and phosphorus. Quite often one or more special elements, such as nickel, chromium, molybdenum, aluminum, etc., are present, being added to the molten iron for physical improvement or, in some cases, gaining entrance through the use of scrap iron and steel.

Structurally, white cast iron consists of cementite embedded in a matrix of pearlite, resulting in the combination of all the carbon present. The presence of excess cementite renders this form of cast iron very hard and of low shock resistance. Therefore, in order to be of any commercial value, the iron must be given a suitable heat treatment producing a soft and ductile alloy.

Foundrymen are quite familiar with the fact that the use of scrap in making up the melt for white cast iron must be done judiciously. The presence of chromium in many grades of scrap is one of the primary factors contributing to this fact. It has been quite definitely established by several investigators that chromium greatly inhibits the proper an-

nealing of white cast iron.

The present study was undertaken with a two-fold object in view: First, to make a quantitative study of the effect of chromium on graphitization rates of white cast iron; and, second, to determine the graphitization rates and microstructure of alloys containing constant amounts of chromium with varying amounts of silicon.

II. HISTORICAL

A. The Graphitization of White Cast Iron.

The graphitization of white cast iron is essentially the conversion of the combined carbon into free temper carbon and soft ductile ferrite. Both Hayes (7) and Honda (9) have proposed a theory as to the mechanism of this conversion. According to Hayes (7), graphitization takes place in two stages. First, by holding the iron at a temperature well above the A_{c1} point for a sufficient length of time and by cooling slowly from this high temperature to the eutectoid, the free or massive cementite is graphitized with the production of free carbon. Second, the remaining combined carbon is graphitized by holding the alloy at a temperature corresponding to or slightly below the A_1 point.

Although there are some differences of opinion as to the exact mechanism of graphitization of white cast iron, it is quite generally agreed that the rate at which graphitization proceeds is influenced by several factors.

B. The Effect of Physical Factors.

The data of Kikuta (14), showing the effect of the pouring temperature on the rate of graphitization during the first stage are shown in Table I. This alloy contains 2.70 per cent

carbon, .98% silicon, and was poured in a dry sand mould.

TABLE I
THE EFFECT OF POURING TEMPERATURE
ON FIRST STAGE GRAPHITIZATION

Pouring temperature	Time required to complete the first stage of graphitization.	
1300° C. (2372° F.)	5 hours	0 minutes
1350° C. (2462° F.)	5	30
1400° C. (2552° F.)	6	20
1450° C. (2642° F.)	7	0
1500° C. (2732° F.)	8	0
1550° C. (2822° F.)	8	20

Table II, after Kikuta (14) shows the effect of the cooling period on the rate of graphitization, both at 925C. and at the eutectoid. This alloy contained 2.17% carbon and 1.07% silicon.

TABLE II
THE EFFECT OF COOLING PERIOD
ON GRAPHITIZATION RATES

Temperature of mould	Time to complete graphitization:			
	Time at 925° C.:		Time at eutectoid:	
Green sand	5 hrs. 0 mins.			
Dry sand	6	0	15 hrs. 0 mins.	
Sand at 400° C. (752° F.)	7	30	22	0
Sand at 600° C. (1112° F.)	9	0	21	0
Sand at 800° C. (1472° F.)	9	20	22	0
Sand at 1100° C. (1832° F.)	10	0		

The effect of different annealing temperatures upon the time required for the graphitization of an alloy containing 2.72% carbon and 1.29% silicon are shown in Tables III and IV. These data are also taken from the work of Kikuta (14).

TABLE III
THE EFFECT OF ANNEALING TEMPERATURE
ON FIRST STAGE GRAPHITIZATION

Annéealing temperature	Time to complete first stage of graphitization
875° C. (1607° F.)	9 hours 0 minutes
900° C. (1652° F.)	4 30
925° C. (1691° F.)	2 50
950° C. (1742° F.)	2 0
975° C. (1787° F.)	1 20

TABLE IV
THE EFFECT OF ANNEALING TEMPERATURE
ON SECOND STAGE GRAPHITIZATION

Annéealing temperature	Time to complete second stage of graphitization
730° C. (1346° F.)	4 hours 0 minutes
710° C. (1310° F.)	5 0
690° C. (1274° F.)	6 20
670° C. (1238° F.)	8 0
650° C. (1202° F.)	11 0

This same factor has been studied by White (24), Hayes (8), and Flanders. White found that the logarithm of the time required at the high temperature for the graphitization of free carbide bears a straight line relation to the temperature. The results of Hayes and of Kikuta show the same relationship.

C. The Effect of Chemical Composition.

When the work of Hayes and Diederichs on the production of malleable iron by using a shortened annealing cycle was in progress in this laboratory, it became apparent that the common elements as well as any special elements present in the cast iron affected the rate of graphitization. In 1925 Hayes (8) and Flanders studied the effect of sulphur on the rate of graphitization. Schwartz (21) and Guiler determined quantitatively the effects of different concentrations of alloying elements on graphitization. Each of the elements antimony, boron, cerium, chromium, molybdenum, selenium, tellurium and tin were found to have a deleterious effect on commercial graphitization. Kikuta (14) investigated the effects of the common elements, carbon, silicon, manganese, sulphur and phosphorus, found in commercial white cast iron, on rates of graphitization both in the first and second stages.

Sawamura (20), in an extensive study, has determined the

effects of the special elements aluminum, nickel, copper, cobalt, gold, platinum, titanium, chromium, tungsten, molybdenum, and vanadium in addition to the four common elements silicon, manganese, sulphur and phosphorus.

It seems to be quite generally agreed among investigators that of the common elements found in white cast iron, silicon is a very powerful promoter of graphitization. However, there is an upper limit above which silicon should not rise because of its great tendency to produce free or primary graphite during solidification of the metal.

Other factors being equal, the silicon content should vary inversely with the carbon content, that is, the higher the carbon the lower the silicon. Otherwise there will be a tendency for primary graphitic separation.

Manganese retards the graphitization of white cast iron, especially during the second stage. Kikuta recommends a content of less than .5% of that element for good black-heart malleable iron.

Sulphur also retards the rate of graphitization in the second stage, and to an even greater extent than manganese.

Sawamura (20) states that phosphorus favors graphitization of white cast iron, reaching a maximum effect at about 1.2% of the element. Further increase of phosphorus, however, produces no increase in graphitization.

As regards the effects of special elements upon the graphitization rates of white cast iron, it may be stated that, in general, those elements which when present form either single or double carbides with iron, retard graphitization. Those elements which do not form carbides, but rather go into solid solution with the iron, promote graphitization.

D. Alloys of the Iron-Chromium-Carbon System.

The earliest work on the iron-chromium equilibrium diagram is that of Treitschke and Tammann (23). The irregularities noted in the liquidus curve pointed toward the gradual formation of a compound, such that the system behaved as a pseudo-ternary system.

Janecke (12), from his thermal data and microsections, concluded that the two metals, iron and chromium, form a simple eutectiferous series as shown in Figure I.

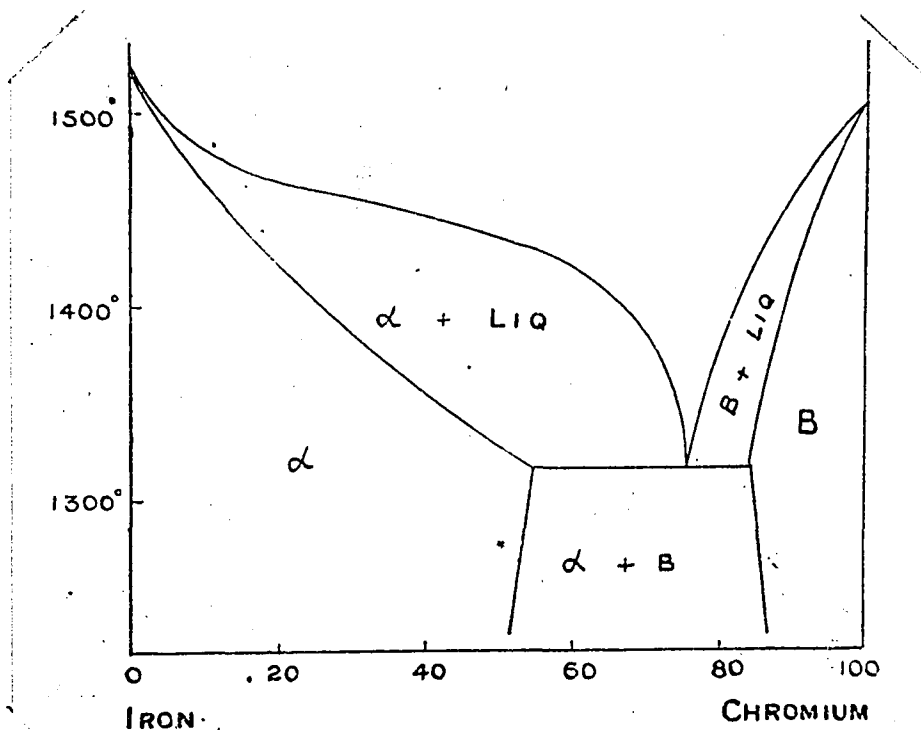


Figure I. The Iron-Chromium System

Murakami (18) attributes the presence of the apparent eutectic, which he found in some iron-chromium alloys, to lack of diffusion during solidification. He concludes that the two metals, iron and chromium, form a complete series of solid solutions.

Some years ago, Bain, (1) by means of the x-ray, investigated a series of iron-chromium alloys of various compositions which had been rapidly cooled near the melting point. A single metallic phase, having the body-centered cubic arrangement, characteristic of both iron and chromium atoms, was found. Bain also found that the addition of 13% chromium to carbonless iron suppressed the gamma transformation causing the alpha and delta modifications to completely merge. His diagram showing the effect of chromium on the gamma transition is reproduced in Figure II.

