Influence of the various Elements on the Graphitization in Cast Iron

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Influence of the various Elements on the Graphitization in Cast Iron.

BY

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INTRODUCTION.

Recently with the development of various industries, various special properties have come to be required for cast iron which is one of the basal materials of industry.

Thus, investigations to improve the properties of cast iron and endow it with some special properties by adding various elements to common cast iron are being intended everywhere. However, there are some fundamental problems in the course of these investigations: (1) What effect have the elements on the graphitization in cast iron? and (2) What is the degree of the effect?

Up to the present, of course, experiment in this direction has been made by many investigators. But, to our regret, their methods have been rather primitive and moreover their works have been restricted to the investigation of the influences of some few special elements.

The principal object of the present work is to solve very clearly the above fundamental problems by new methods of investigation. The results of the investigation will be described in Part I. In Part II, the theory of the graphitization in cast iron will be argued based on the results of the investigation described in Part I, and those of some investigations carried out supplementarily.

Part. I. INFLUENCE OF THE VARIOUS ELEMENTS ON THE GRAPHITIZATION IN WHITE CAST IRON.

§ I. MATERIALS

The kinds and the results of analysis of raw materials used in the present work are summarised in Table 1.

Table 1.

Raw Materials No.	Kinds of Raw Materials	Composition (%)						
		C	Si	Mn	P	S	Cu	Other Element
A	White Cast Iron	3.45	0.15	0.15	0.113	0.045	0.190	—
B	White Cast Iron	1.99	0.018	0.033	0.070	0.017	trace	—
C	Gray Cast Iron	3.46	3.73	0.41	0.023	0.008	0.015	—
D	Soft Steel	0.24	0.02	0.48	0.034	0.040	0.151	—
E	Metallic Silicon	—	99.01	—	—	—	—	—
F	Metallic Aluminium	—	0.04∼0.16	—	—	—	0∼0.11	Fe=0.30∼0.40
G	Metallic Nickel	—	—	—	—	—	—	Ni=98
H	Metallic Copper		Electrolytic Copper.					
I	Metallic Cobalt	—	—	—	—	—	—	Co=98.
J	Metallic Gold		Pure Gold					
K	Metallic Platinum		Pure Platinum					
L	*Ferro-Sulphur	—	—	—	—	19.87	—	—
M	Ferro-Silicon	0.10	24.90	0.57	0.028	0.009	trace	—
N	Ferro-Titanium	8.04	7.47	0.45	0.057	0.012	—	Ti=24.96 Al=0.96
O	Ferro-Chromium	1.39	13.06	0.31	0.018	0.33	—	Cr=58.08 Al=0
P	Ferro-Vanadium	0.45	5.23	1.80	0.003	0.28	—	V=30.94 Al=0
Q	Ferro-Tungsten	0.58	2.91	1.15	0.015	0.37	—	W=80.22 Al=0.03
R	Ferro-Molybdenum	—	—	—	—	—	—	Mo=97
S	Ferro-Phosphorus	0.31	0.28	0.72	17.84	0.044	—	—
T	Ferro-Manganese	6.79	0.42	79.55	0.32	0.001	—	—

* Prepared from raw material No. D and sulphur.

The raw material No. A and three other kinds of white cast irons which were prepared by melting together the raw materials No. A, D and M in proper proportion in a graphite crucible lined with alumina or alundum cement were adopted as the starting materials of the present experiments, to which another raw material was added to get a white cast iron containing some special element whose influence on the graphitization was to be examined. The approximate compositions of these starting materials is given in Table 2.

Table 2.

Starting Materials No.	Composition (Approximate per Cent)		
	C	Si	Other Impurities
I	3·45	0.15	Minute
II	2.50	0.15	Minute
III	1.80	0.15	Minute
IV	2.50	0.80	Minute

§ II. METHOD OF INVESTIGATION.

White cast iron having no other elements consists of cementite and ferrite in normal state. By complete decomposition of cementite to carbon and iron, the white cast iron having 3.4 per cent of carbon expands about 4 per cent by volume. Hence, by the measurement of the thermal expansion of white cast irons, we shall be able to trace the process of the graphitization in them in detail. For this purpose, the present writer adopted Honda's dilatometer.[1]

In order to investigate the subject in a range as wide as possible, the present writer adopted chill cast white cast irons as the specimens for the dilatometer experiment, which were prepared as follows.

100 to 200 grs. of the starting material were melted in a graphite crucible lined with alumina or alundum cement in a kryptol furnace. In a few minutes after the charging of the crucible, when all the metals were melted together, a weighed amount of the special raw material was added, and after well stirring and then allowing proper time in the furnace, the melt was cast in an iron mould with a thick wall into several ingots 5 m.m. in dia. The specimen was then prepared by cutting the ingot to a length of 70 m.m..

Heating and cooling of the specimen were always carried out in

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1) Sci. Rep. Tohoku Imp. Univ. 6, (1917), 203.

vacuo at the following rate:

— Heating rate —

room temp.→(5°C per. min.)→required temp. (about 1,070°C).

— Cooling rate —

required temp. (about 1,070°C)→(5°C per min.)→Ar_1→(furnace cooling)→ room temp.

The distance from the mirror of the meter to the scale was kept constant throughout the experiments.

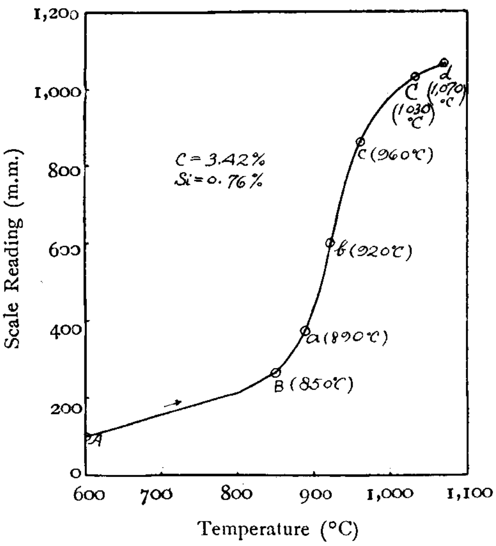
The electric resistance furnace employed for heaing the specimen was made so as to keep the uniformity of temperature less than 2° C in the range of 150 m.m. in the middle of the furnace.

The temperature of the specimen was measured with a thermocouple consisting of platinum and platinum—rhodium wires, the hot junction of which was placed at an extreme adjacent point to one end of the specimen.

Before entering into the main subject, the present writer will show how clearly the process of the graphitization can be developed by this new method of investigation with a typical example.

Figs. 1 and 2 show the two kinds of curves obtained from the same dilatometer experiment on a specimen having the following compositions: C=3.42%, Si=0.76%, other impurities=minute.

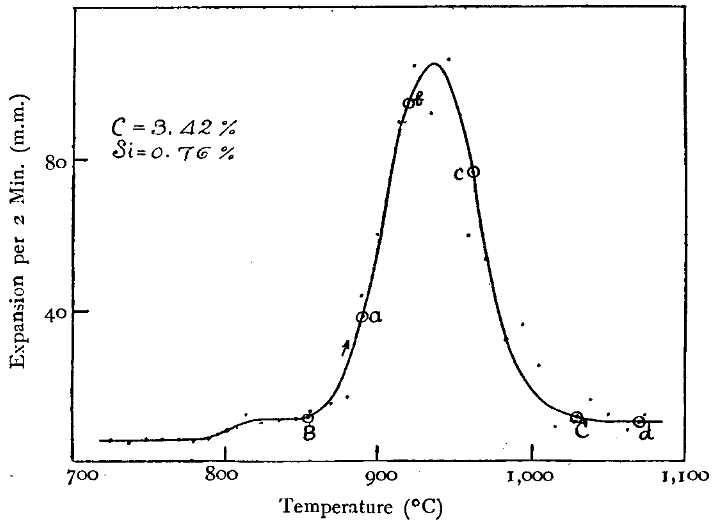
Fig. 1.



In these figures, the abscissa represents temperature, the ordinate scale reading in Fig. 1, andt he linear expansion per 2 min. in Fig. 2.

These curves show that an irreversible expansion begins at B(850°C) and ends at C(1,030° C). The present writer found that it was entirely due to the graphitization in the alloy by

Fig. 2.



other methods, and that B and C were the beginning and end temperatures of the graphitization of the alloy respectively.

Chemical analysis and microscopic study were, of course, always carried out on all specimens both in the cast and in the annealed state.

As supplementary work, the specific gravity of the specimens both in the cast and in the annealed state was always measured after Archimedes' principle, and the volume change of the specimens due to graphitization was calculated. The magnetic analysis by Honda's magnetometric method¹⁾ was also adopted in some cases.

In the present experiments, when the element was one which favours the graphitization in cast iron, not only its characteristic effect upon practically pure white cast iron, taking the starting materials No. I, II or III, but also its effect in the presence of a moderate amount of silicon, taking the starting material No. IV, was studied. When the element was one which hinders graphitization, only its effect in the presence of a moderate amount of silicon, taking the starting material No. IV, was

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1) Sci. Rep. Tohoku Imp. Univ. 5, (1916), 285.

studied, and its characteristic property was only conjectured since its characteristic effect upon pure white cast iron could not be found by the experimental method adopted in the present work.

§ III. INFLUENCE OF SILICON.

It is a well known fact that silicon strongly favours graphitization in cast iron as we see from the works of previous investigators.[1] But the clear relation between the silicon content in cast iron and the degree of its effect on the graphitization has not yet been shown. Nor has the reason why silicon favours graphitization been fully explained. As regards the last point, recently Profs. Honda and Murakami[2] imputed the readiness of the graphite formation in cast iron having silicon to the following three facts:

(1) The non-magnetic silico-carbide primarily separated is very unstable,

(2) Silicon diminishes the solubility of carbon in the melt or austenite,

(3) Silicon raises eutectic and eutectoid temperatures.

Of course, all these conditions must favour graphitization. But the reason why silicon favours the graphitization of the magnetic cementite which covers the most of the constituents to be graphitised in common cast iron was not explained by them.

A. Constitution of the specimens in the tempered state.

Honda and Murakami[3] deduced the constitutional diagram of iron, carbon and silicon system from the results of magnetic analysis and microscopic observation.

The present writer also investigated the constitution of chill cast white cast irons having silicon by the same method.

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1) Charpy and Grenet: Bull. Société dencouragement (1902), 399.
Wüst and Schlösser: Stahl u. Eisen 24, (1904), 1120.
Liszner: Ferrum 11, (1912), 44.

2) Sci. Rep. Tohoku Imp. Univ. 12, (1924), 287.

3) ditto.

Magnetic analysis :— 23 specimens with varied carbon and silicon contents were subjected to measurement. They were always 5 m.m. thick and 70 m.m. long. The deflection of the magnetometer was observed during heating and cooling at the rate of 5°C per min.. The maximum heating temperature was limited to 600°C, above which graphitization may occur in the specimens.

Classifying the form of the cooling curves into three groups, a constitutional diagram has been deduced as shown in Fig. 3.

Fig. 3.

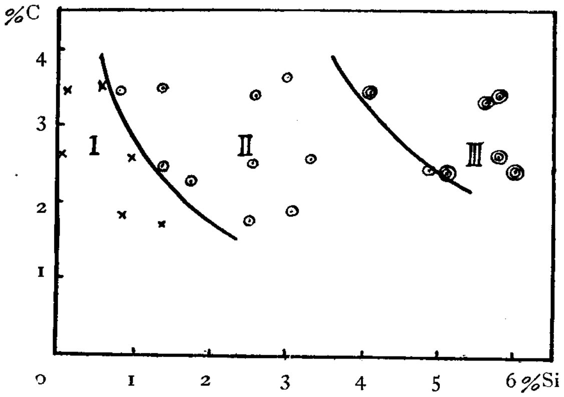
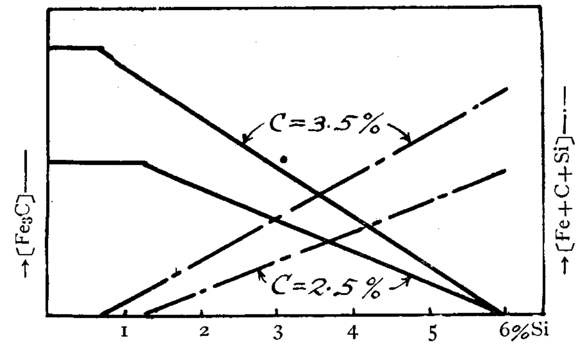


Fig. 4.



The constituents belonging to fields I, II, and III, are as follows:

I. silico-ferrite + cementite,

II. silico-ferrite + cementite + solid solution consisting of iron, carbon and silicon ; (Fe + C + Si),

III. silico-ferrite + cementite + (Fe + C + Si) + graphite.*

The results well coincide with those obtained by the professors before referred to.

Examining the intensity of the magnetic transformations at about 200° C and 500° C with the specimens, the fallowing facts were found :

(1) The amount of the cementite in the tempered alloys gradually decreases as the silicon

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* Found by microscopic study.

content increases to about 6 per cent, the alloys having more than 6 per cent of the element having no cementite.

(2) The amount of the solid solution (Fe + C + Si) increcses replacing cementite as the silicon content increases.

These relations are diagramatically shown in Fig. 4.

Although the real nature of the constituent having a magnetic transformation at about 500°C has not been definitely determined, it should be a substance containing carbon since its amount increases replacing cementite as the silicon content increases as above mentioned, and moreover it should be a solid solution consisting of iron, carbon and silicon for the same reason as described by the professors in their paper.