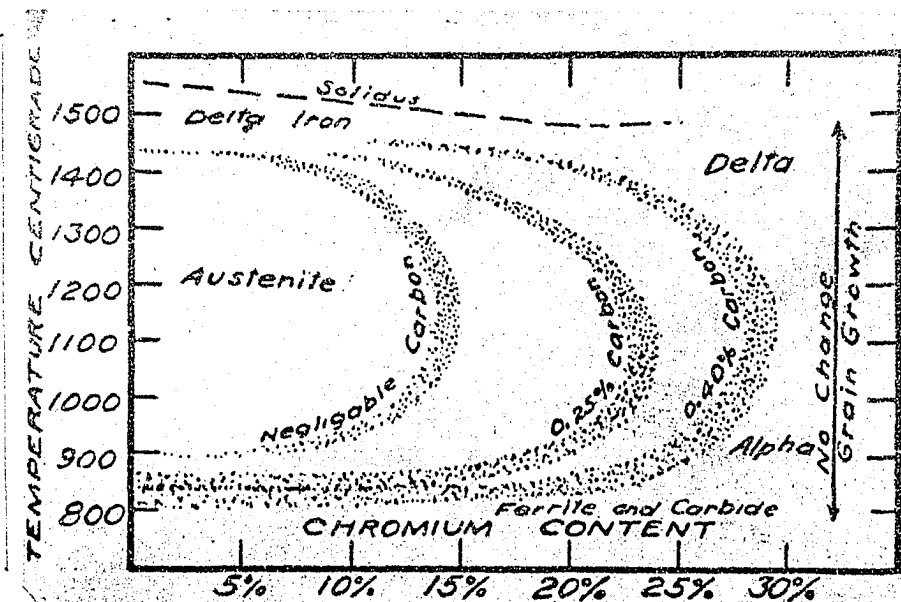


Figure II. Effect of Chromium on the Gamma Transition

Maurer (16), using a Saladin differential thermocouple recorder, obtained the diagram shown in Figure III, showing the effect of chromium on the gamma transformation and on the magnetic change point.

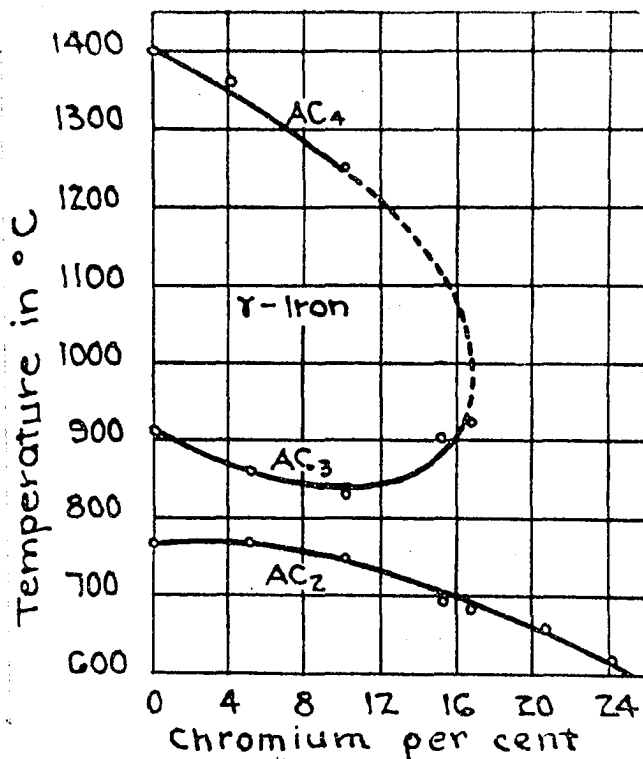


Figure III. Effect of Chromium on the Gamma Transition and Magnetic Change.

The liquidus of the chromium-carbon system was determined by Ruff and Foehr (19). The carbide Cr₅C₂, containing 8.5% carbon, and chromium solid solution of 0.5% carbon form an eutectic containing 9.3% carbon. Their diagram is shown in Figure IV.

Murakami (18) differs with Ruff and Foehr as to the carbide which forms the eutectic. He states that the compound Cr_4C and chromium form an eutectic alloy containing 1.7% carbon.

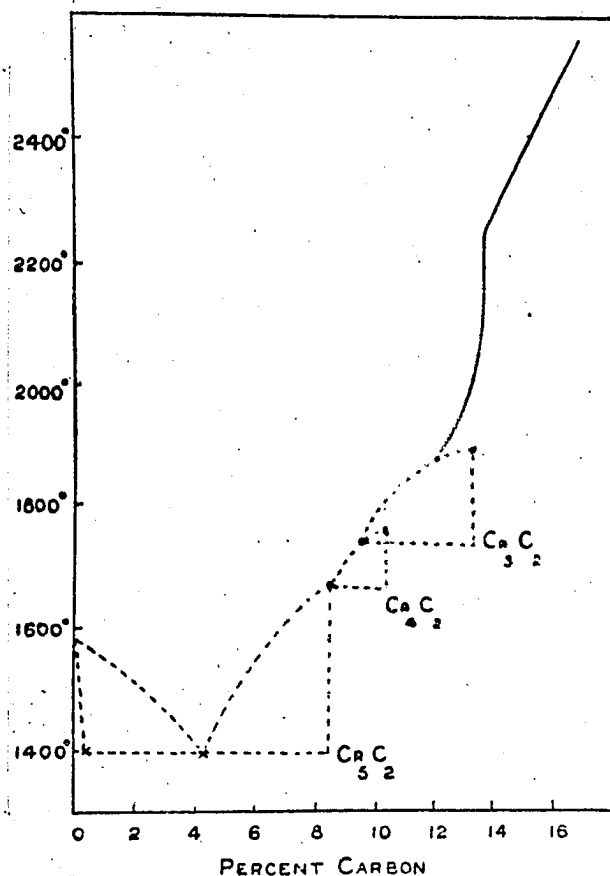


Figure IV. Liquidus of the Chromium-Carbon System

Monypenny (17) has determined the influence of chromium on the solubility of cementite and of the pearlitic carbide. In Figure V the full lines represent the solubility of cementite and the dotted lines that of the pearlitic carbide. Figure VI, after Monypenny, shows the carbon content of the eutectoid for varying amounts of chromium.

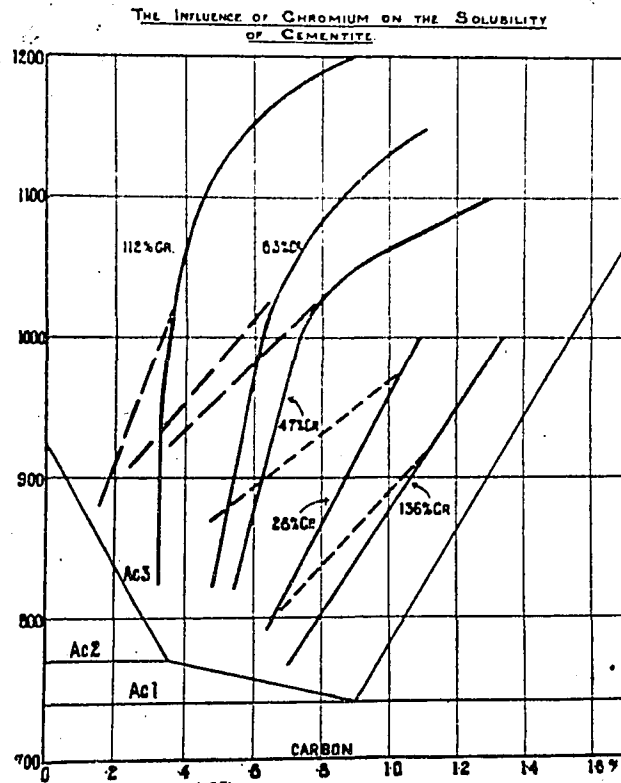


Figure V. The Influence of Chromium on the Solubility of Cementite and Pearlitic Carbide.

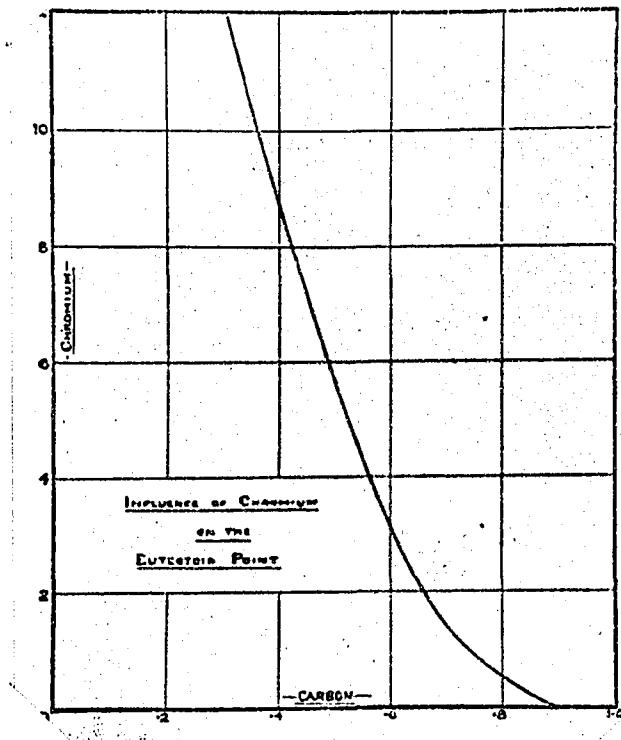
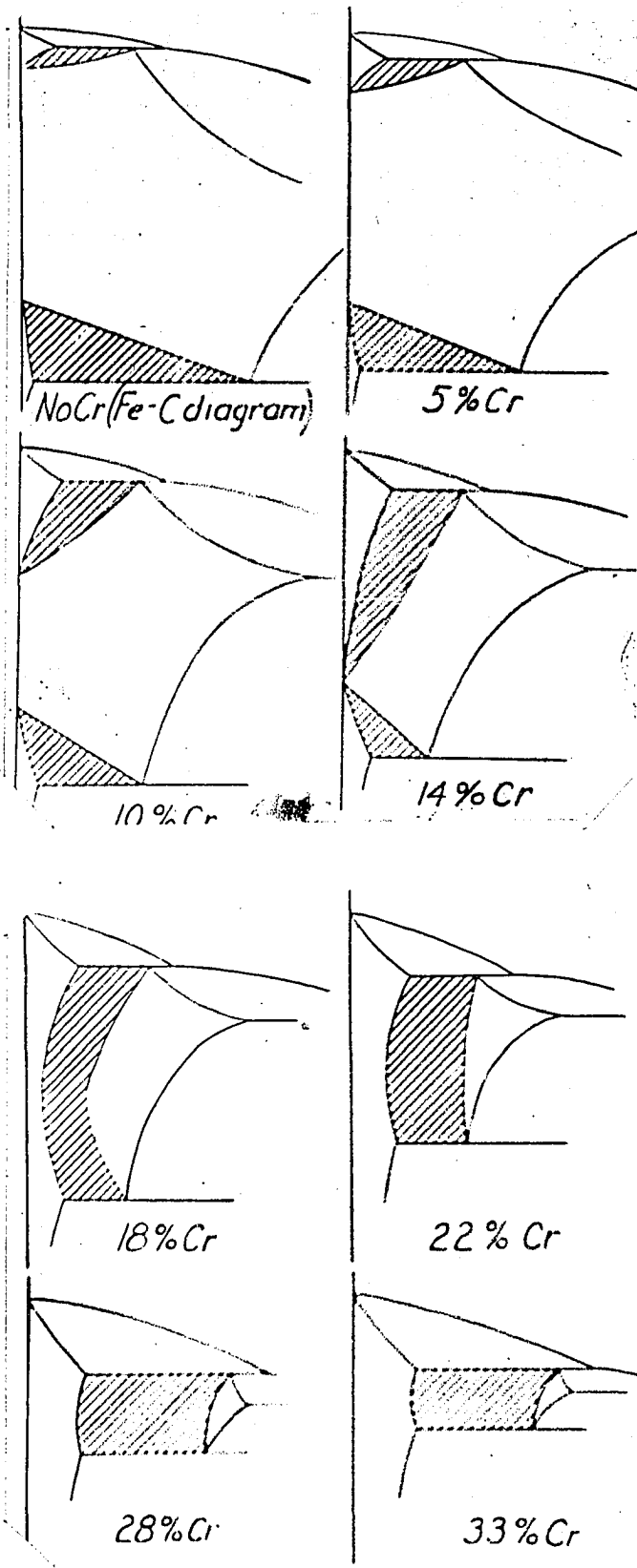


Figure VI. The Effect of Chromium on the Carbon Content of the Eutectoid.

Krivobok and Grossmann (15) examined the changes in microstructure produced in alloys of iron-chromium-carbon by increasing the chromium up to 35% and varying carbon up to 0.60%. Their sectional views of the ternary constitutional diagram (Figures VIIa and VIIb) show that, with increase of chromium content, the shaded region above in which austenite is associated with delta iron, approaches the shaded region below, in which austenite is in equilibrium with alpha iron. The two areas become continuous, as shown, when chromium is in excess of 18%.

Goerens and Stadeler (5) found that with increasing quantities of chromium, the per cent of carbon corresponding to the eutectic increases. With chromium rising from 0% to 66%, the carbon rises from 4% to 9.2%. The melting point is not affected until a percentage of 10.4% chromium is reached, after which the melting point is gradually increased. In alloys of over 21% chromium, the pearlite point disappears.



Figures VIIa and VIIb. Sectional Views of the Iron-chromium-carbon system

Chromium has the effect of opposing both the disintegration and the reconstitution of cementite, so that it raises the Ar range and lowers the Ac range. Each 0.10% chromium up to 4% raises Acl by about 2 degrees C. Four per cent chromium, therefore, will raise the Acl of a 0.5% carbon alloy from 720 C. to 800 C.

In a mild steel with 0.2% carbon, a 5% addition of chromium will cause Ar3 to coincide with Ar1. One of the principal effects of chromium is to decrease the rate at which the transformations take place. This promotes stability of the austenite and martensite, so that chromium tends to produce great hardness. Chromium also tends to increase the hysteretic gap, though not to such an extent as to produce irreversible steels.

The influence of chromium on cast iron, particularly gray cast iron, has been studied by many investigators. Perhaps the earliest work is that of Keep (13), who employed chromium additions up to 2% in gray cast iron. The strength was slightly increased by chromium additions up to 1%, but decreased with further additions. Hurst (11) states that in a cast iron containing 1% silicon, an addition of 0.9% chromium rendered the fracture quite mottled, while in an iron containing 1.5% silicon, the fracture was rendered perfectly white by the addition of 4% chromium. Drastic annealing at a temperature of

900°C. to 950°C. (1652 to 1742 degrees F.) failed to produce graphite in these alloys. Further experiments by Hurst showed that an increase in silicon rapidly reduced the stability of the carbide. Test bars containing 3.5% silicon and as much as 7.5 to 8.5% of chromium were found to be graphitic, and could be filed and drilled with some difficulty. A cast iron containing 3.15% silicon and 6.94% chromium, gave a Brinell figure of 460 on a sand cast bar, and a chill-cast bar could be filed with difficulty. The same alloy containing 1.46% silicon was glass hard and of white fracture with no sign of graphite.

Smalley's (22) investigations, using ordinary gray iron with chromium additions, showed that small additions of 0.11% and 0.85% chromium increased the strength and hardness slightly. With 0.78% chromium the tensile strength fell to that obtained from an ordinary gray iron, the transverse strength was little affected, but the Brinell figure was raised 40 points.

Donaldson's (2) investigations show that additions of 0.19% and 0.39% chromium to a good cylinder iron give an increase of 5% and 10% in strength and 5% and 11% in Brinell hardness, respectively. Chromium to the extent of 0.39% hindered growth of cast iron to a much greater degree than manganese.

The effect of chromium additions to malleable cast iron has not been studied as thoroughly as has been the case with gray cast iron. This, no doubt, is due to the very great stabilizing effect upon the carbide produced by small additions of chromium, thus necessitating a greater annealing period. Makers of malleable iron castings seem to agree that the presence of chromium is injurious to the quality of their product. It is said to give a picture frame structure which results in low tensile strength and elongation.

Gilmore (4) states that about 0.25% chromium added to normal malleable is effective in holding a pearlitic matrix (about .80% combined carbon) after annealing.

Hurren (10), in discussing the effects of common elements on white heart malleable, states that chromium appears to have an action similar to that which it exerts on gray iron; namely, to increase the stability of the combined carbon.

Schwartz and Guiler (21) mention some experiments on the annealing of nearly silicon free alloys. These alloys contain less than .05% silicon, about .02% phosphorus, .043% sulphur and .16% chromium. One alloy, washed metal, contained no manganese, another contained .23% of that element. Neither of these alloys showed the slightest trace of free carbon, chemically or microscopically, after 2075 hours (about three months)

at 1650 degrees F. (900 degrees C.) This distinct stability of the carbide was attributed to the approximate absence of silicon rather than to the presence of chromium. Speaking on qualitative evidence only, the writers said they would not expect a commercially noticeable effect below .02% chromium, and would feel that at .05 to .07% chromium only an extremely slight retardation of annealing might be noticed. Toward .10%, they state the matter would grow serious, while at .25% the process would probably become commercially inoperative.

Evans and Peace (3), in discussing the effects of chromium on black heart malleable, state that chromium definitely retards annealing even in as small an amount as .01%. Most pig iron, they say, contains chromium in quantities up to .10%; therefore, care must be taken in the choice of pig iron. The same authors state that higher chromium content is permissible in white heart malleable than in black heart malleable, as its stabilizing effect upon the carbide is not so detrimental. Up to a certain amount, the effect is even beneficial. Quantities above .20%, however, appear to reduce the rate of decarburisation.

Hadfield (6) says the action of chromium on cast iron is probably twofold:

1. By crystallizing with the carbide it renders the combined carbon more stable. The addition of chromium, therefore,

tends to harden cast iron, and will be found to increase the chill. Graphite separates with increasing difficulty as the percentage of chromium increases.

2. It is most probable that the chromium remaining in the ferrite definitely modifies the characteristics of that constituent; and, since ferrite frequently constitutes the matrix of cast irons, this phase is worth considering.

III. EXPERIMENTAL

A. Materials Used.

The materials used in the preparation of the alloys were ferro-chrome containing 73.18% chromium, ferro-silicon containing 46% silicon, ferro-manganese containing 46% manganese, crushed graphite and commercial white cast iron test bars of the following compositions:

	I.	II.
Carbon	2.42	2.45
Silicon	0.88	0.87
Manganese	0.23	0.21
Sulphur	0.050	0.031
Phosphorus	0.149	0.141

B. Preliminary Study and Discussion.

As a preliminary study of the effect of chromium on the stability of cementite, three series of alloys of varying percentages of chromium were prepared. From 200 to 300 grams of iron No. I were melted in magnesia crucibles heated in an Ajax induction furnace. The calculated amount of ferro-chrome (about 20 mesh) was added to the molten metal, and the melt stirred several times with an Armco iron rod. Bars were then cast vertically into small magnesia tubes of 5/8 inch diameter

and 5 to 6 inches in length. The pouring temperature, as measured by a Leeds and Northrup optical pyrometer, was approximately 1375°C. (2507°F.). The alloys were allowed to cool completely before they were removed from the moulds.

Chemical analysis for carbon and chromium contents are given in Table V. It is quite probable the other elements present remained approximately constant in amount; therefore, any variations noted in the stability of the cementite could be attributed to the variations in chromium content.

TABLE V.

Alloy No.	% Carbon	% Chromium	Remarks
A - 1	2.20	0.339	
A - 2	2.23	0.656	
A - 3	2.18	0.862	
A - 4	2.24	1.260	
A - 5	2.20	1.477	
B - 1	1.90	0.088	
B - 2	1.88	0.181	
B - 3	1.85	0.287	
C - 1	2.26	0.053	C series of
C - 2	2.20	0.062	alloys cast
C - 3	2.23	0.102	vertically in:
			sand moulds.

Each of the above alloys were broken into 5 samples of nearly equal length. A sample of each alloy was then put into each of 5 graphite crucibles, packed with powdered graphite,

placed in a vertical hump furnace and then heated to a temperature of 1700-1720°F. during a period of about 3 hours. The crucibles were removed consecutively at intervals of 2 hours and the contents examined microscopically. All the samples, with the exception of the very low chromium ones, were found to be very incomplete as regards the graphitization of the cementite.

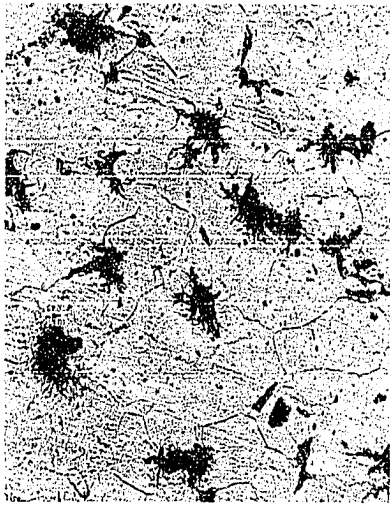
Duplicate samples from each series of alloys and from each chromium content were repacked in each of two graphite crucibles and reheated to a temperature of 1700°F. In addition to the chromium samples, a sample of the original white iron stock bar was included in each crucible.