Microscopic study :— When an alcoholic solution of nitric acid was used as the etching reagent, all the specimens displayed similar dendritic structures as shown in Photogr. 65. The cementite and the solid solution (Fe + C + Si) should correspond to the white part since its area does not practically vary with the silicon content. The cementite could be distinguished, however, from the solid solution (Fe + C + Si), since the former was more deeply colored than the latter by a hot alkaline solution of sodium picrate.

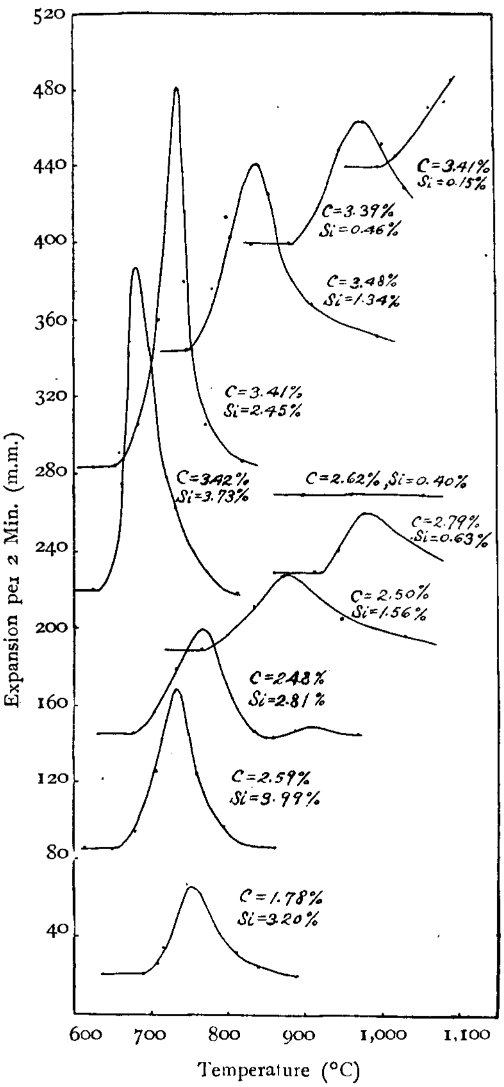
Photogrs. 1 to 6 show the typical structure of the alloys in the cast state. Photogrs. 3 to 6 show that the amount of primary cementite in acicular form decreases and that of the solid solution (Fe + C + Si) represented by the colored matrix increases as the silicon content increases. Photogr. 5 shows the graphite produced by the direct decomposition of the cementite.

By microscopic stuby of the alloys, it was also ascertained that the tempering of the alloys only meant the transformation of the residual austenite and martensite to troostite, consequently a part of the cementite in Fig. 4 was that produced by tempering from austenite and martensite.

B. Graphitization Experiment.

The compositions of the specimens are given in Table 3. Figs. 5 and 6 show typical graphitization curves of the alloys.

Fig. 6.



In these curves, two irreversible changes at about 170°C and 500°C are due to the tempering of the alloys in the cast state.

Important data concerning the graphitization of the alloys are summarised in Table 3, where

A = the heating temperature (°C),

B = the beginning temperature of graphitization (°C),

C = the end tmperature of graphitization (°C),

D = the temperature at which the maximum expansion of the specimens takes place (°C),

E = the maximum height of graphitization curves (m.m.),

F = the total linear expansion in the graphitization period referred to 100 m.m. of the specimen in the cast state; that is,

$$\frac{\text{the difference of the scale readings at the beginning and at the end temperatures of the graphitization of the specimens}}{\text{true length of the specimens (L)}} \times 100 \text{ (m.m.)},$$

G = the decrease in specific gravity or the increase in volume of the specimens due to graphitization; that is,

Fig. 5–a

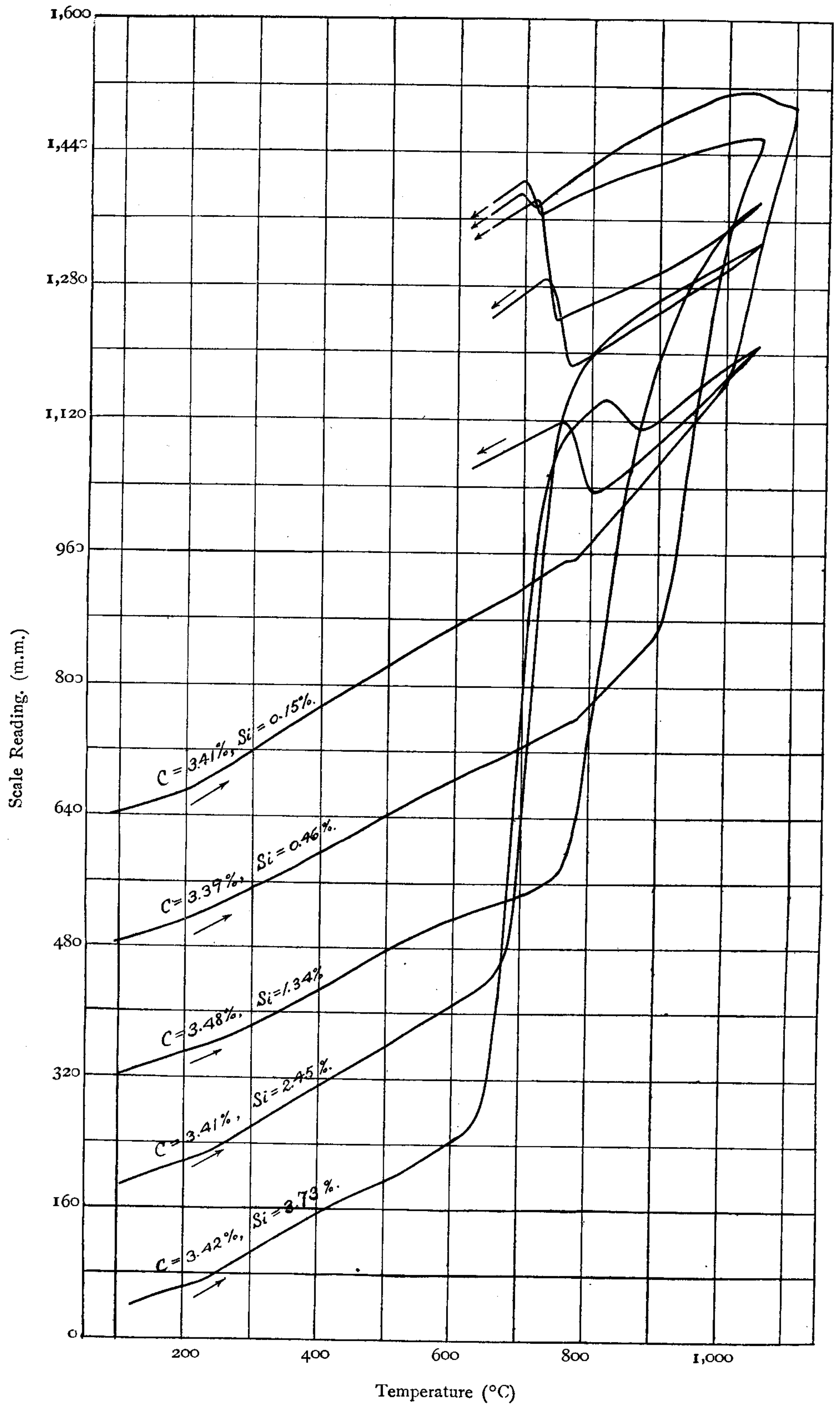


Fig. 5–b

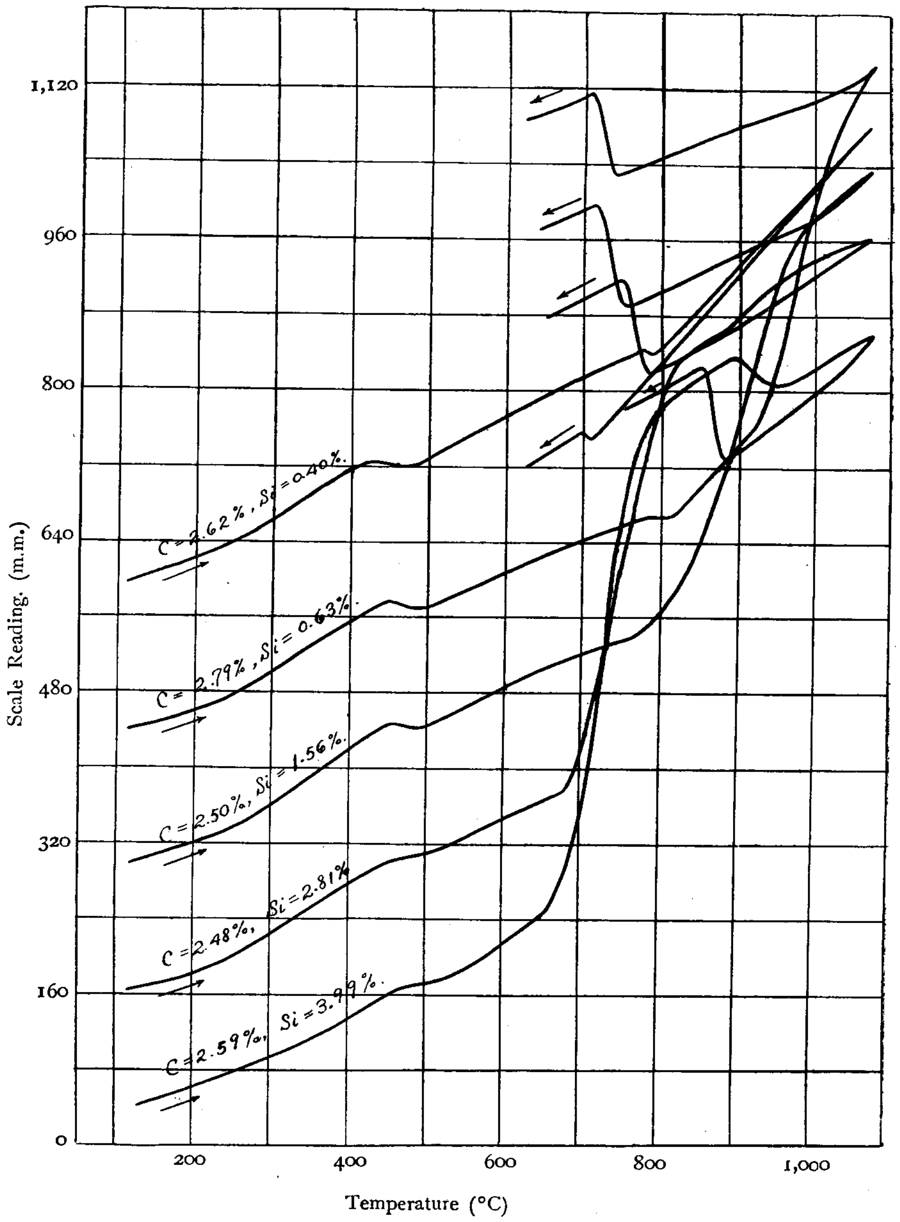
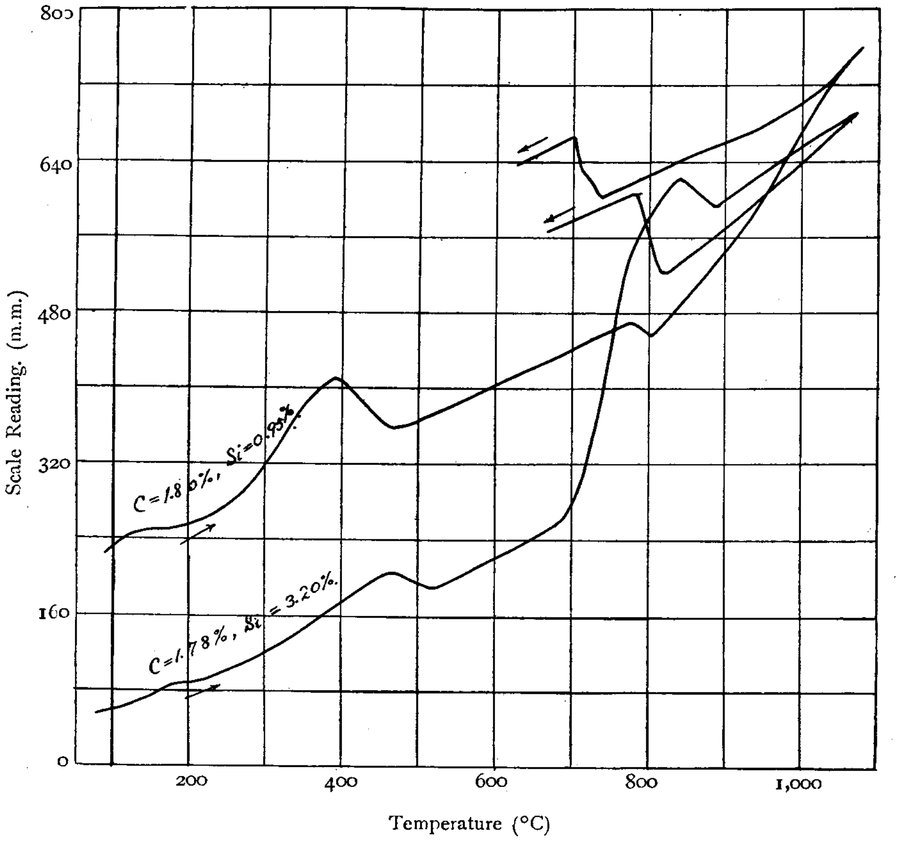


Fig. 5–c



$$\frac{\text{the difference of the specific gravity of the specimens in the cast and in the annealed state}}{\text{specific gravity of the specimens in the cast state}} \times 100 \ (\%),$$

H = the amount of the combined carbon in the annealed specimens (%).