The purpose of this second heat treatment was to leave the samples in the furnace long enough for the non-chromium samples to reach equilibrium with respect to carbide decomposition. The samples were then to be cooled slowly from the high temperature to below the critical range.

A thorough microscopic examination was made of the resulting products, and photographs taken.

A study of the photographs, pages 27 to 29 inclusive, points out very well the effect of increasing chromium content on the graphitization of cementite at 1700°F. It is to be noted that the original white iron sample (containing no

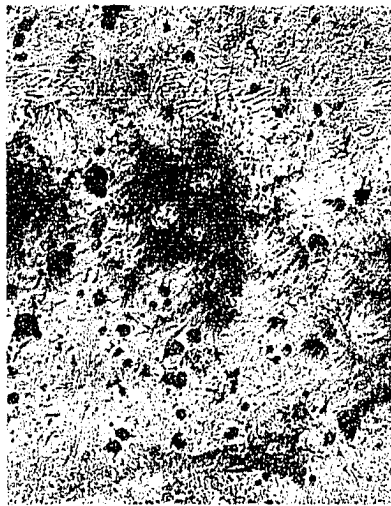
chromium) is completely annealed. The alloy containing 0.033% chromium contains no free cementite, while 0.062% is effective in retaining traces of cementite after 75 hours at 1700° F.



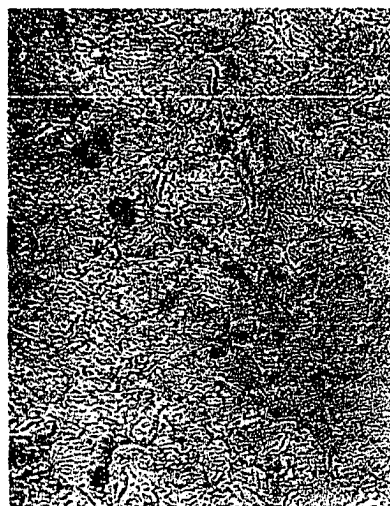
Alloy C-0. 0.00% chromium.
Annealed at 1700° F. (927° C.)
for 70 hours, cooled to
1100 F. during 13 hours.
Nitric acid etched. 75 X.



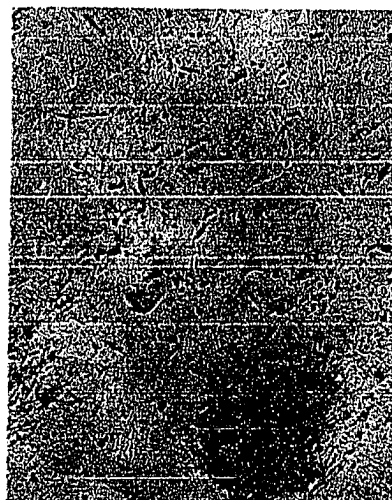
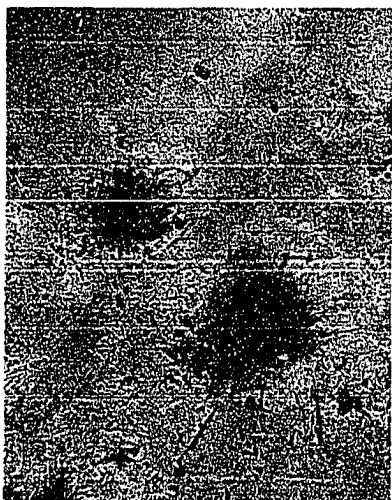
Alloy C-1. 0.033% chromium.
Annealed at 1700° F. (927° C.)
for 70 hours, cooled to
1100° F. during 13 hours.
Nitric acid etched. 75 X.



Alloy C-2. 0.062% chromium.
Annealed at 1700° F. (927° C.)
for 75 hours, cooled to
1100° F. during 13 hours.
Nitric acid etched. 75 X.

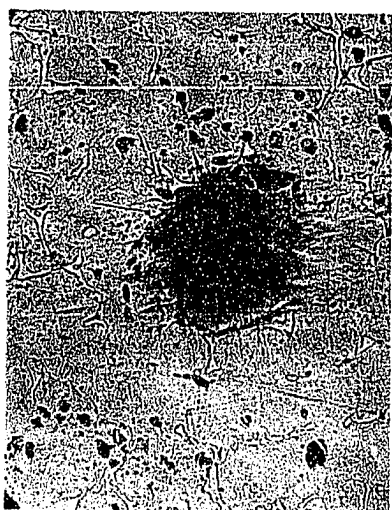


Alloy C-3. 0.102% chromium.
Annealed at 1700° F. (927° C.)
for 75 hours, cooled to
1100° F. during 13 hours.
Nitric acid etched. 75 X.



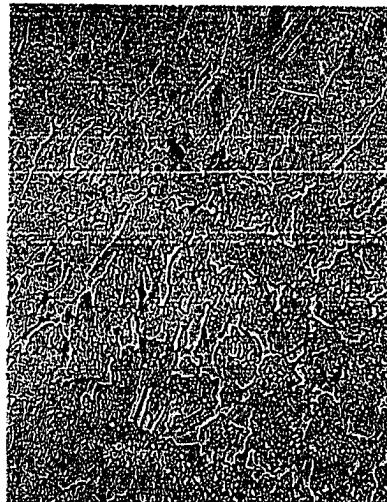
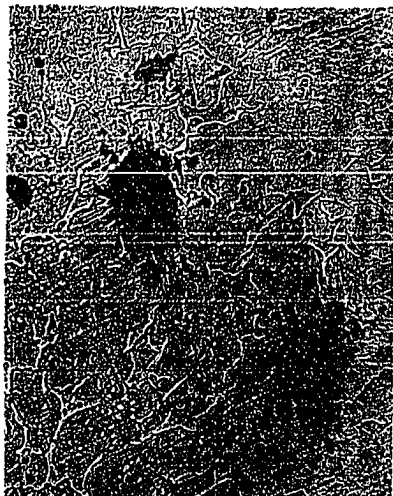
Alloy B-1. 0.088% chromium.
Annealed at 1700°F.(927°C.)
for 71 hours, cooled to
1100°F. during 13 hours.
Nitric acid etched. 75 X.

Alloy B-2. 0.18% chromium.
Annealed at 1700°F.(927°C.)
for 71 hours, cooled to
1100°F. during 13 hours.
Nitric acid etched. 75 X.



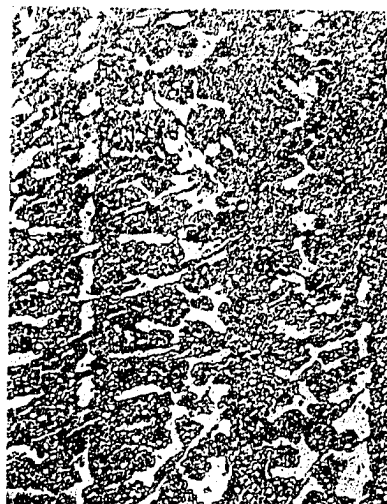
Alloy B-3. 0.287% chromium.
Annealed at 1700°F.(927°C.)
for 73 hours, cooled to
1100°F. during 13 hours.
Nitric acid etched. 75 X.

Alloy A-1. 0.34% chromium.
Annealed at 1700°F.(927°C.)
for 70 hours, cooled to
1100°F. during 13 hours.
Nitric acid etched. 75 X.



Alloy A-2. 0.66% chromium.
Annealed at 1700°F. (927°C.)
for 75 hours, cooled to
1100°F. during 13 hours.
Nitric acid etched. 75 X.

Alloy A-3. 0.86% chromium.
Annealed at 1700°F. (927°C.)
for 68 hours, cooled to
1100°F. during 13 hours.
Nitric acid etched. 75 X.



Alloy A-4. 1.26% chromium.
Annealed at 1700°F. (927°C.)
for 72 hours, cooled to
1100°F. during 13 hours.
Nitric acid etched. 75 X.

Alloy A-5. 1.48% chromium.
Annealed at 1700°F. (927°C.)
for 70 hours, cooled to
1100°F. during 13 hours.
Nitric acid etched. 75 X.

C. Preparation of Alloys.

The foregoing preliminary anneal has shown chromium, even in small amounts, to have a very pronounced stabilizing effect on the cementite of white cast iron at 1700°F. That silicon has a powerful graphitizing effect on cementite at this temperature has been known for some time. Several writers have suggested the possibility of effecting graphitization of chromium bearing white cast iron by increasing the silicon content, but, to the writer's knowledge, no published work of such a nature has appeared.

Therefore, it was decided to make several new series of chromium bearing alloys and study the effects of constant chromium content and increasing silicon content on rates of graphitization.

The first step was the preparation of series N and M alloys which contain 0.18% chromium and 0.43% chromium respectively. The melting and casting procedure differed materially from that used in the preparation of series A, B and C alloys. About 4000 grams (8.82 pounds) of white cast test bars, No. II, (page 23) were melted in a 6-inch Plumbago crucible in connection with an Ajax induction furnace. Ferrochromium, calculated to give a chromium content of approximately 0.20%, was added to the molten metal and the mass stirred several

times with an Armco iron rod. When the metal had reached a temperature of 2500°F., a single bar of 5/8 inch diameter and 12 inches in length was poured horizontally into a sand mould which had been air dried from 36 to 40 hours. The crucible, containing the remainder of the molten charge, was returned to the furnace and ferro-silicon sufficient to produce an increase of about 0.25% silicon was added. After thorough stirring of the resulting melt, another bar was poured.

This procedure was repeated, each time sufficient ferro-silicon being added to result in an increase of 0.25% silicon, until a total of 7 bars had been prepared. After cooling to room temperature, the bars were removed from the moulds and broken into pieces of about one-half inch length. A portion of each bar, taken from the central portion, was reserved for analytical purposes.

The above procedure was repeated in the preparation of series M alloys with the exception that enough ferro-chrome to result in an alloy of 0.40% chromium was added.

It was thought advisable to prepare additional series of alloys containing chromium in smaller amounts than series N. The results obtained on such alloys may have some commercial application, since white cast iron is frequently made from pig iron containing 0.05% to 0.10% chromium. Due to the oxidation

losses of carbon and manganese during the preparation of series N bars, a new method was employed in the preparation of the remaining alloys.