The graphical expression of these symbols* are shown in Fig. 7.

Fig. 7.

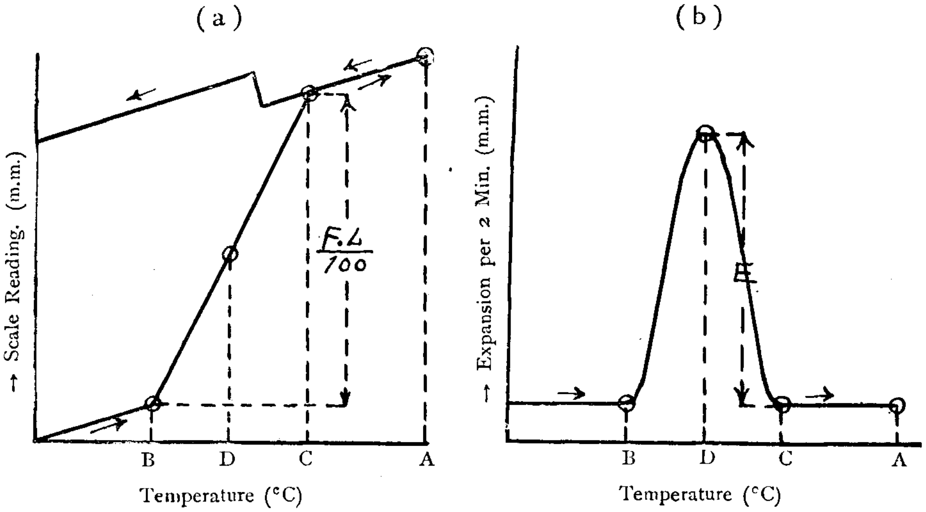


Table 3.

Specimens. No.	Composition (%)						A	B	C	D	E	F	G	H
	C	Si	Mn	S	P	Cu								
1	3.41	0.15	0.17	0.040	0.115	0.185	1,100	1,000	—	—	—	—	4.65	1.35
2	3.42	0.18					1,050	980	—	—	—	—	4.51	2.05
3	3.35	0.27	0.17	0.041	0.113	0.189	1,050	960	—	1,040	80	—	4.55	1.57
4	3.44	0.32	0.18	0.040	0.101	0.180	1,010	940	—	990	70	—	4.67	1.50
5	3.41	0.40					1,010	910	—	1,010	80	—	5.05	—
6	3.47	0.44					1,050	890	—	950	90	—	4.81	0.94
7	3.39	0.46	0.21	0.035	0.089	0.139	1,050	890	—	979	70	—	4.85	1.18
8	3.45	0.48					1,050	890	—	960	80	—	—	0.83
9	3.40	0.52					1,050	880	1,070(?)	970	90	880	—	0.70
10	3.46	0.53					1,050	870	1,070(?)	940	100	930	5.00	0.77

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* The same symbols will be used without any further remarks in the tables of the same kind which will be given in the following pages.

Specimens. No.	Composition (%)						A	B	C	D	E	F	G	H
	C	Si	Mn	S	P	Cu								
11	3.43	0.58					1,050	860	1,100(?)	920	70	890	5.30	1.08
12	3.43	0.61					1,050	870	1,070(?)	950	70	930	5.34	0.76
13	3.42	0.72					1,050	830	1,040	910	80	930	5.16	—
14	3.48	0.81					1,050	830	1,050	940	100	1,000	5.36	0.72
15	3.38	0.85					1,050	830	1,050	920	90	1,100	5.07	0.50
16	3.44	1.05					1,050	810	1,010	890	80	1,070	5.71	0.14
17	3.48	1.34					1,050	750	990	840	100	1,140	5.71	trace
18	3.43	1.36					1,050	780	1,000	880	120	1,220	6.05	(*) 0
19	3.46	1.59					1,010	730	950	800	120	1,230	—	(*) 0
20	3.35	1.60					1,050	720	940	800	140	1,210	6.20	(*) 0
21	3.41	1.71	0.32	0.029	0.060	0.113	1,050	710	920	790	140	1,240	6.16	(*) 0
22	3.37	1.95	0.35	0.021	0.058	0.121	1,050	690	890	760	130	1,250	—	(*) 0
23	3.45	2.00	0.35	0.021	0.049	0.075	1,050	690	900	780	140	1,250	6.48	(*) 0
24	3.40	2.39					1,050	670	860	750	140	1,300	—	(*) 0
25	3.41	2.45					1,010	660	800	740	200	1,320	6.86	(*) 0
26	3.42	2.72					1,010	650	830	720	150	1,300	6.49	(*) 0
27	3.45	2.87					1,010	650	830	710	190	1,310	7.26	(*) 0
28	3.40	3.33					1,010	650	820	720	160	1,330	7.21	(*) 0
29	3.42	3.73	0.45	0.008	0.021	0.013	1,050	630	800	680	170	1,320	7.43	(*) 0
30	2.58	0.19	0.21	0.044	0.093	0.190	1,080	—	—	—	—	—	0.31	2.46
31	2.51	0.33					1,080	—	—	—	—	—	0.50	2.24
32	2.62	0.40					1,080	—	—	—	—	—	0.22	1.67
33	2.56	0.52					1,080	930	—	1,020	40	—	3.50	—
34	2.55	0.58					1,080	940	—	1,020	40	—	3.38	—
35	2.79	0.63					1,080	920	—	980	40	—	4.22	0.95
36	2.55	0.78					1,080	900	—	970	40	—	—	—
37	2.51	0.81	0.25	0.048	0.080	0.105	1,080	870	—	950	40	—	4.33	—
38	2.54	0.85					1,080	880	—	950	30	—	4.00	—
39	2.49	0.99					1,080	850	—	920	40	—	4.35	0.26
40	2.60	1.24					1,080	820	—	900	40	—	—	—
41	2.65	1.37					1,080	790	1,100(?)	870	40	680	4.67	0.23
42	2.50	1.56					1,080	770	1,100(?)	880	50	650	—	0.07
43	2.61	1.79					1,080	730	970	830	50	710	4.65	(*) 0
44	2.68	2.04					1,080	680(?)	930	790	60	770	5.44	(*) 0
45	2.57	2.37					1,080	710	950	800	60	800	5.60	(*) 0
46	2.48	2.81					1,080	680	890	770	60	850	5.22	(*) 0
47	2.52	2.93					1,080	680	920	760	70	870	5.50	(*) 0
48	2.53	2.96					1,080	690	920	750	80	870	5.52	(*) 0
49	2.50	3.47					1,080	660	850	740	80	870	—	(*) 0
50	2.59	3.99					1,080	660	820	730	90	880	5.63	(*) 0

Speci-mens. No.	Composition (%)						A	B	C	D	E	F	G	H
	C	Si	Mn	S	P	Cu								
51	1.55	0.65					1,080	940	1,020	980	18	200	2.2	1.26
52	1.80	0.95					1,080	900	990	930	20	200	2.6	0.80
53	1.71	1.93					1,080	750	980	840	30	390	3.4	0.11
54	1.78	3.20					1,080	690	870	750	50	500	3.7	(*) 0

* Determined by microscopic study and magnetic analysis.

The relation between the beginning and the end temperature of graphitization of the alloys and the silicon content is shown in Figs. 8, 9 and 10. The relation between the amount of the combined carbon in the annealed alloys and the silicon content is shown in Figs. 11, 12 and 13. From these data, the following facts are found :

(1) The beginning and the end temperature of graphitization descends rapidly in the alloys having lower silicon, and gradually in the alloys having higher silicon, as the silicon content increases, but there is a minimum limit in the temperatures under discussion.

(2) As regards the specimens having the same amount of silicon, the higher the carbon content, the lower the beginning temperature of graphitization.

(3) The alloys having more than about 1 per cent of silicon in the alloys having 3.45 per cent of carbon, or more than about 1.5 per cent of silicon in the alloys having 2.5 per cent of carbon, begin to graphitise at a temperature lower than their Ac_1, and some of them having higher silicon completely graphitise until their temperature rises to their Ac_1.

(4) Since the most of the carbon in the completely graphitised alloys exists in a free state, it is evident that both the cementite and the solid solution (Fe+C+Si) are concerned with the graphitization, and also that the stability of these two constituents decreases to a certain limit as the silicon content or the carbon content increases.

C. Constitution of the specimens in the annealed state.

Magnetic analysis :— From the results of the usual magnetic analysis

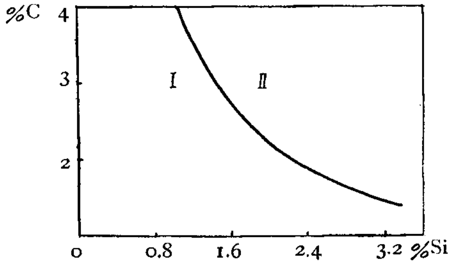


Fig. 14.

of the annealed alloys, a constitutional diagram was obtained as shown in Fig. 14.

The constituents belonging to the fields in the diagram are as follows:

I. cementite + silico-ferrite + temper carbon,

II. silico-ferrite + temper carbon.

The solid solution (Fe + C + Si) was not found at all in any of the annealed alloys.

Microscopic study:— It was observed in the microstructure of the annealed alloys that the alloys having more than about 1.4 per cent of silicon in the alloys having 3.45 per cent of carbon, or more than about 1.8 per cent of silicon in the alloys having 2.5 per cent of carbon contained almost no carbon in the combined state. The form of the temper carbon gradually changes from nodular to flaky, as the silicon content increases. The size of the temper carbon gradually decreases while its number increases as the silicon content increases. Photogrs. 51 and 7 show the relations above mentioned.

D. Summary.

The results so far obtained may be summarised as follows:

(1) The effect of silicon up to about 4 per cent on the graphitization in practically pure white cast iron with varied carbon content has been definitely determined.

(2) Silicon strongly favours the graphitization in the alloys, but it has a limit in its effect.

(3) The alloys having a higher silicon content begin to graphitize at a temperature lower than their Ac_1, or completely graphitize until their temperatures rise to their Ac_1.

(4) The constitution of the alloys has been examined by means of magnetic analysis and microscopic observation.

(5) Both the cementite and the solid solution (Fe+C+Si) in the alloys are graphitised by annealing. Their stability decreases as the carbon content or the silicon content of the alloys increases.

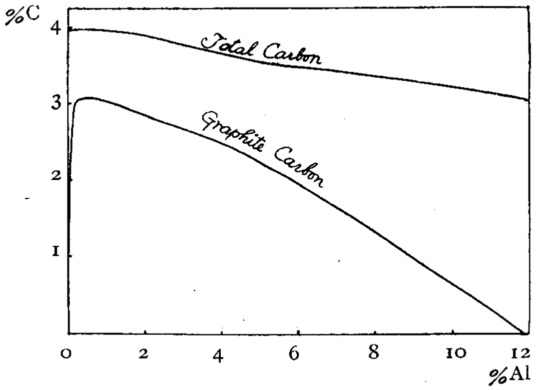
(6) Why the stability of the cementite, which has a magnetic transformation point at about 200° C, decreases as the carbon content or the silicon content of the alloys increases is an important question which remains yet unsolved.

(7) The form of the temper carbon produced in the annealed alloys changes from nodular to flaky as the silicon content increases. The size of the temper carbon gradually decreases while its number gradually increases as the silicon content increases.

§ IV. INFLUENCE OF ALUMINIUM.

The fact that aluminium favours graphitization in cast iron has been known from the investigations of Keep[1] and Hogg.[2] Melland and Waldron[3] were the last investigators who studied the subject in a systematic manner. Fig. 15 shows the results obtained by them from the slowly cooled cast iron containing aluminium.

Fig. 15.



A. Influence of aluminium on the graphitization in white cast iron having a minute amount of other impurities.

(a) Constitution of the specimens in the tempered state.

The constitution of the specimens used for the graphitization experiments was studied by the usual magnetic analysis and microscopic

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1) Trans. Amer. Inst. Min. Eng. 18, (1889–90), 102.
2) Journ. Ir. St. Inst. (1894), No. II, 104.
3) Journ. Ir. St. Inst. (1900), No. II, 244.

observation.

The compositions of the specimens are given in Table 4.

Table 4.

Specimens No.	Composition. (%)		A	B	C	D	E	F	G	H
	C	Al								
1	3.43	0.08	1,070	950	—	1,050(?)	40(?)	—	4.88	—
2	3.78	0.13	1,070	890	—	1,050(?)	40(?)	—	5.09	—
3	3.56	0.16	1,070	860	—	950	50	—	5.27	0.84
4	3.45	0.60	1,070	780	1,030	830	50	930	6.05	0.17
5	3.47	1.23	1,070	780	1,030	910	40	940	5.82	0.08
6	3.55	1.36	1,070	780	1,030	900	100	930	5.96	0.11
7	3.39	2.09	1,070	780	970	810	120	930	6.15	0.15
8	3.69	2.90	1,070	780	950	840	140	890	6.00	0.10
9	3.49	3.50	1,070	780	950	820	140	810	5.49	0.09
10	3.54	4.22	1,070	770	920	820	100	630	5.02	0.10
11	3.42	5.65	1,070	770	910	800	90	540	3.17	0.65
12	3.35	6.42	1,070	780	920	830	60	400	2.91	0.98
13	3.48	6.89	1,070	780	920	820	70	250	1.55	1.40
14	3.45	7.81	1,070	780	920	820	30	180	1.21	2.78
15	3.43	8.82	1,070	—	—	—	—	—	−0.13	3.43
16	2.83	10.09	1,070	—	—	—	—	—	−0.21	2.83
17	2.89	10.23	1,070	—	—	—	—	—	−0.20	2.89
18	2.65	13.49	1,070	—	—	—	—	—	−0.06	2.65
19	2.58	15.51	1,070	—	—	—	—	—	−0.24	2.58
20	2.37	17.89	1,070	—	—	—	—	—	−0.27	2.37
21	2.47	0.32	1,070	970	—	1,020(?)	20	—	2.13	—
22	2.53	0.70	1,070	850	1,040	900–1,010	20	530	2.69	0.62
23	2.51	1.01	1,070	830(?)	1,030	870–1,000	20	550	2.45	0.69
24	2.50	1.22	1,070	800	1,010	850	30	510	—	0.58
25	2.56	1.54	1,070	760	850	800	50	480	3.14	0.41
26	2.53	2.64	1,070	730	830	760	140	590	2.97	0.06
27	2.55	3.51	1,070	740	850	780	60	480	3.02	0.10
28	2.59	4.50	1,070	760	860	780	40	450	2.79	0.09
29	2.48	5.95	1,070	800	900(?)	820	30	400(?)	3.21	1.17
30	2.49	6.21	1,070	800	900(?)	820	30	260(?)	2.10	1.43
31	2.21	7.61	1,070	—	—	—	—	—	1.07	2.21
32	2.28	7.72	1,070	—	—	—	—	—	1.29	2.28
33	2.29	8.19	1,070	—	—	—	—	—	−0.32	2.29
34	2.34	9.68	1,070	—	—	—	—	—	−0.12	2.34
35	2.21	10.72	1,070	—	—	—	—	—	−0.08	2.21
36	2.02	13.49	1,070	—	—	—	—	—	−0.15	2.02
37	1.88	14.45	1,070	—	—	—	—	—	−0.12	1.88
38	1.79	15.05	1,070	—	—	—	—	—	−0.20	1.79
39	1.75	17.33	1,070	—	—	—	—	—	−0.47	1.75

Magnetic analysis:— The specimens were always 5 m.m. thick and 70 m.m. long. The heating temperature was limited to a temperature lower than the beginning temperature of the graphitization of the specimens found by the dilatometer experiment.

Typical magnetization—temperature curves are shown in Fig. 16.

Fig. 16–a.

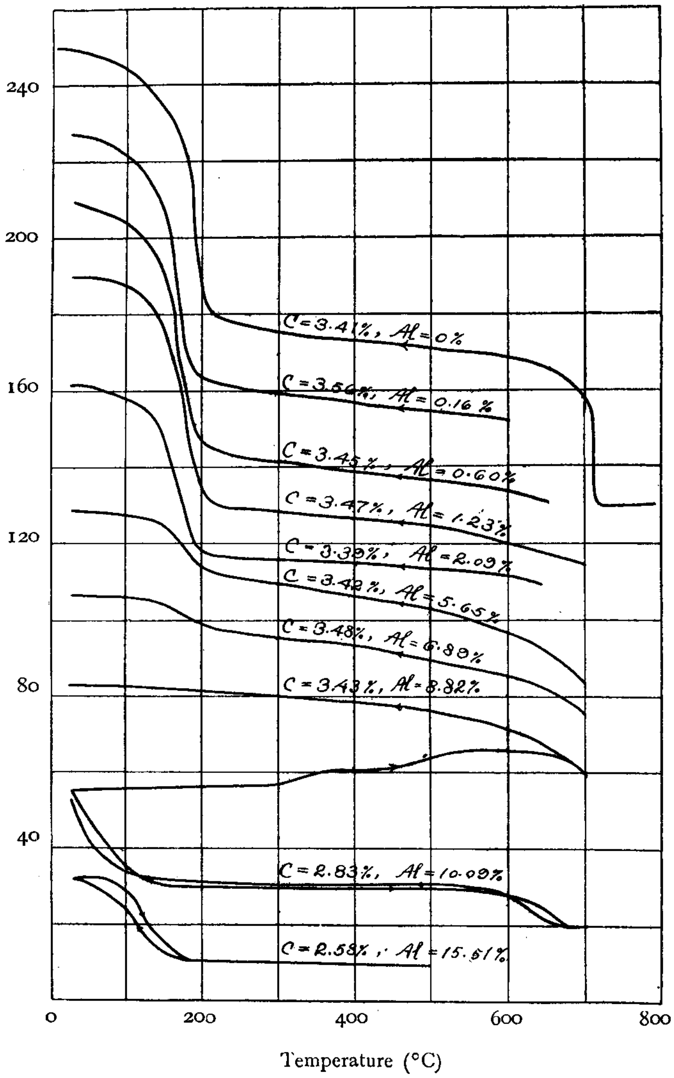
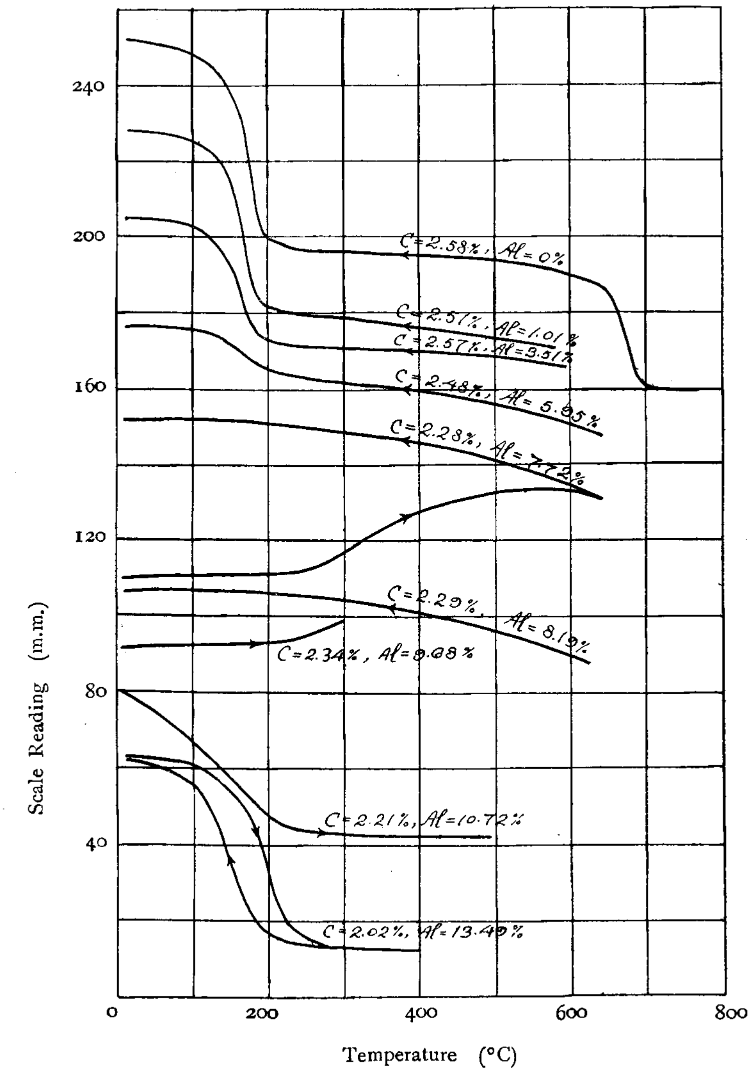


Fig. 16–b.



In these curves the ordinate represents the deflections of the magnetometer, which is proportional to the intensity of magnetization, and the abscissa the temperature of the specimens. The rate of heating and cooling was 5° C per min.

From these curves, two constituents, cementite and alumino-ferrite, are found in the alloys having up to 7 or 8 per cent of aluminium according to the carbon content of the alloys. In the alloys having 7 or 8 up to 10 per cent of aluminium, only alumino-ferrite is found, and in those having more than 10 per cent of aluminium, two constituents, alumino-ferrite and a substance (X) which has a magnetic transformation point at about 150°C. The amount of cementite found in the tempered alloys remains almost invariable up to about 3 per cent of aluminium, and afterwards gradually decreases as the aluminium content increases. Accordingly, it is evident that carbon exists in some combined form different from cementite (Y_1) in the alloys having a content higher than about 3 per cent of aluminium.

Microscopic study:— The results of the microscopic study on the higher carbon alloys (C=about 3.5 per cent) in the cast state will be first described.

Photogr. 8 shows the typical structure of the alloys in the cast state having less than about 3 per cent of aluminium. The white part is primary cementite and the colored part austenite and its derivatives. The area of the white part and the colored part remains almost constant until the aluminium content exceeds about 3 per cent, but afterwards the former contracts and the latter extends as the aluminium content increases from about 3 per cent to about 6 per cent, at which the latter reaches a maximum. No carbon in a combined state different from cementite is observed in the primary state in the alloys having about 3 to 6 per cent of aluminium. It should, therefore, exist in the austenite area in a secondary state.

Primary cementite is not found in the alloys having more than about 6 per cent of aluminium. When the aluminium exceeds this content, a new non–magnetic constituent (Y_2) first appears in the primary state (Y_2 in Photogr. 10) in place of the primary cementite in the alloys having less than about 6 per cent of aluminium. As aluminium increases from about 6 per cent to about 10 per cent the amount of the constituent Y_2 increases, and on the other hand, that of the primary austenite rapidly decreases.

Photogr. 11 shows a mass of the constituent Y_2 (white crystals) and a minute amount of austenite (dark colored).

When the aluminium exceeds about 10 per cent, the structure of the alloys is entirely re-formed as shown in Photogr. 12.

Fig. 17.

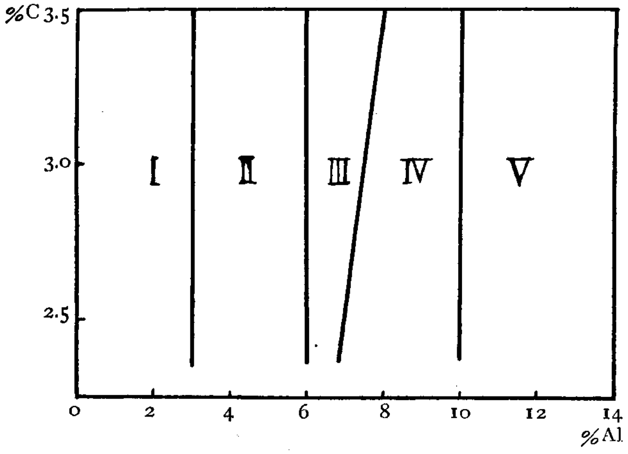


Fig. 18.

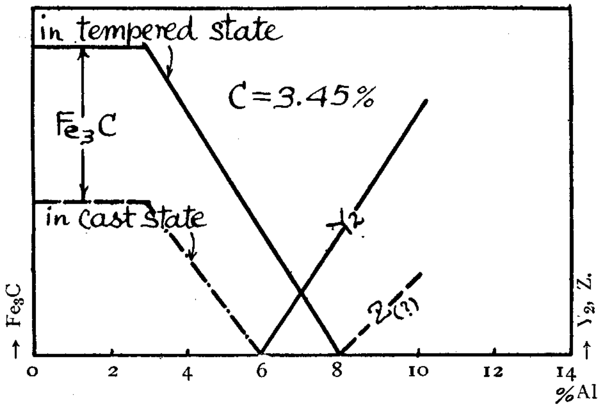
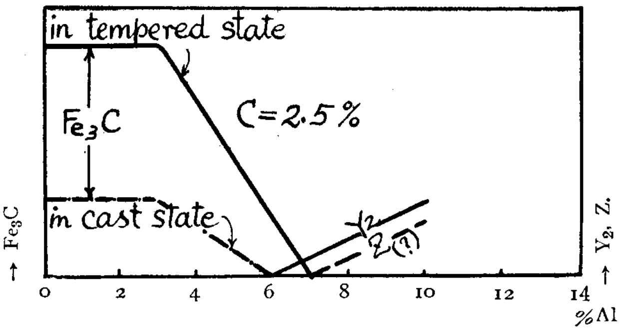


Fig. 19.



The structure of the lower carbon alloys (C=about 2.5 per cent) also changes in the same manner as that of the higher carbon alloys. In this case, however, the degree of increase in the amount of the constituent Y_2 is not so remarkable as in the former case. Photogr. 13 shows the small islets of the constituent Y_2 imbedded in the austenite. An abrupt change in the structure is found also in this case in the alloys having about 10 per cent of aluminium.

It was found by this study that only austenite and martensite in the alloys in the cast state were transformed to troostite by tempering.

Moreover, examining the results of the magnetic analysis of the alloys having 7 or 8 to 10 per cent of aluminium, another non-magnetic constituent (Z) seems to be separated out of the austenite and martensite.

From the results obtained above, a constitutional diagram of cast iron containing aluminium in the tempered state is deduced as shown in Fig. 17.