Twenty-five pounds of white iron test bars, No. II, (page 23) were melted in a large Plumbago crucible covered by a close fitting plumbago cover. When molten, ferro-chromium calculated to give an alloy containing 0.03% chromium, was added. This molten metal was poured into an open shallow mould giving a thin slab of iron which could be broken easily into small pieces. From 2 to $2\frac{1}{2}$ pounds of this stock alloy were remelted in small Plumbago crucibles. A weighed quantity of 20 mesh graphite was added to compensate for oxidation losses, and the melt poured into a dry sand mould. This remelting procedure was repeated, each time sufficient ferro-silicon being added to increase the silicon content of the bar by approximately 0.05%, until a total of 9 bars, designated series D, had been prepared. This procedure was repeated in the preparation of series E and F alloys, with the exceptions that sufficient ferro-chromium was added to result in alloys of approximately 0.10% chromium and 0.07% chromium respectively.

In order to have some basis with which to compare the relative graphitization rates of the different alloys, one bar, designated O, containing no chromium, was prepared under the same conditions as obtained in the preparation of the other alloys.

D. Analysis of Alloys.

Table VI gives the complete chemical analysis of alloys of series D, E, F, N, M and O. The nature of the fracture of each cast alloy is also included. The analytical methods used in each case were those recommended by the American Society for Testing Materials. Duplicate determinations were made in each case, and, when necessary, a third determination was made. All titrating solutions used were standardized in terms of the element sought by use of Bureau of Standard cast iron samples. All determinations were corrected by running blanks under identical conditions.

Carbon was determined by direct combustion in oxygen, the carbon dioxide being absorbed by Ascarite.

Chromium was determined by the sodium bicarbonate separation-sodium peroxide fusion method.

Silicon was determined by the Nitro-Sulphuric acid dehydration method.

Manganese was determined by the sodium bismuthate method.

Sulphur was determined by the gravimetric, barium sulphate precipitation method.

Phosphorus was determined by the alkali-acid titration method.

TABLE VI
CHEMICAL COMPOSITION OF ALLOYS

Alloy	Per cent Chemical Composition						Fracture as cast
	C	Cr	Si	Mn	S	P	
O - 1	2.30	0.000	0.82	0.21	0.036	0.142	white
D - 1	2.39	0.025	0.81	0.27	0.045	0.139	white
D - 2	2.32	0.026	0.88	0.29	0.047	0.137	"
D - 3	2.31	0.026	0.90	0.28	0.046	0.140	"
D - 4	2.34	0.026	0.93	0.29	0.047	0.141	"
D - 5	2.31	0.026	1.05	0.28	0.049	0.139	"
D - 6	2.37	0.026	1.06	0.25	0.043	0.136	"
D - 7	2.27	0.026	1.09	0.27	0.048	0.137	"
D - 8	2.32	0.026	1.16	0.28	0.049	0.135	"
D - 9	2.32	0.025	1.20	0.28	0.049	0.139	slight gray
F - 1	2.25	0.086	0.84	0.23	0.050	0.141	white
F - 2	2.26	0.086	0.93	0.24	0.048	0.142	"
F - 3	2.28	0.086	0.94	0.23	0.048	0.142	"
F - 4	2.28	0.085	0.96	0.24	0.049	0.142	"
F - 5	2.25	0.084	1.01	0.24	0.051	0.140	"
F - 6	2.27	0.084	1.08	0.23	0.051	0.143	"
F - 7	2.26	0.084	1.07	0.23	0.049	0.141	"
F - 8	2.25	0.084	1.13	0.23	0.049	0.145	"
E - 1	2.39	0.111	0.86	0.17	0.042	0.135	white
E - 2	2.33	0.113	0.91	0.18	0.041	0.137	"
E - 3	2.37	0.113	0.96	0.18	0.040	0.138	"
E - 4	2.36	0.112	0.99	0.18	0.043	0.140	"
E - 5	2.36	0.114	1.04	0.18	0.040	0.136	"
E - 6	2.31	0.108	1.07	0.17	0.042	0.136	"
E - 7	2.39	0.101	1.08	0.16	0.041	0.135	"
E - 8	2.25	0.111	1.14	0.17	0.041	0.140	"
E - 9	2.32	0.112	1.17	0.18	0.042	0.138	"
N - 1	2.35	0.189	0.84	0.17	0.040	0.148	white
N - 2	2.34	0.186	1.01	0.16	0.040	0.148	"
N - 3	2.29	0.186	1.26	0.16	0.039	0.149	"
N - 4	2.26	0.197	1.44	0.16	0.041	0.146	"
N - 5	2.19	0.188	1.57	0.16	0.040	0.147	"
N - 6	2.18	0.185	1.89	0.13	0.039	0.149	mottled
N - 7	2.19	0.184	2.35	0.11	0.039	0.145	very dark
M - 1	2.62	0.445	0.83	0.23	0.046	0.145	white
M - 2	2.51	0.434	1.01	0.23	0.048	0.144	"
M - 3	2.50	0.448	1.15	0.23	0.048	0.146	"
M - 4	2.47	0.461	1.39	0.23	0.049	0.148	"
M - 5	2.45	0.443	1.55	0.23	0.049	0.147	"
M - 6	2.50	0.439	1.74	0.22	0.047	0.149	"
M - 7	2.45	0.427	1.80	0.22	0.045	0.147	"
M - 8	2.54	0.429	1.91	0.23	0.046	0.146	"

E. Heat Treatment of Alloys.

Samples of each bar of series N, M, D, E, F and O were placed in iron pipes (2x8 inches) and packed in powdered graphite. They were then heated to a temperature of 1700°F. during about 3½ hours. Some of the samples, those of high silicon content, were removed at intervals of 5 hours; those of low silicon content were removed at 10 hour intervals. Each sample was examined microscopically, both unetched and etched, and the times required for the complete graphitization of the cementite determined in each case. With the high silicon alloys, this time was determined within an interval of 5 hours; with the lower silicon alloys it was determined to the nearest 10 hour interval.

It was found that the 0.43% chromium alloys, even those high in silicon, retained considerable cementite after 200 hours (8 1/3 days) at 1700°F. Due to the fact that the supply of several alloys of this series was nearly exhausted, it was thought inadvisable to attempt the complete graphitization of this series.

For the second stage of graphitization, several new samples of each alloy of series N, D, E, F and O were packed in powdered graphite and held at 1700°F. for the times necessary for the graphitization of the cementite. The furnace and samples were then cooled to 1300°F. over a period of 8 hours. After being at 1300°F. for definite lengths of time, samples were removed

and examined microscopically. The complete absence of pearlite was taken as the criterion of complete graphitization.

The furnace temperature was regulated and recorded by a Leeds and Northrup automatic recorder in conjunction with an iron-constantin thermocouple. Thermocouples were replaced each 24 hours during the 1700°F. anneal and each 48 hours during the 1300°F. anneal. The recorder and thermocouples were standardized frequently by means of a standard platinum-rhodium thermocouple.

IV. EXPERIMENTAL DATA AND DISCUSSION

In Table VII, are shown the times necessary for the first and second stages of graphitization of the alloys. The times stated are those during which the samples were held at 1700°F. and 1300°F. respectively, and do not include the 8 hours required in cooling from 1700°F. to 1300°F. By time necessary is meant the interval during which the last traces of cementite or pearlite, as the case might be, disappeared. With some alloys this interval is seen to be 5 hours, while with some of the high chromium-low silicon alloys it is as great as 20 hours. In some cases it was difficult to detect any material progress in graphitization during a 10 hour interval.

TABLE VII.
TIMES OF COMPLETE GRAPHITIZATION OF ALLOYS

Alloy	Weight Per cent:		Times for Complete Graphitization :	
	Cr	Si	Time at 1700°F.	Time at 1300°F.
O - 1	0.000	0.82	25 to 30 hours	35 to 40 hours
D - 1	0.025	0.81	30 to 40 hours	50 to 60 hours
D - 2	0.026	0.88	20 to 30	30 to 40
D - 3	0.026	0.90	20 to 30	30 to 40
D - 4	0.026	0.93	20 to 30	30 to 40
D - 5	0.026	1.05	10 to 20	20 to 30
D - 6	0.026	1.06	10 to 20	20 to 30
D - 7	0.026	1.09	10 to 15	10 to 20
D - 8	0.026	1.16	5 to 10	10 to 20
D - 9	0.025	1.20	5 to 10	10 to 20
F - 1	0.086	0.84	60 to 70 hours	110 to 120 hours
F - 2	0.086	0.93	50 to 60	80 to 90
F - 3	0.086	0.94	50 to 60	70 to 80
F - 4	0.085	0.96	50 to 60	70 to 80
F - 5	0.084	1.01	40 to 50	50 to 60
F - 6	0.084	1.08	40 to 50	50 to 60
F - 7	0.084	1.07	30 to 40	50 to 60
F - 8	0.084	1.13	20 to 30	30 to 40
E - 1	0.111	0.86	70 to 80 hours	140 to 150 hours
E - 2	0.113	0.91	70 to 80	140 to 150
E - 3	0.113	0.96	60 to 70	130 to 140
E - 4	0.112	0.99	60 to 70	120 to 130
E - 5	0.114	1.04	50 to 60	90 to 100
E - 6	0.108	1.07	40 to 50	90 to 100
E - 7	0.101	1.08	40 to 50	90 to 100
E - 8	0.111	1.14	20 to 30	80 to 90
E - 9	0.112	1.17	10 to 20	50 to 60
N - 1	0.189	0.84	130 to 150 hours	More than 160 hr.
N - 2	0.186	1.01	70 to 90	More than 150 hr.
N - 3	0.186	1.26	40 to 50	More than 140 hr.
N - 4	0.197	1.44	20 to 30	90 to 100 hours
N - 5	0.188	1.57	15 to 20	70 to 80
N - 6	0.185	1.89	5 to 10	40 to 50
N - 7	0.184	2.35	5 to 10	5 to 10

From a study of Table VII, it is quite evident that chromium has a decided inhibiting effect on rates of graphitization of white cast iron.

Sample D-1, which is of about the same silicon content as the reference sample (0.00% chromium), requires from 20 to 30 hours longer for complete graphitization. This slower rate might be contributed, in part, to the higher manganese content of the D series of alloys. However, if a comparison be made between the standard alloy and alloy F-1, containing 0.084% chromium, a marked difference is found. This alloy required from 170 to 190 hours for complete graphitization, which is from 110 to 120 hours longer than for the standard alloy.

Since, in this case, the small difference in manganese content is of but meager importance, we may conclude that 0.084% chromium with medium silicon presents a serious problem to the manufacturer of malleable iron.