The constituents belonging to the fields are as follows:

I. cementite + alumino-ferrite,

II. cementite + alumino-ferrite + (Y_1),

III. cementite + alumino-ferrite + (Y_2),

IV. alumino-ferrite + (Y_2)+(Z ?),

V. alumino-ferrite + (X).

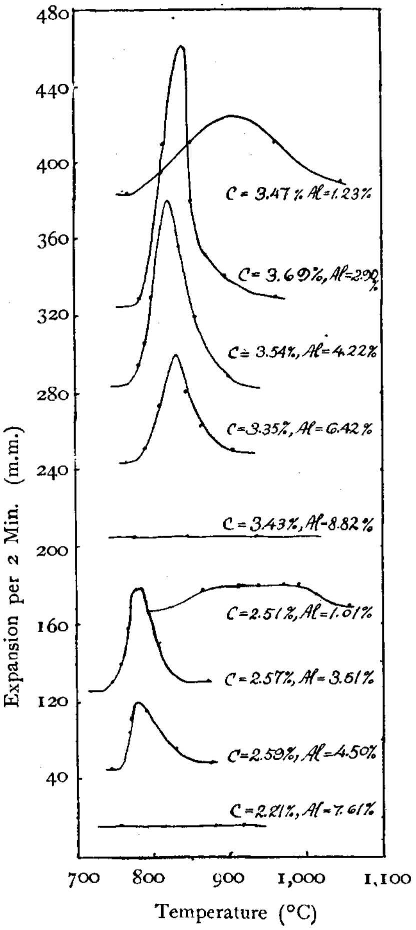
The variation of the amount of the constituents with the aluminium content is diagramatically shown in Figs. 18 and 19. Of course, it requires further investigation to determine the true nature of the constituents (X), (Y_1), (Y_2), and (Z).

(b) Graphitization experiment.

The compositions of the specimens are given in Table 4. The other impurities in the specimens were not analysed as the present writer knew in the previous experiments that the remelting of the starting materials did not cause any considerable change in the composition of other impurities in the charge if the melting were carried out with sufficient care and discretion as before mentioned.

Figs. 20 and 21 show the typical graphitization curves of the alloys. Important data concerning the graphitization of the alloys are summarised in Table 4. The relation between the beginning temperature of the graphitization of the alloys and the aluminium content is shown in Figs. 8 and 9.

Fig. 21.



From these curves the following facts are derived:

(1) Even a minute amount of aluminium has a favorable effect on the graphitization in the alloys, but the effect reaches a maximum at about 0.5 per cent of aluminium in the higher carbon alloys and 1.5 per cent in the lower carbon alloys. Further additions of the element have little effect on the temperature in question.

(2) Alloys having more than about 7 or 8 per cent of aluminium according to the carbon content of the alloys do not graphitise at all by annealing.

(3) Alloys having more than about 3 per cent of aluminium in the higher carbon alloys and about 1.5 per cent of aluminium in the lower carbon alloys completely graphitise until their temperature rises to their Ac_1.

The relation of the amount of

Fig. 22–a.

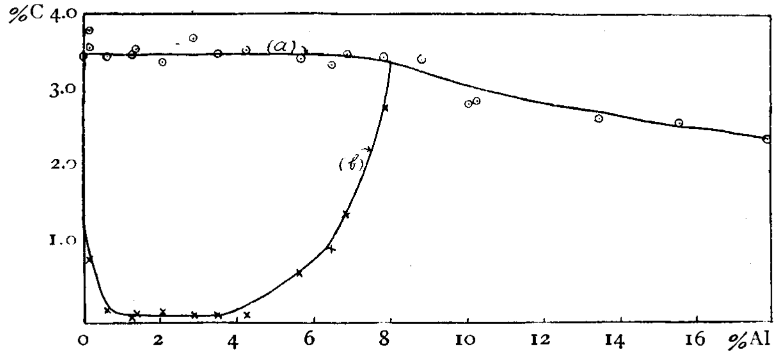


Fig. 20–a.

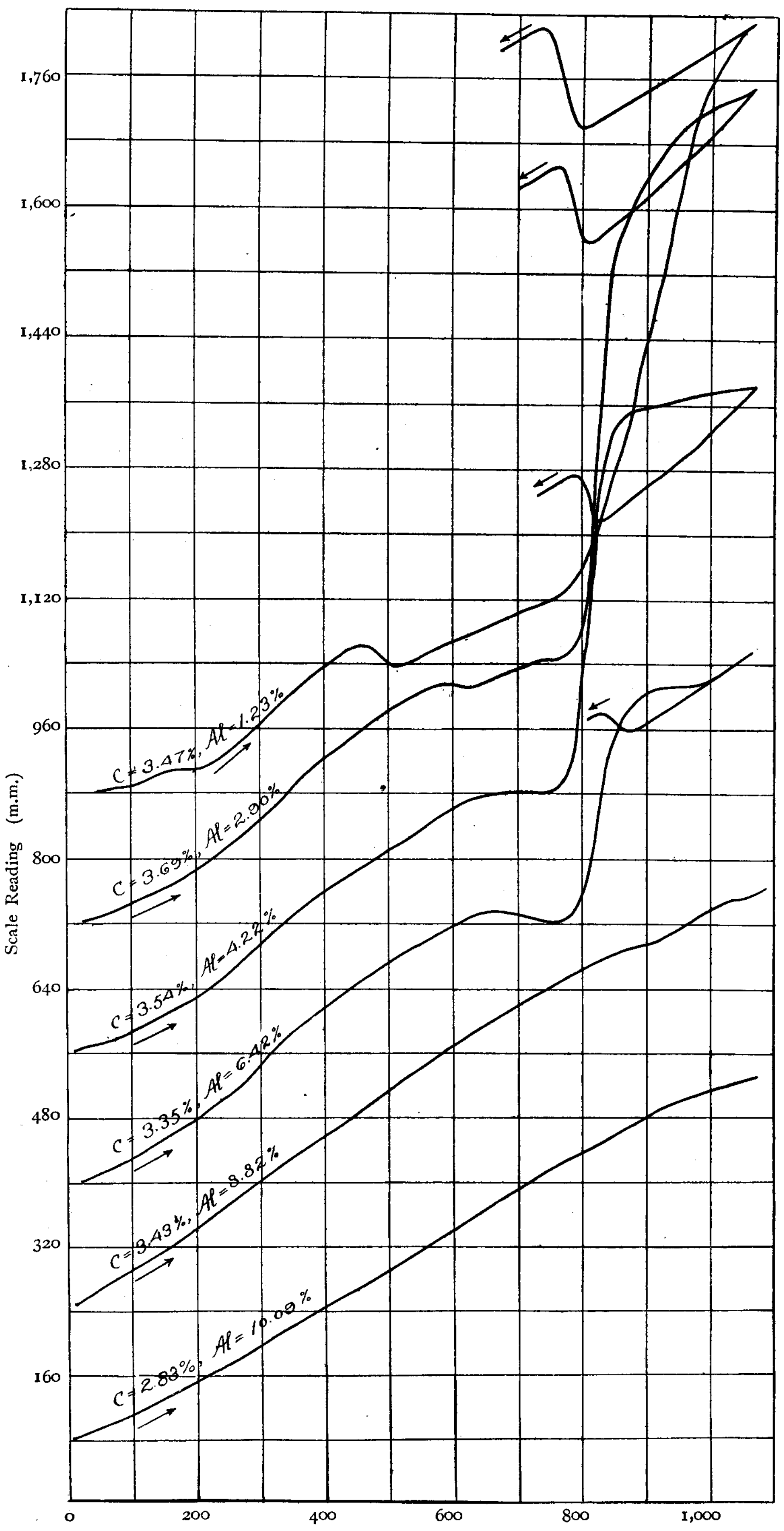


Fig. 20–b.

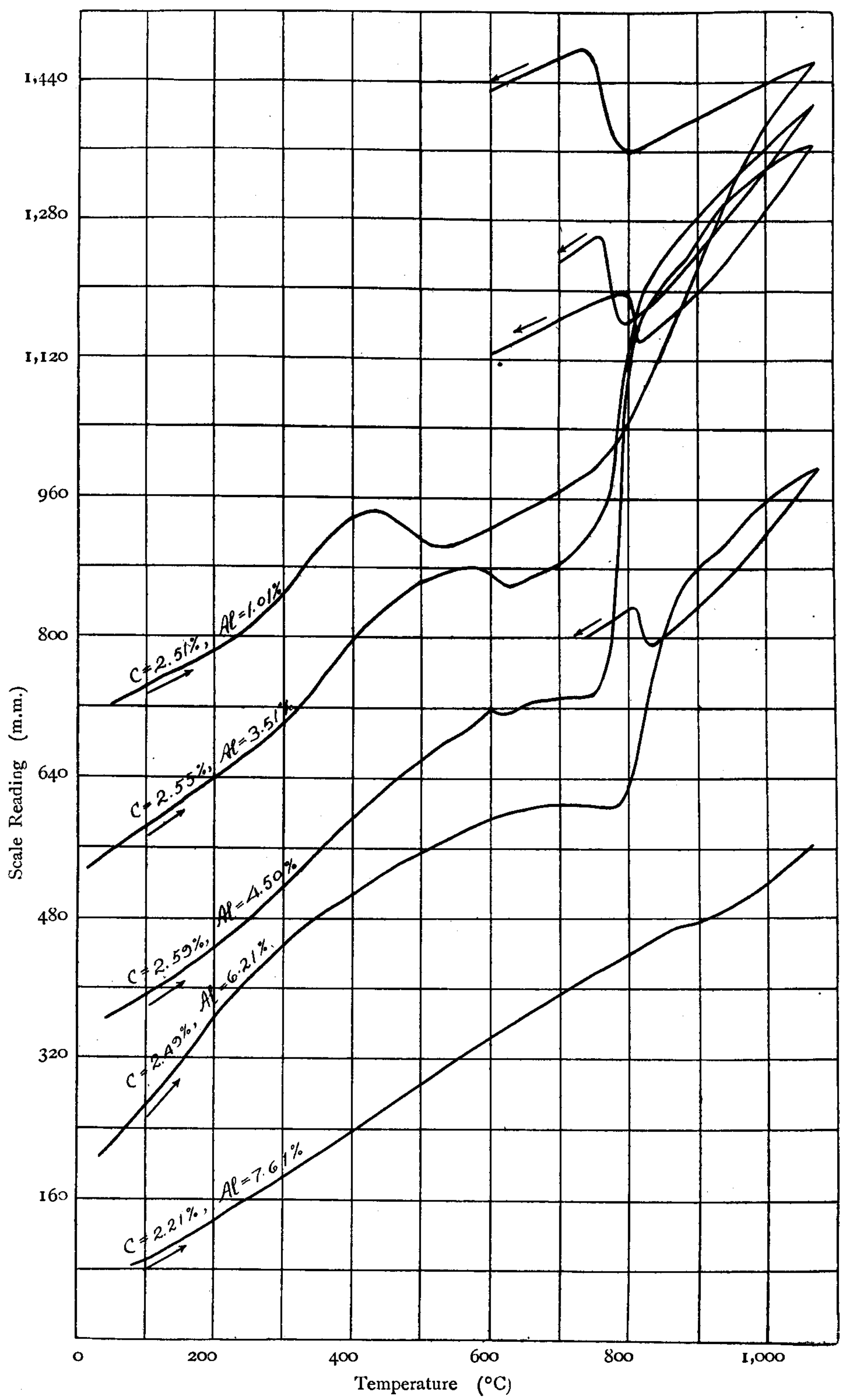
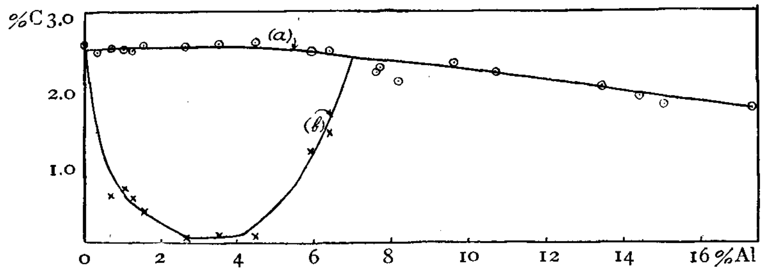


Fig. 22-b.



the total carbon and the combined carbon in the annealed alloys to the aluminium content is shown in Fig. 22.

In these figures the curve (a) represents the former relation and the curve (b) the latter relation.

Hence, the area enclosed by the curves (a) and (b) should correspond with the amount of the temper carbon produced by the annealing which rapidly increases to a maximum at about 0.5 per cent of aluminium in the higher carbon alloys and about 2 per cent of aluminium in the lower carbon alloys, and then remains practically constant while the aluminium content increases to about 4 per cent, and afterwards rapidly decreases as the aluminium content increases and at last vanishes at about 7 or 8 per cent of aluminium according to the carbon content of the alloys.

Comparing Figs. 18, 19 and 22, it is evident that it is the carbon in the form of cementite in the alloys which is graphitised by the annealing, and that the combined carbon in other forms is neutral to graphitization.

The close examination of both the volume increase of the alloys due to graphitization, and the total linear expansion of the alloys in the graphitization period which should change with the amount of the temper carbon produced in the alloys leads to recognition of the above conclusions.

(C) Constitution of the specimens in the annealed state.

Magnetic analysis :— By the results of the usual magnetic analysis of all the annealed alloys, it was found that minute amounts of cementite and of alumino-ferrite were present in the specimens No. 1 to 3 and 21 to 25 ; only alumino-ferrite in the specimens No. 4 to 15 and 26 to 34 ; and alumino-ferrite and (X) in the specimens No, 16 to 20 and 35 to 39. It was also found that the intensity of the magnetic transformation of (X) was indifferent to the heat treatment.

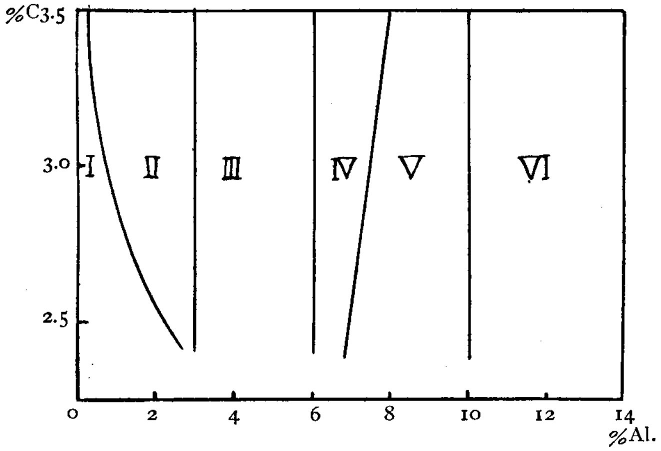
Microscopic study :— The microscopic study of the annealed alloys also leads to the conclusion that only cementite is concerned with the graphitization of the alloys. The form of the temper carbon produced is controlled by the form of the mother constituent; the flaky temper carbon (Photogr. 14) is produced from the elongated cementite (Photogr. 8), and the nodular temper carbon (Photogr. 15) from the nodular cementite (Photogr. 9).

The substance (Y_2) is stable and its amount is practically indifferent to annealing.

It is also observed microscopically that the alloys having more than 10 per cent of aluminium are very stable.

From the results above obtained, a constitutional diagram of the annealed alloys is deduced as shown in Fig. 23.

Fig. 23.



The constituents belonging to the fields are as follows :

I. cementite + alumino-ferrite + temper carbon,

II. alumino-ferrite + temper carbon,

III. alumino-ferrite + (Y_1) + temper carbon,

IV. alumino-ferrite + (Y_2) + temper carbon,
V. alumino-ferrite + (Y_2) + (Z ?),
VI. alumino-ferrite + (X).

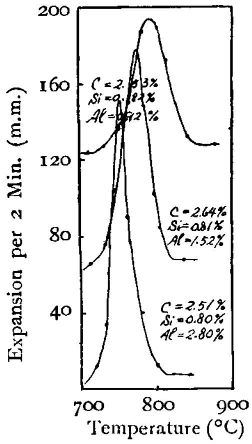
B. Influence of aluminium on the graphitization in white cast iron having 2.5 per cent of carbon, 0.8 per cent of silicon and a minute amount of other impurities.

The compositions of the specimens are given in Table 5. Fig. 24 shows the typical graphitization curves of the alloys. Important data concerning the graphitization of the alloys are summarised in Table 5.

Table 5.

Specimens No.	Composition (%)			A	B	C	D	E	F	G	H
	C	Si	Al								
1	2.67	0.81	0.09	1,070	800	—	870	40	—	4.97	0.47
2	2.58	0.80	0.25	1,070	760	—	810	60	—	5.13	0.31
3	2.50	0.80	0.39	1,070	750	1,030	820	30	700	5.10	0.54
4	2.61	0.83	0.56	1,070	730	970	810	40	720	5.28	0.26
5	2.52	0.79	0.78	1,070	720	900	790	60	700	5.26	0.13
6	2.53	0.82	0.92	1,070	720	850	790	80	660	5.46	0.04
7	2.64	0.81	1.52	1,070	720	820	770	120	750	5.37	0.09
8	2.60	0.82	1.98	1,070	720	820	750	120	750	5.62	0.11
9	2.50	0.84	2.31	1,070	710	820	750	140	780	5.57	0.08
10	2.51	0.80	2.80	1,070	710	810	750	150	800	5.75	0.05

Fig. 24.



The relation between the beginning and the end temperatures of the graphitization of the alloys and the aluminium content is shown in Fig. 25.

The relation between the amount of the combined carbon in the annealed alloys and the aluminium content is shown in Fig. 26. These data show that aluminium promotes the effect of silicon on the graphitization in the alloys, and the effect of the element reaches a maximum at about 0.6 per cent of aluminium. It is also found that the alloys having more than 1 per cent of aluminium completely graphitise until their temperatures reach their Ac_1.

The microstructure of the alloys in the cast state is almost the same as that of the alloys used in the former experiments.

The form of the temper carbon produced is governed also in this case by the form of the mother cementite.

C. Summary.

The results so far obtained may be summarised as follows:

(1) The effect of aluminium up to about 17 per cent on the graphitization in white cast irons with varied carbon contents and a minute amount of other impurities, has been definitely determined.

(2) The constitution of cast iron containing aluminium has been examined by means of magnetic analysis and microscopic study.

(3) It has been found that the combined carbon in very stable forms different from cementite appears in the alloys having more than about 3 per cent of aluminium, and that the amount of the cementite, on the other hand, remains almost constant while the aluminium content increases from 0 to about 3 per cent, but afterwards rapidly decreases as the aluminium content increases, and at last vanishes at about 7 or 8 per cent of aluminium according to the carbon content of the alloys.

(4) It has been found that only cementite is concerned with the graphitization of the alloys.

(5) The alloys having higher aluminium begin to graphitise at temperatures lower than their Ac_1, or completely graphitise until their temperatures reach their Ac_1.

(6) From the above conclusions it is evident that the beginning temperature of the graphitization of the alloys may mean the beginning temperature of the decomposition of the cementite in the alloys.

(7) The stability of the cementite in the alloys rapidly decreases as the aluminium content of the alloys increases up to about 0.5 or 1.5 per cent and further addition of aluminium has almost no effect on it.

(8) The effect of aluminium up to about 3 per cent on the graphitization in white cast iron containing 2.5 per cent of carbon, 0.8 per cent

of silicon, and a minute amount of other impurities has been definitely determined.

(9) Aluminium promotes the effect of silicon on the graphitization in the alloys, but its effect reaches a maximum at about 0.6 per cent of the element.

(10) The form of the temper carbon produced in the annealed alloys having higher aluminium is entirely dependent on the form of the mother cementite.

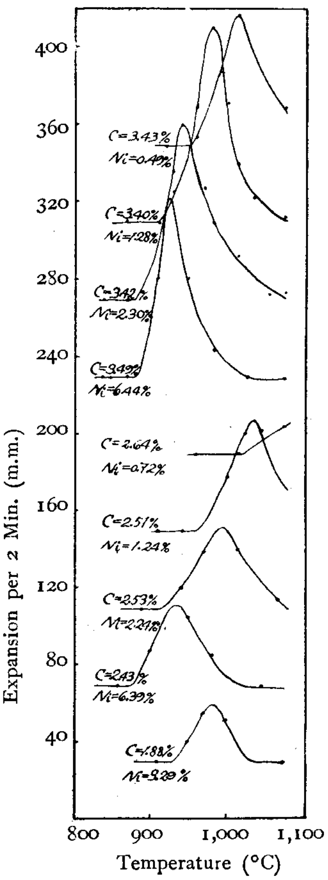
§ V. INFLUENCE OF NICKEL.

It is qualitatively known from the works of previous investigators,[1] that nickel favours the formation of graphite in cast iron, but the effect has not been shown quantitatively. The theory on the effect of this element has not yet been formulated, although Kase's paper[2] recently published threw some light on the constitution of iron, carbon and nickel alloys.

A. Influence of nickel on the graphitization in white cast iron having a minute amount of other impurities.

The compositions of the specimens are given in Table 6. Fig. 27 shows the typical graphitization curves of the alloys. Important data concerning graphitization are summarised in Table 6. The relation between the beginning and the end temperature of the graphitization of the alloys and the nickel

Fig. 27.



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1) Guillet: Rev. Mét. 5, (1908), 306.
Hatfield: Cast Iron in the Light of recent Research, (1918), 101.
Bauer u. Piwowarsky: Stahl u. Eisen. 40, (1920), 1300.
Piwowarsky u. Ebbefeld: ditto. 43, (1923), 967.

2) Sci. Rep. Tohoku Imp. Univ. 14, (1925), 173.

Table 6.

Specimens No.	Composition (%)		A	B	C	D	E	F	G	H
	C	Ni								
1	3.33	0.10	1,080	980	—	—	—	—	4.75	1.64
2	3.41	0.30	1,080	970	—	—	—	—	4.90	1.50
3	3.46	0.48	1,080	950	—	1,010	60	—	4.72	0.98
4	3.43	0.49	1,080	950	—	1,010	80	—	4.86	1.33
5	3.39	0.68	1,080	950	—	1,010	90	—	4.84	0.93
6	3.48	0.75	1,080	690	—	1,000	100	—	5.31	1.21
7	3.40	1.28	1,080	910	—	980	110	—	5.35	0.66
8	3.47	1.33	1,080	900	1,080(?)	950	130	880	6.19	0.54
9	3.45	1.50	1,080	900	1,080(?)	960	140	890	5.93	0.73
10	3.42	1.71	1,080	890	1,080(?)	940	150	920	6.03	0.55
11	3.38	1.87	1,080	890	1,080(?)	950	110	900	6.16	0.44
12	3.42	2.30	1,080	880	1,080(?)	940	100	960	6.38	0.51
13	3.40	3.00	1,080	880	1,060	940	100	970	6.31	0.41
14	3.38	4.08	1,080	880	1,030	920	80	900	6.60	0.23
15	3.49	6.44	1,080	880	1,020	920	100	900	6.54	0.54
16	2.63	0.09	1,080	—	—	—	—	—	0.96	2.23
17	2.59	0.19	1,080	—	—	—	—	—	1.34	2.16
18	2.71	0.31	1,080	—	—	—	—	—	1.78	2.05
19	2.50	0.44	1,080	—	—	—	—	—	1.25	1.90
20	2.53	0.58	1,080	1,060	—	—	—	—	1.71	1.38
21	2.64	0.72	1,080	1,020	—	—	—	—	1.82	1.40
22	2.65	0.84	1,080	1,000	—	1,050	70	—	3.17	1.51
23	2.58	1.09	1,080	990	—	1,020	60	—	4 23	1.09
24	2.51	1.24	1,080	960	—	1,030	70	—	4.52	—
25	2.55	1.28	1,080	950	—	1,010	70	—	4.26	0.68
26	2.48	1.74	1,080	930	—	1,020	60	—	4.47	0.70
27	2.53	2.24	1,080	910	—	990	50	—	5.12	0.51
28	2.50	2.90	1,080	890	—	950	50	—	5.14	0.45
29	2.45	4.29	1,080	880	1,030	930	50	520	5.13	0.02(?)
30	2.43	6.39	1,080	880	1,010	930	50	500	5.12	0.31
31	1.85	0.79	1,080	—	—	—	—	—	-0.35	1.63
32	1.99	1.27	1,080	1,070(?)	—	—	—	—	1.37	1.16
33	1.93	2.14	1,080	980	—	1,050	30	—	2.71	0.87
34	1.88	3.29	1,080	930	1,030	980	40	—	3.55	0.65

content is shown in Figs. 8, 9 and 10. The relation between the amount of the combined carbon in the alloys in the annealed state and the nickel content is shown in Figs. 11, 12 and 13.

From these curves it is ascertained that nickel favours the formation of graphite in cast iron. It is also found that there is a limit on the effect of this element on the beginning temperature of graphitization; the temperature under discussion gradually sinks as the nickel content increases up to 2 or 3 per cent according to the carbon content of the alloys, and afterwards remains almost constant though the nickel content increases beyond the above amount.

Typical structure of the alloys in the cast state is shown in Photogr. 16. The relative amount of white crystal and the colored substance is almost invariable in the alloy series having the same amount of carbon, while nickel increases 0 to 6 per cent. Of course, it is evident that most of the white crystal is cementite in the alloys having a small amount of nickel; but it requires further investigation to determine whether or not it is likewise in the alloys having a large amount of nickel.

By the microscopic study of the graphitized alloys, it was found that the amount of the white crystal above mentioned decreased as the nickel content increased (Photogrs. 17, 18).

Temper carbon produced in the graphitised alloys having higher nickel has a tendency to take a flaky form in a sorbitic matrix as shown in Photogr. 18.

B. Influence of nickel on the graphitization in white cast iron having 2.5 per cent of carbon, 0.8 per cent of silicon and a minute amount of other impurities.

The compositions of the specimens are given in Table 7. Fig. 28 shows the typical graphitization curves of the alloys. Important data concerning the graphitization of the alloys are aummarised in Table 7. The relation between the beginning and the end temperature of graphitization and the nickel content is shown in Fig. 25. The relation between the amount of the combined carbon in the graphitised alloys and the nickel

Table 7.