Alloy E-1, somewhat higher in silicon than the standard, is seen to have a much slower rate of graphitization. There are two factors in connection with this alloy which should favor rapid graphitization; higher silicon and lower manganese. However, the presence of 0.111% chromium is much more effective in its inhibiting action than the higher silicon and lower manganese are in promoting graphitization.

An alloy of 0.189% chromium with medium silicon (0.84%) requires more than 300 hours (12 days) for graphitization. This amount of chromium exerts such a great stabilizing effect on combined carbon as to render the complete graphitization of this alloy commercially impractical. An increase of silicon from 0.84% to 1.57%, as in alloy N-5, will give an alloy of this same chromium content which can be completely graphitized in 3 to 3½ days.

A study of the higher silicon members of each series points out very well the powerful graphitizing influence of silicon. It is of interest to study the total times for complete graphitization of alloys D-2, F-8, E-9, and N-6.

In the case of D-2, we find an increase of 0.06% silicon will correct the retarding effect of 0.026% chromium. With alloy F-8, an increase of approximately 0.30% silicon corrects for 0.084% chromium. Following this comparison through series E, we find the retarding effect of 0.111% chromium to be corrected by an increase of slightly more than 0.35% silicon. Table VI has shown that the addition of 1.86% silicon to 0.188% chromium alloy produced a mottled structure. However, if we employ this alloy, N-6, in our comparison, it is found to require an increase of 1.07% silicon to offset the effect of 0.188% chromium.

Using this data for the four cases stated above, we may

calculate the ratio of silicon increase, required to produce a normal alloy in so far as rates of graphitization are concerned, to the percentage of chromium present.

For the D series this ratio becomes $0.06/0.026 = 2.30$

For the F series this ratio becomes $0.300/0.084 = 3.57$

For the E series this ratio becomes $0.350/0.111 = 3.15$

For the N series this ratio becomes $1.07/0.188 = 5.69$

These ratios are based on the normal alloy of 0.82% silicon.

Although in commercial practice silicon is generally present in greater amounts than 0.82%, the above ratios are of theoretical interest in making a comparative study of the chromium-silicon combinations.

Using the same alloys as mentioned above, it is interesting to calculate the ratios of total silicon required to the per cent chromium present.

These ratios become:

$$\text{Alloy D - 2} \quad 0.88/0.26 = 33.84$$

$$\text{Alloy F - 8} \quad 1.13/0.084 = 13.45$$

$$\text{Alloy E - 9} \quad 1.17/0.111 = 10.54$$

$$\text{Alloy N - 6} \quad 1.89/0.185 = 10.21$$

Since, in the case of alloy N-6, the fracture was slightly mottled, as shown in Table VI, it may be concluded that for

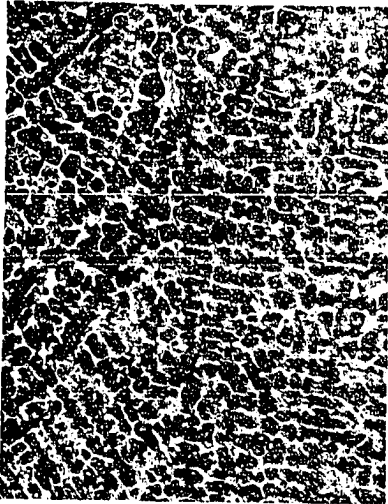
alloys of higher chromium content the above ratio would continue to grow smaller.

Photographs of alloys M-1, M-3, M-5 and M-8 are shown on pages 43 to 46 inclusive. The effect of increasing silicon content on the stability of cementite is well shown by these photographs. It is to be noted in the case of alloy M-1, that graphitization of the cementite is most rapid between 80 and 150 hours at 1700°F. With alloys M-5 and M-8 the greatest rate of graphitization occurs during the first 40 hours of heating. The last alloy of this series, M-8, containing 1.91% silicon, retains traces of cementite after 200 hours of heating at 1700°F.

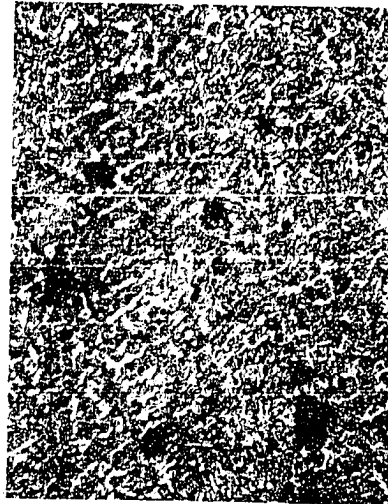
Pages 47 to 54, inclusive, contain photographs of several representative alloys of the D, E, F, N and O series. These photographs show the effect of chromium-silicon combinations on the cast structure and on the progressive annealing of these alloys. The times given under each photograph do not include the 8 hour interval in which the alloys cooled from 1700°F. to 1300°F.

Photographs D-9, N-6, N-7, as cast, show the only alloys of the entire group in which primary graphitization was produced while cooling in the mould.

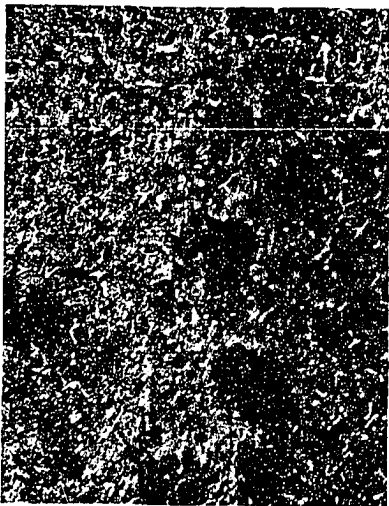
Alloy N-2 is very incompletely graphitized even after 150 hours at 1300°F. as shown on page 52.



Alloy M-1.
0.445% Cr., 0.83% Si.
Structure as cast.
Nitric acid etched. 75 X.



Alloy M-1.
0.445% Cr., 0.83% Si.
Annealed at 1700°F. (927°C.)
for 80 hours.
Nitric acid etched. 75 X.



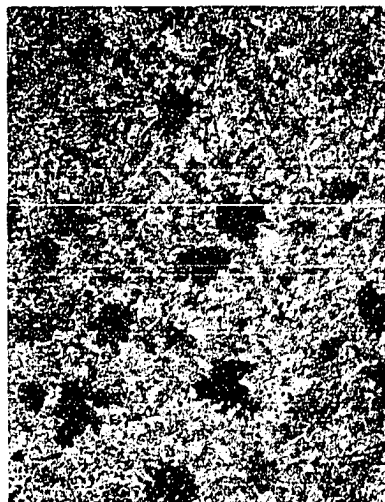
Alloy M-1
0.445% Cr., 0.83% Si.
Annealed at 1700°F. (927°C.)
for 150 hours.
Nitric acid etched. 75 X.



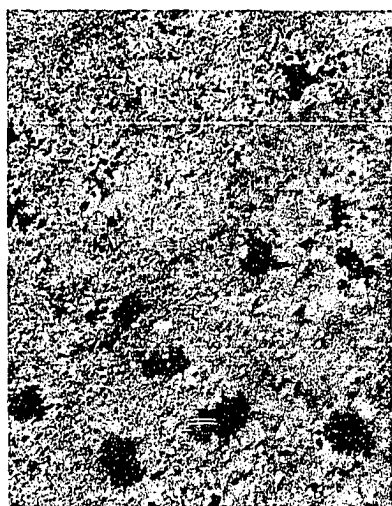
Alloy M-1.
0.445% Cr., 0.83% Si.
Annealed at 1700°F. (927°C.)
for 200 hours.
Nitric acid etched. 75 X.



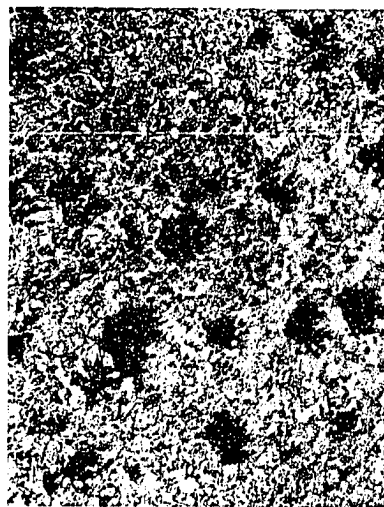
Alloy M-3.
0.448% Cr., 1.15% Si.
Structure as cast.
Nitric acid etched. 75 X.



Alloy M-3.
0.448% Cr., 1.15% Si.
Annealed at 1700°F. (927°C.)
for 80 hours.
Nitric acid etched. 75 X.



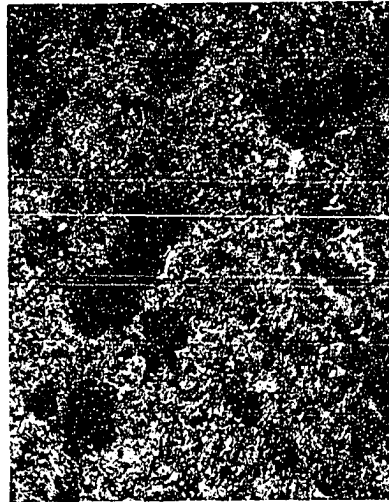
Alloy M-3.
0.448% Cr., 1.15% Si.
Annealed at 1700°F. (927°C.)
for 120 hours.
Nitric acid etched. 75 X.



Alloy M-3.
0.448% Cr., 1.15% Si.
Annealed at 1700°F. (927°C.)
for 200 hours.
Nitric acid etched. 75 X.



Alloy M-5.
0.443% Cr., 1.55% Si.
Structure as cast.
Nitric acid etched. 75 X.



Alloy M-5.
0.443% Cr., 1.55% Si.
Annealed at 1700° F. (927° C.)
for 40 hours.
Nitric acid etched. 75 X.



Alloy M-5.
0.443% Cr., 1.55% Si.
Annealed at 1700° F. (927° C.)
for 80 hours.
Nitric acid etched. 75 X.



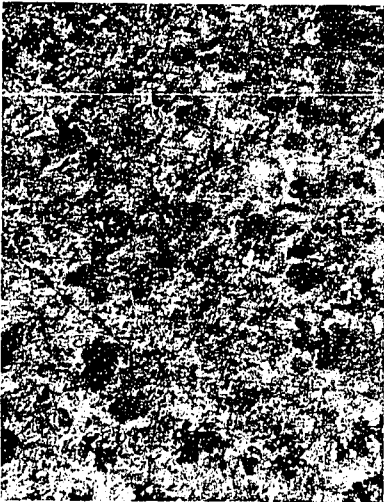
Alloy M-5.
0.443% Cr., 1.55% Si.
Annealed at 1700° F. (927° C.)
for 200 hours.
Nitric acid etched. 75 X.