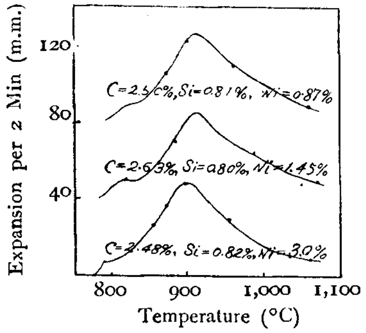
Specsmens No.	Composition (%)			A	B	C	D	E	F	G	H
	C	Si	Ni								
1	2.52	0.84	0.51	1,080	850	—	950	40	—	4.39	0.41
2	2.50	0.81	0.87	1,080	830	—	910	50	—	4.84	0.42
3	2.63	0.80	1.45	1,080	830	1,080(?)	900	50	700	4.57	0.24
4	2.48	0.82	1.89	1,080	820	1,080(?)	900	50	760	4.81	0.09
5	2.54	0.81	2.04	1,080	820	1,050	880	50	830	5.26	0.17
6	2.56	0.79	2.41	1,080	800	1,040	880	50	800	5.02	0.15
7	2.50	0.80	2.76	1,080	810	1,040	900	50	800	5.27	0.26
8	2.48	0.82	3.00	1,080	800	1,020	890	50	830	5.53	0.18

content is shown in Fig. 26.

All these data show that nickel promotes the effect of 0.8 per cent silicon in white cast iron on the formation of temper carbon.

The microscopic structure of the alloys both in the cast and in the annealed state is practically the same as in the former case.

Fig. 28.



C. Summary.

The results so far obtained may be summarised as follows :

(1) The effect of nickel on the graphitization in white cast irons has been definitely determined.

(2) Nickel favours the formation of temper carbon in practically pure white cast iron, but its effect reaches a maximum at 2 to 3 per cent of the element according to the carbon content of white cast iron.

(3) Nickel promotes the effect of silicon of 0.8 per cent in white cast iron having 2.5 per cent of carbon on the formation of temper carbon.

(4) White cast iron having higher nickel has a tendency to produce temper carbon in flaky form.

§ VI. INFLUENCE OF COPPER.

According to Lupin[1] and Hamazumi,[2] Copper is practically indifferent to the formation of graphite in cast iron. But the results of their investigations have not shown the characteristic property of the element, because the specimens used for their experiments always contained a moderate amount of silicon.

Recently Ishiwara[3] has published the results of his investigation on the ternary system of iron, carbon and copper, but the theory on the effect in question of the element has remained untouched.

A. Influence of copper on the graphitization in white cast iron having a minute amount of other impurities.

The compositions of the specimens are given in Table 8. Fig. 29 shows the typical graphitization curves of the alloys. Important data concerning the graphitization are summarised in Table 8. The relation between the beginning temperature of the alloys and the copper content is shown in Fig. 8. The relation between the amount of the combined carbon in the graphitised alloys and the copper content is shown in Fig. 11.

All the data conclusively show that copper favours the formation of temper carbon. Its effect is moderately remarkable up to about 2 per cent of the element, but further addition of the element makes practically no difference to its effect.

Microscopic study of the alloys also proves the above conclusion.

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[1] Stahl u. Eisen 20, (1900), 536.

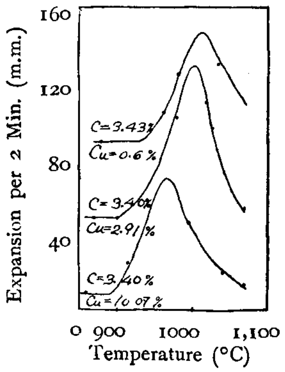
[2] Sci. Rep., Tohoku Imp. Univ., 13, (1924), 169.

[3] Kinzoku no Kenkyu. 1, (1924), 1.

Table 8.

Specimens No.	Composition (%)		A	B	D	E	G	H
	C	Cu						
1	3.43	0.34	1,070	1,000	—	—	4.65	1.52
2	3.39	0.41	1,070	970	1,050	70	5.61	1.24
3	3.43	0.60	1,070	930	1,010	70	5.72	0.70
4	3.40	0.84	1,070	950	1,020	80	5.70	0.98
5	3.33	1.01	1,070	910	1,040	90	6.33	1.19
6	3.46	1.54	1,070	910	1,010	80	6.48	0.65
7	3.44	1.76	1,070	910	1,000	80	6.46	0.46
8	3.45	2.09	1,070	910	1,010	80	6.09	0.42
9	3.41	2.67	1,070	910	1,010	90	6.23	0.26
10	3.40	2.91	1,070	900	1,000	80	5.97	0.42
11	3.40	10.07	1,070	890	970	70	5.30	0.11

Fig. 29.



Photogr. 19 shows a typical structure of the alloys in cast state. The relative amount of the white area and the colored area is almost invariable with the copper content. The white part, cementite which may accompany combined carbon in another form, was found to be graphitised by annealing. Photogrs. 20 and 21 show the typical structure of the graphitised alloys; in the former, a great amount of the combined carbon remains ungraphitised (white islets), in the latter a minute amount of the combined carbon is shown as eutectoid cementite.

The temper carbon produced in the alloys has a tendency to be nodular.

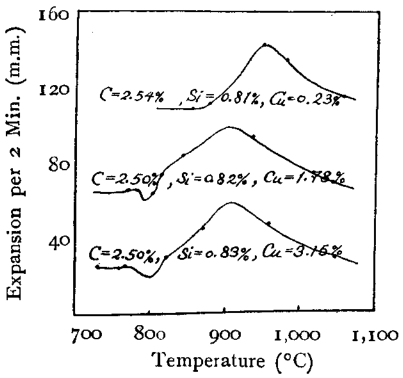
B. Influence of copper on the graphitization in white cast iron having 2.5 per cent of carbon, 0.8 per cent of silicon and a minute amount of other impurities.

The compositions of the specimens are given in Table 9. Fig. 30 shows the typical graphitization curves of the alloys.

Table 9.

Specimens No.	Composition (%)			A	B	C	D	E	F	G	H
	C	Si	Cu								
1	2.54	0.81	0.23	1,070	870	—	950	40	—	4.15	0.78
2	2.48	0.80	0.43	1,070	860	—	950	40	—	4.08	0.53
3	2.56	0.79	0.59	1,070	840	1,070(?)	920	40	780(?)	4.36	0.66
4	2.71	0.80	1.04	1,070	830	1,070(?)	900	40	800(?)	4.30	0.91
5	2.60	0.83	1.35	1,070	820	1,070(?)	900	40	800(?)	4.46	0.89
6	2.50	0.82	1.78	1,070	810	1,060(?)	900	40	800(?)	4.94	0.20
7	2.63	0.79	1.91	1,070	810	1,060(?)	900	40	810(?)	4.53	0.31
8	2.41	0.81	2.04	1,070	810	1,070(?)	900	40	800(?)	4.71	0.24
9	2.52	0.84	2.27	1,070	810	1,070(?)	900	40	850(?)	4.56	0.39
10	2.50	0.83	3.15	1,070	810	1,060(?)	900	40	800(?)	4 80	0.01

Fig. 30.



Important data concerning the graphitization of the alloys are summarised in Table 9. The relation of the beginning temperature of the graphitization of the alloys to the copper content is shown in Fig. 25. The relation of the amount of the combined carbon in the graphitised alloys to the copper content is shown in Fig. 26. All the data is sufficient to prove the fact that copper also promotes the effect of the silicon in the alloys under discussion, and that the effect reaches a maximum at about 2 per cent of copper.

The microstructure of the alloys in the cast state is the same as in the former case. Photogr. 22 shows the typical structure of the graphitised alloys.

The temper carbon is liable to be formed in nodular form in this case also.

C. Summary.

The results so far obtained are summarised as follows:

(1) The effect of copper on the graphitization in white cast iron has been definitely determined.

(2) Copper favours the formation of temper carbon in practically pure white cast iron and the effect reaches a maximum at about 2 per cent of the element, the further addition of the element beyond this amount being practically indifferent to the effect.

(3) Copper promotes the effect of 0.8 per cent silicon in white cast iron having 2.5 per cent of carbon on the formation of temper carbon but the effect reaches a maximum at about 2 per cent of the element.

(4) White cast iron having copper has a tendency to produce temper carbon in nodular form.

§ VII. INFLUENCE OF COBALT.

According to Piwowarsky and Bauer,1) cobalt hinders the graphite formation in cast iron. But their experiments were carried out on specimens having a moderate amount of silicon. Hence, it is in doubt whether its nature found by them is characteristic of cobolt or not.

A. Influence of cobalt on the graphitization in white cast iron having a minute amount of other impurities.

The compositions of the specimens are given in Table 10. Fig. 31

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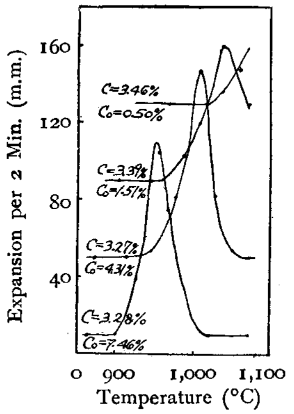
1) Stahl u. Eisen, 40, (1920), 1300

shows the typical graphitization curves of the alloys. Important data concerning graphitization are summarised in Table 10. The relation of the beginning temperature of graphitization to the cobalt content is shown in Fig. 8. The relation of the amount of the combined carbon in the annealed alloys to the cobalt content is shown in Fig. 11.

Table 10.

Specimens No.	Composition (%)		A	B	C	D	E	F	G	H
	C	Co								
1	3.45	0.21	1,080	1,060	—	—	—	—	3.82	2.67
2	3.46	0.50	1,070	1,020	—	—	—	—	4.16	2.35
3	3.51	0.75	1,070	1,020	—	—	—	—	3.93	1.81
4	3.40	0.92	1,070	1,000	—	—	—	—	4.44	2.16
5	3.45	1.33	1,070	970	—	—	—	—	4.26	1.59
6	3.39	1.51	1,070	960	—	1,040	80	—	4.13	1.24
7	3.48	2.22	1,070	950	—	1,040	80	—	4.91	0.84
8	3.39	3.37	1,070	930	—	1,030	100	—	5.12	0.56
9	3.27	4.31	1,070	930	1,060	1,010	110	850	5.67	0.58
10	3.28	7.46	1,070	900	1,010	950	110	830	5.83	0.36

Fig. 31.



These data evidently show that cobalt favours the formation of temper carbon in practically pure white cast iron, though its effect is feeble.

The present writer proceeds to prove the conclusion by microscopic study of the alloys. Photogr. 23 shows a typical structure of the alloys in the cast state. The white area which corresponds to cementite or cementite accompanying combined carbon in another form practically does not vary with the cobalt content. Photogrs. 24 and 25 show the typical structures of the annealed alloys. In the former, most of the combined carbon remains undecomposed as white islets, but in the latter the small amount of combined carbon appears as eutectoid cementite. It is very interesting to find that well developed temper carbon is produced in the alloys and that the number of the temper corbon is far smaller and its size is far larger than expected from the structure of the alloys in the cast state.

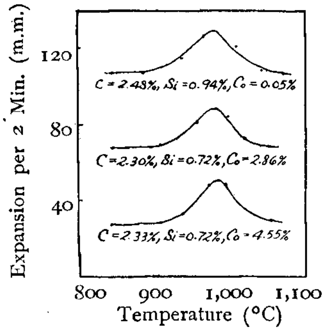
B. Influence of cobalt on the graphitization in white cast iron having 2.5 per cent of carbon, 0.8 per cent of silicon and a minute amount of other impurities.

The compositions of the specimens are given in Table 11. Fig. 32 shows the typical graphitization curves of the specimens. Important data concerning graphitization of the alloys are summarised in Table 11. The relation of the beginning temperature of the graphitization of the alloys to the cobalt content is shown in Fig. 25. The relation of the amount of the combined carbon in the annealed alloys to the cobalt content is shown in Fig. 26. These data show that cobalt is practically indifferent to the

Table 11.

Specimens No.	Composition (%)			A	B	C	D	E	F	G	H
	C	Si	Co.								
1	2.48	0.94	0.05	1,070	900	1,070(?)	980	30	380	4.29	0.54
2	2.43	0.72	0.37	1,070	900	1,050	980	30	340	3.42	0.60
3	2.41	0.74	0.53	1,070	900	1,050	980	30	350	3.20	0.65
4	2.38	0.75	0.95	1,070	900	1,040	980	30	340	3.27	0.57
5	2.41	0.69	1.24	1,070	900	1,040	980	30	350	3.84	0.63
6	2.36	0.73	1.76	1,070	900	1,040	980	30	350	3.49	0.55
7	2.31	0.75	2.20	1,070	900	1,040	980	30	350	4.07	0.41
8	2.30	0.72	2.86	1,070	900	1,040	980	30	350	3.38	0.42
9	2.33	0.77	3.37	1,070	900	1,040	980	30	350	3.33	0.53
10	2.33	0.72	4.55	1,070	900	1,040	980	30	350	3.46	0.39

Fig. 32.



beginning temperature of the graphitization of the alloys. The amount of the combined carbon in the annealed alloys, however, seems to decrease gradually as the cobalt content increases. As regards the form of the temper carbon, it is found that when the cobalt content is small it is flaky (Photogr. 26), but it changes from flaky to nodular as the cobalt content increases (Photogr. 27). It is also found in this case that the number of the nodular temper carbon is far smaller and its size is far larger than expected from the structure of the alloys in the cast state.

C. Summary.

The results so far obtained are summarised as follows:

(1) The effect of cobalt on the graphitization in white cast irons has been definitely determined.

(2) Cobalt favours the graphitization of practically pure white cast iron, but the effect is feeble.

(3) Cobalt promotes the effect of silicon of 0.8 per cent in white cast iron having 2.5 per cent of carbon, on the formation of temper carbon, but the effect is very feeble.

(4) White cast iron having cobalt has a strong tendency to produce well-developed nodular temper carbon.