Alloy M-8.
0.429% Cr., 1.91% Si.
Structure as cast.
Nitric acid etched. 75 X.



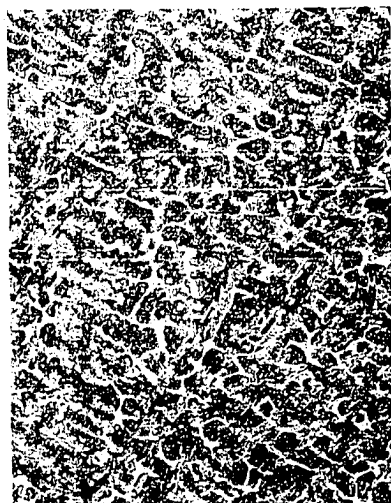
Alloy M-8.
0.429% Cr., 1.91% Si.
Annealed at 1700° F. (927° C.)
for 40 hours.
Nitric acid etched. 75 X.



Alloy M-8.
0.429% Cr., 1.91% Si.
Annealed at 1700° F. (927° C.)
for 80 hours.
Nitric acid etched. 75 X.



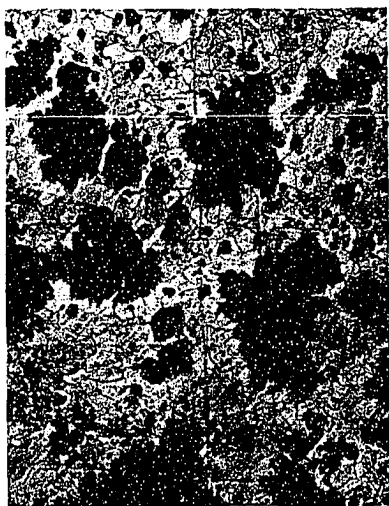
Alloy M-8.
0.429% Cr., 1.91% Si.
Annealed at 1700° F. (927° C.)
for 200 hours.
Nitric acid etched. 75 X.



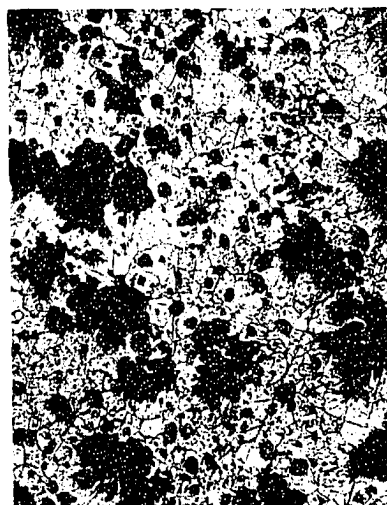
Alloy O-1.
0.00% Cr., 0.82% Si.
Structure as cast.
Nitric acid etched. 75 X.



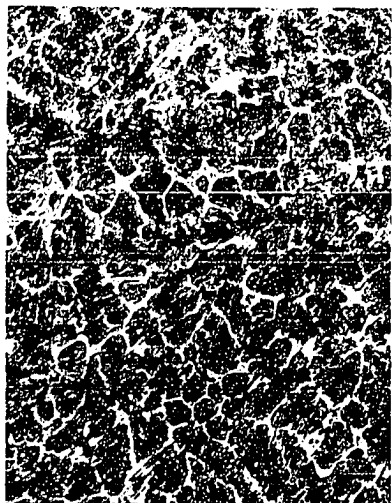
Alloy O-1.
0.00% Cr., 0.82% Si.
Annealed at 1700° F. (927° C.)
for 30 hours.
Nitric acid etched. 75 X.



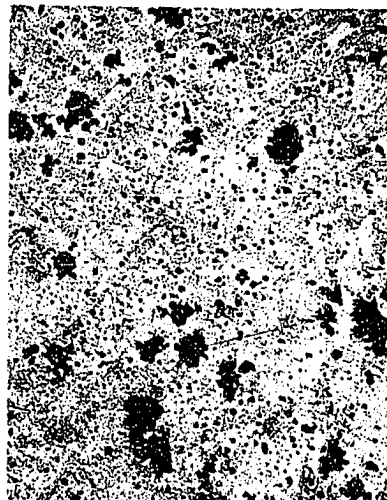
Alloy O-1.
0.00% Cr., 0.82% Si.
Annealed at 1700° F. (927° C.)
for 30 hours and at 1300 F.
for 15 hours.
Nitric acid etched. 75 X.



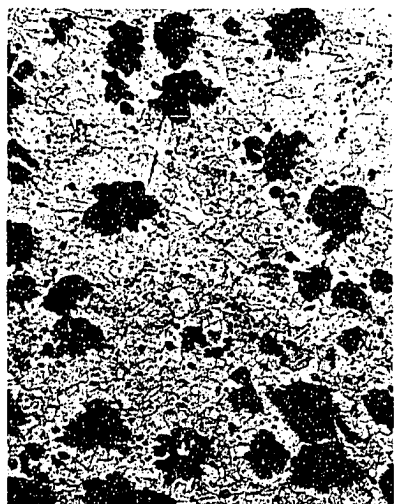
Alloy O-1.
0.00% Cr., 0.82% Si.
Annealed at 1700° F. (927° C.)
for 30 hours and at 1300 F.
for 35 hours.
Nitric acid etched. 75 X.



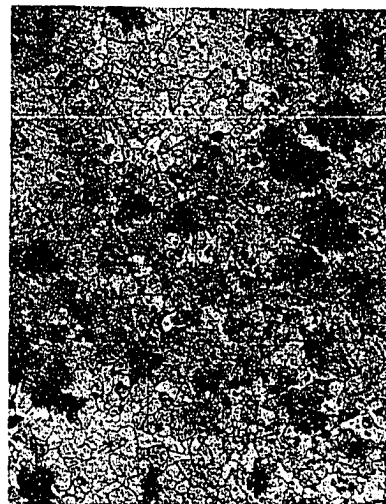
Alloy D-6.
0.026% Cr., 1.06% Si.
Structure as cast.
Nitric acid etched. 75 X.



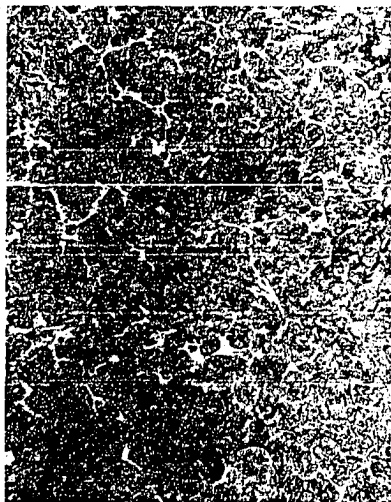
Alloy D-6.
0.026% Cr., 1.06% Si.
Annealed at 1700°F. (927°C.)
for 20 hours.
Nitric acid etched. 75 X.



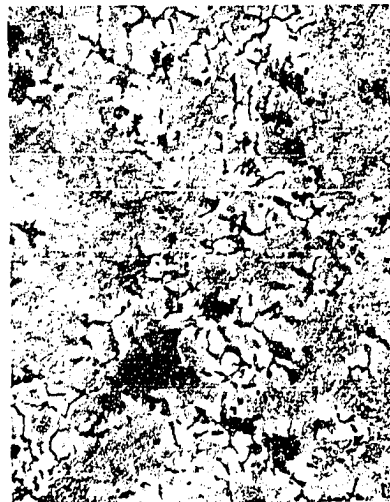
Alloy D-6.
0.026% Cr., 1.06% Si.
Annealed at 1700°F. (927°C.)
for 20 hours and at 1300°F.
for 20 hours.
Nitric acid etched. 75 X.



Alloy D-6.
0.026% Cr., 1.06% Si.
Annealed at 1700°F. (927°C.)
for 20 hours and at 1300°F.
for 30 hours.
Nitric acid etched. 75 X.



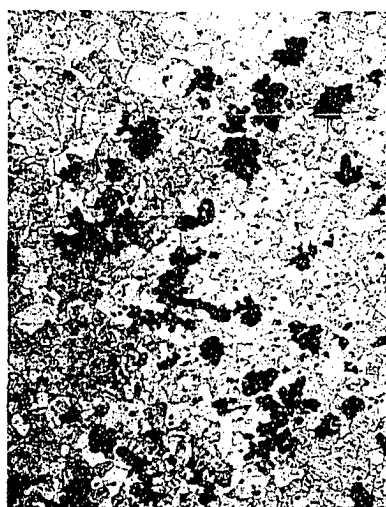
Alloy D-9.
0.025% Cr., 1.20% Si.
Structure as cast.
Nitric acid etched. 75 X.



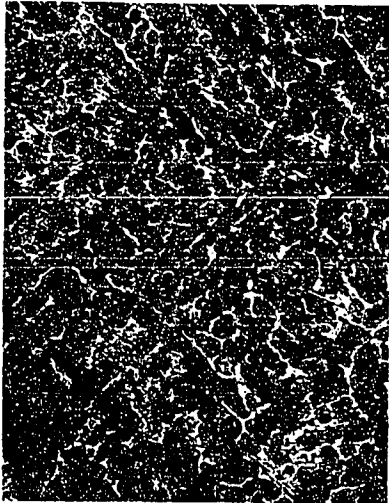
Alloy D-9.
0.025% Cr., 1.20% Si.
Annealed at 1700°F. (927°C.)
for 10 hours.
Nitric acid etched. 75 X.



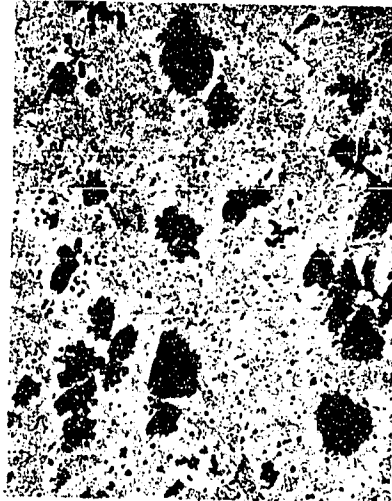
Alloy D-9.
0.025% Cr., 1.20% Si.
Annealed at 1700°F. (927°C.)
for 10 hours and at 1300°F.
for 10 hours.
Nitric acid etched. 75 X.



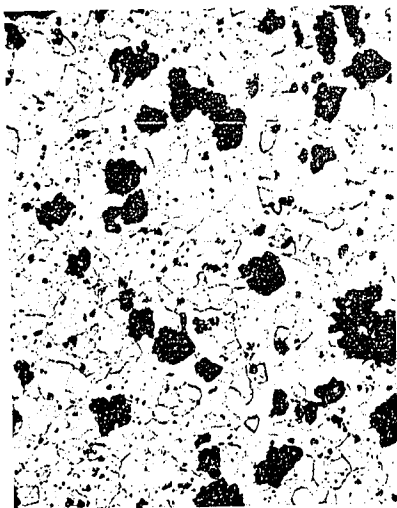
Alloy D-9.
0.025% Cr., 1.20% Si.
Annealed at 1700°F. (927°C.)
for 10 hours and at 1300°F.
for 20 hours.
Nitric acid etched. 75 X.



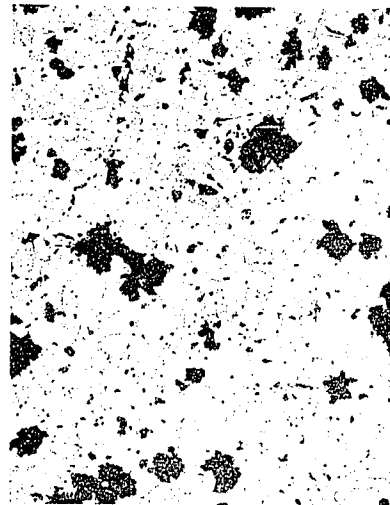
Alloy F-7.
0.084% Cr., 1.07% Si.
Structure as cast.
Nitric acid etched. 75 X.



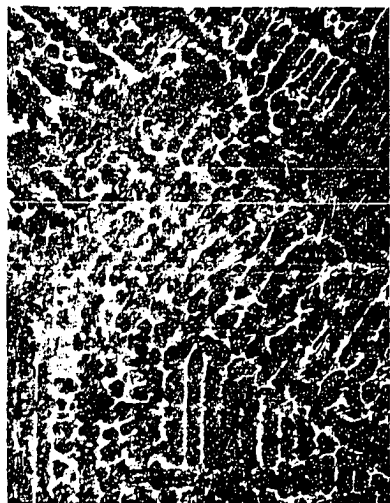
Alloy F-7.
0.084% Cr., 1.07% Si.
Annealed at 1700°F. (927°C.)
for 40 hours.
Nitric acid etched. 75 X.



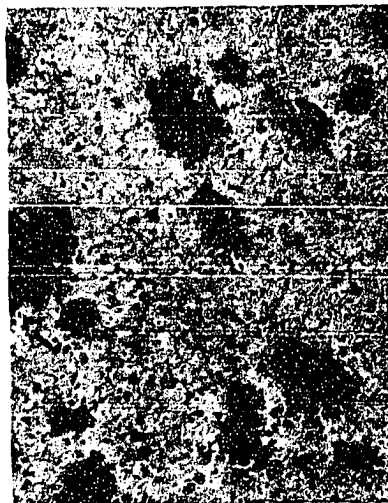
Alloy F-7.
0.084% Cr., 1.07% Si.
Annealed at 1700°F. (927°C.)
for 40 hours and at 1300°F.
for 50 hours.
Nitric acid etched. 75 X.



Alloy F-7.
0.084% Cr., 1.07% Si.
Annealed at 1700°F. (927°C.)
for 40 hours and at 1300°F.
for 60 hours.
Nitric acid etched. 75 X.



Alloy E-6.
0.108% Cr., 1.07% Si.
Structure as cast.
Nitric acid etched. 75 X.



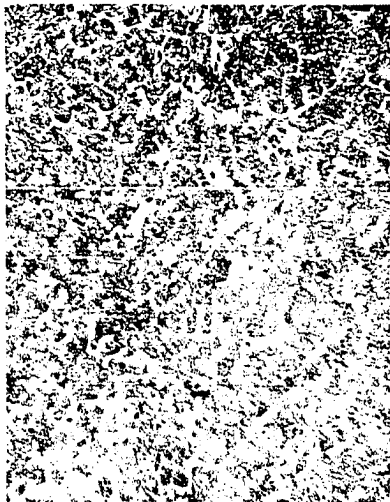
Alloy E-6.
0.108% Cr., 1.07% Si.
Annealed at 1700°F. (927°C.)
for 50 hours.
Nitric acid etched. 75 X.



Alloy E-6.
0.108% Cr., 1.07% Si.
Annealed at 1700°F. (927°C.)
for 50 hours and at 1300°F.
for 90 hours.
Nitric acid etched. 75 X.



Alloy E-6.
0.108% Cr., 1.07% Si.
Annealed at 1700°F. (927°C.)
for 50 hours and at 1300°F.
for 100 hours.
Nitric acid etched. 75 X.



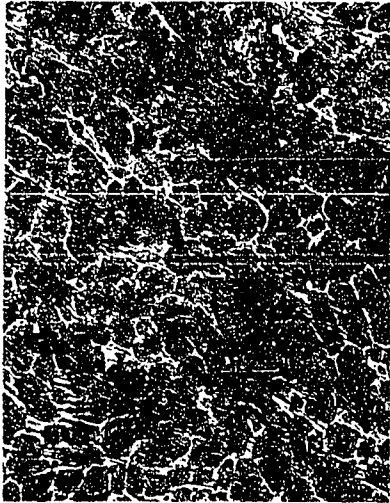
Alloy N-2.
0.186% Cr., 1.01% Si.
Structure as cast.
Nitric acid etched. 75 X.



Alloy N-2.
0.186% Cr., 1.01% Si.
Annealed at 1700°F. (927°C.)
for 70 hours.
Nitric acid etched. 75 X.



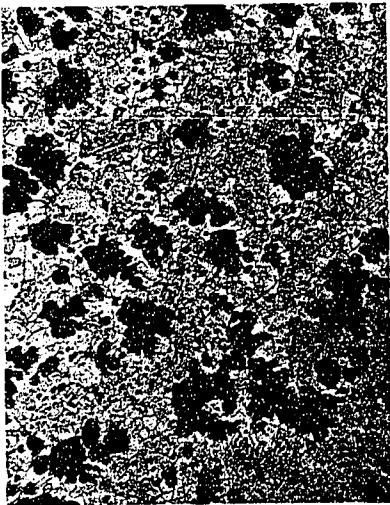
Alloy N-2.
0.186% Cr., 1.01% Si.
Annealed at 1700°F. (927°C.)
for 70 hours and at 1300°F.
for 150 hours.
Nitric acid etched. 75 X.



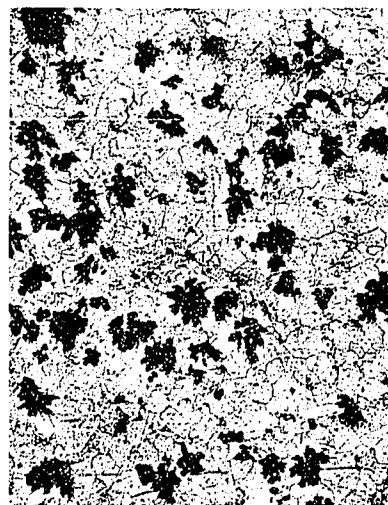
Alloy N-6.
0.185% Cr., 1.89% Si.
Structure as cast.
Nitric acid etched. 75 X.



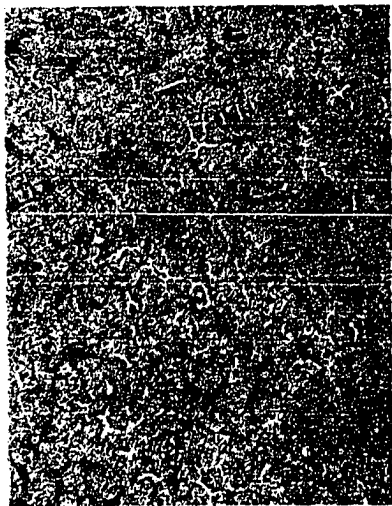
Alloy N-6.
0.185% Cr., 1.89% Si.
Annealed at 1700°F. (927°C.)
for 10 hours.
Nitric acid etched. 75 X.



Alloy N-6.
0.185% Cr., 1.89% Si.
Annealed at 1700°F. (927°C.)
for 10 hours and at 1300°F.
for 40 hours.
Nitric acid etched. 75 X.



Alloy N-6.
0.185% Cr., 1.89% Si.
Annealed at 1700°F. (927°C.)
for 10 hours and at 1300°F.
for 50 hours.
Nitric acid etched. 75 X.



Alloy N-7.
0.184% Cr., 2.35% Si.
Structure as cast.
Nitric acid etched. 75 X.



Alloy N-7.
0.184% Cr., 2.35% Si.
Annealed at 1700° F. (927° C.)
for 10 hours.
Nitric acid etched. 75 X.



Alloy N-7.
0.184% Cr., 2.35% Si.
Annealed at 1700° F. (927° C.)
for 10 hours and at 1300° F.
for 5 hours.
Nitric acid etched. 75 X.

V. CONCLUSIONS

Chromium, when present in white cast iron, exhibits a very marked stabilizing effect on combined carbon. That the combined carbon of the eutectoid as well as that of the cementite is stabilized, is shown by the greatly extended times required for graphitization of chromium bearing alloys, both at 1300°F. and 1700°F.

Silicon, by its powerful graphitizing tendency, is an effective agent for correcting the inhibiting influence of chromium. However, in order to prevent the separation of primary graphite during solidification, an upper limit of silicon for each chromium content must not be exceeded. For 0.025% chromium alloys this upper limit is between 1.15 and 1.20% silicon, while for 0.18% chromium alloys this limit is about 1.8% silicon.

When large amounts of scrap are used in the manufacture of pig iron, it is practically impossible to hold the chromium content much below 0.05%. By adding the proper amounts of silicon such pig iron can be annealed satisfactorily, resulting in a marked saving to the manufacturer of malleable iron.

No attempt has been made to correlate physical properties with chemical composition. It is quite possible that the alloys of higher silicon content, i.e., those requiring relatively short annealing periods, would show inferior physical properties.

VI. SUMMARY

1. A study of the quantitative effects of chromium on cementite stability has been made.
2. Rates of first and second graphitization stages have been determined for several alloy series containing constant amounts of chromium and varying amounts of silicon.
3. Several ratios of theoretical interest have been calculated.
4. Photographs, showing the effects of chromium and of chromium-silicon combinations on graphitization rates, are included.

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