(5) In the graphitised alloys, the number of nodular temper carbon is far smaller and its size is far larger than expected from the structure of the alloys in the cast state.

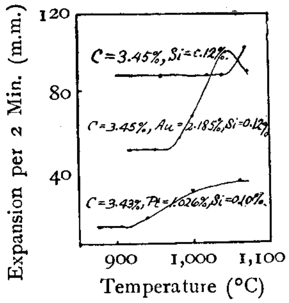
§ VIII. INFLUENCE OF GOLD AND PLATINUM.

Three specimens were prepared, one having a minute amount of other impurities, and two others having gold and platinum respectively. The compositions of the alloys are given in Table 12. Fig. 33 shows the

Table 12.

Specimens No.	Composition (%)			A	B	D	E	G	H
	C	Si	Special Element						
1	3.45	0.12	0	1,070	1,050	—	—	0.79	2.99
2	3.43	0.10	Pt = 1.026	1,070	920	—	—	4.39	1.81
3	3.45	0.12	Au = 2.185	1,070	970	1,040	60	4.87	1.20

Fig. 33.



graphitization curves of the alloys. Important data concerning the graphitization of the alloys are summarised in Table 12. These data evidently show that these elements favour the graphitization of practically pure white cast iron. The conclusion can be microscopically proved. The amount of the combined carbon in the annealed alloy having a minute amount of other impurities (Photogr. 28) is far greater than that of the others (Photogrs. 29 and 30).

§ IX. INFLUENCE OF TITANIUM.

According to Piwowarsky[1], titanium favours the formation of graphite in cast iron and the effect is stronger than that of silicon. The theory of the effect of the element has not ever been explained though the ternary system of iron, carbon and titanium has been investigated by Vogel[2] and by Tamaru.[3]

In the present work, to his regret, the present writer has been compelled to study the effect of the element on alloys having always a moderate amount of silicon, and has not been able to determine its characteristic effect under discussion, as he has not been able to obtain pure ferro-titanium as raw material.

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1) Stahl u. Eisen 43, (1923), 1491.
2) Ferrum. 14, (1917), 177.
3) Sci. Rep. Tohoku Imp. Univ. 14, (1925), 25.

A. Experiment.

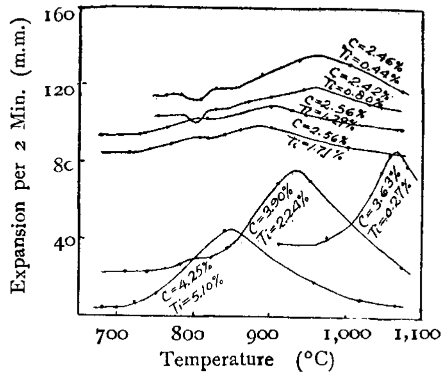
The compositions of the specimens are given in Table 13. The alloys always contain aluminium as an impurity, but its effect is practically negligible as the amount of it is very minute. Fig. 34 shows the typical graphitization curves of the alloys.

Important data concerning the graphitization are summarised in Table 13. In the table, the numbers in the brackets are data found from the results

Table 13.

Specimens No.	Composition (%)				A	B	C	D	E	F	G	H
	C	Si	Ti	Al								
1	2.42	0.86	0.18	—	1,070	870 (870)	1,070(?) (—)	960 (950)	30 (?) (40)	420 (?) (—)	4.10	0.41
2	2.46	0.95	0.44	—	1,070	860 (860)	1,070(?) (—)	970 (940)	30 (?) (40)	440 (?) (—)	4.11	0.37
3	2.46	0.93	0.61	—	1,070	840 (860)	1,050 (—)	940 (940)	30 (40)	450 (—)	4.06	0.34
4	2.42	0.96	0.80	—	1,070	840 (860)	1,050 (—)	960 (940)	20 (40)	400 (—)	4.05	0.35
5	2.56	1.07	1.29	—	1,070	730 (850)	1,050 (—)	890 (930)	20 (40)	600 (—)	4.44	0.28
6	2.73	1.13	1.37	—	1,070	740 (830)	1,050 (—)	930 (910)	20 (40)	550 (—)	4.24	0.25
7	2.56	1.32	1.71	—	1,070	720 (800)	1,050 (—)	890 (890)	20 (50)	450 (—)	4.14	0.23
8	3.63	0.20	0.27	—	1,070	960 (980)	— (—)	1,060 (1,050)	60 (70)	— (—)	4.05	1.88
9	3.70	0.35	1.10	—	1,070	900 (920)	— (—)	1,000 (990)	70 (70)	— (—)	5.33	1.05
10	3.92	0.45	1.44	—	1,070	850 (900)	— (—)	980 (970)	70 (80)	— (—)	6.04	0.86
11	3.90	0.74	2.24	0.04	1,070	740 (840)	1,070 (1,060)	940 (920)	60 (90)	1,140 (990)	6.84	0.54
12	4.25	0.86	2.81	0.03	1,070	720 (820)	1,070 (1,040)	910 (900)	60 (90)	1,120 (1,020)	6.96	0.40
13	4.25	0.99	5.10	0.05	1,070	700 (790)	1,050 (1,010)	850 (870)	50 (100)	1,020 (1,120)	6.40	0.21

Fig. 34.



of the work on alloys having the same amount of carbon and silicon but having a minute amount of other impurities as the alloys in question.

The relation of the beginning and the end temperature of the graphitization of the alloys to the titanium content is shown in Fig. 35 (real line). If in the same figure the numbers in the brackets given in Table 13 be plotted in the position corresponding to that of the alloys and the effect of the silicon be represented by curves (dotted line) at the same time, the effect of titanium can be approximately found.

Fig. 35-a.

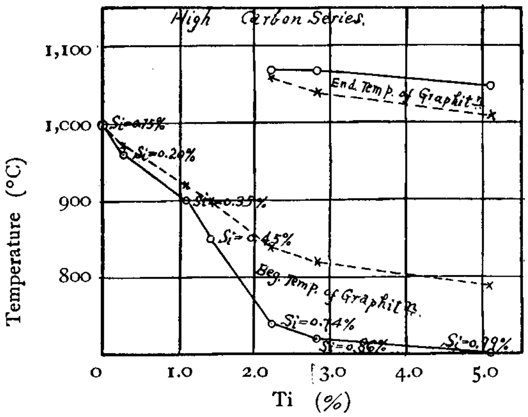
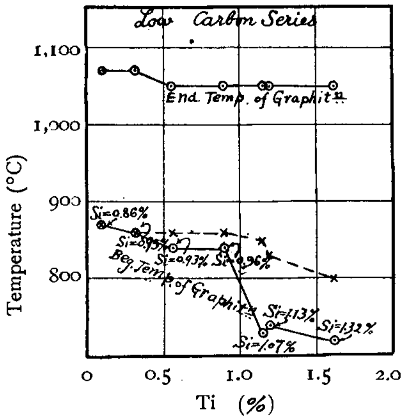


Fig. 35-b.



Since the biginning temperature of the graphitization of the alloys is always lower than that of the alloys having the same composition except titanium, it is evident that titanium promotes the effect of silicon under discussion. The degree of its effect is probably smaller than that of silicon, because the beginning temperature of the graphitization of alloys having silicon and a minute amount of other impurities is always lower than that of alloys having the composition in which a part of the silicon content in the former is replaced by titanium. The microscopic structure of the alloys in the cast state does not show any peculiarities except some hard crystals found in the alloys having higher titanium, as shown in Photogr. 31. As regards the true nature of this substance, further investigation is required, but it has been found that it does not change at all by annealing, as shown in Photogrs. 32 and 33. Consequently it is indifferent to graphitization.

It has been also found that temper carbon is inclined to be nodular in the graphitised alloys having lower titanium, but flaky in those having higher titanium.

B. Summary.

The results so far obtained may be summarised as follows:

(1) The effect of titanium on the graphitization in white cast iron having a moderate amount of silicon has been studied.

(2) Titanium strongly favours graphitization in white cast iron, but the degree of the effect is probably smaller than that of silicon, contrary to Piwowarsky's notion.

(3) A certain substance crystallises out in the alloys having a higher titanium in the primary state, but it is indifferent to graphitization.

(4) White cast iron having higher titanium inclines to produce flaky temper carbon.

§ X. INFLUENCE OF CHROMIUM.

Though it is generally accepted that chromium hinders graphitization in cast iron by forming stable double carbides, the quantitative relation between the element and its effect under discussion has not yet been studied.

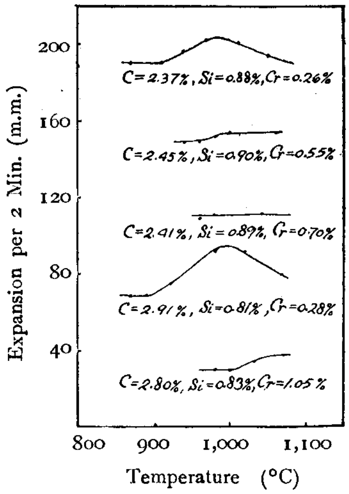
A. Experiment.

The compositions of the specimens are given in Table 14. Fig. 36 shows the typical graphitization curves of the alloys. Important data concerning the graphitization of the alloys are summarised in Table 14.

Table 14.

Specimens No.	Composition (%)			A	B	D	E	G	H
	C	Si	Cr						
1	2.91	0.81	0.28	1,070	900	1,000	50	3.91	0.58
2	2.81	0.80	0.31	1,070	900	1,000	40	3.65	0.77
3	2.86	0.82	0.84	1,070	950	—	—	1.81	1.72
4	2.80	0.83	1.05	1,070	1,010	—	—	0.73	2.31
5	2.37	0.88	0.26	1,070	920	980	30	2.47	0.78
6	2.45	0.90	0.55	1,070	980	—	—	1.54	1.27
7	2.41	0.89	0.70	1,070	—	—	—	0.51	2.04
8	2.46	0.88	0.93	1,070	—	—	—	0.20	2.46
9	2.43	1.00	1.41	1,070	—	—	—	0.08	2.43

Fig. 36.



The relation of the beginning temperature of the graphitization of the alloys to the chromium content is shown in Fig. 25. The relation of the amount of the combined carbon in the annealed alloys to the chromium content is shown in Fig. 26. These data show that chromium strongly hinders the graphitization of the alloys, and that the more remarkable the effect of the element, the lower the carbon content in the alloys.

Photogrs. 34 and 35 show the typical structure of the annealed alloys. In the former, the smaller amount of carbon remains undecomposed in the combined state in a well-developed pearlite matrix. In the latter, most of the carbon in the combined state remains undecomposed in a sorbitic pearlite matrix.

B. Summary.

The results so far obtained may be summarised as follows:

(1) The effect of chromium up to about 1.4 per cent on the graphitization in white cast iron having 2.8 to 2.5 per cent of carbon, 0.8 per cent of silicon and a minute amount of other impurities has been definitely determined.

(2) Chromium strongly hinders the graphitization in white cast iron, and the lower the carbon content in the alloy, the more remarkable the effect of this element.

§ XI. INFLUENCE OF TUNGSTEN.

According to Honda and Murakami[1] and Ozawa,[2] the carbon in cast iron having tungsten may exist in the form of cementite dissolving tungsten or double carbides forming one constituent in pearlite.

What rôle such cementite or carbides play in the graphitization of cast iron has not yet been studied.

A. Experiment.

The compositions of the specimens are given in Table 15. Fig. 37 shows the typical graphitization curves of the alloys. Important data concerning the graphitization of the alloys are summarised in Table 15.

Table 15.

Specimens No.	Composition (%)			A	B	C	D	E	F	G	H
	C	Si	W								
1	2.31	0.74	0.01	1,070	890	1,070(?)	980	30	390	3.03	0.50
2	2.31	0.73	0.53	1,070	880	1,070(?)	980	30	370	3.00	0.61
3	2.34	0.73	1.05	1,070	890	1,070(?)	980	30	380	2.89	0.73
4	2.25	0.71	1.29	1,070	890	1,070(?)	970	30	380	2.99	0.75
5	2.25	0.73	1.61	1,070	890	1,070(?)	980	30	380	2.97	0.71
6	2.30	0.70	2.16	1,070	900	1,070(?)	980	30	380	3.05	0.73
7	2.31	0.73	3.65	1,070	890	1,070(?)	980	30	380	2.83	0.82

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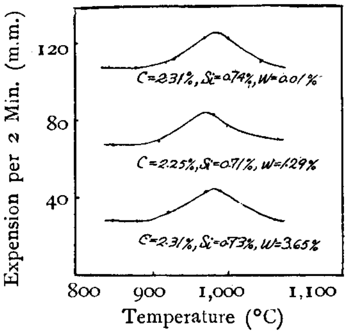
[1] Sci. Rep. Tohoku Imp. Univ. 6, (1918), 235.

[2] ditto. 11, (1922), 333.

Fig. 37.



The relation of the beginning temperature of the graphitization of the alloys to the tungsten content is shown in Fig. 25. The curve shows that tungsten is practically indifferent to the beginning temperature of the graphitization of the alloys. But the amount of the combined carbon in the annealed alloys seems to increase gradually as the tungsten content increases. The last fact has been also proved by microscopic study of the annealed specimens (Photogrs. 36 and 37).

B. Summary.

The results so far obtained may be summarised as follows:

(1) The effect of tungsten up to about 3.5 per cent on the graphitization in white cast iron having 2.3 per cent of carbon, 0.75 per cent of silicon and a minute amount of other impurities has been definitely determined.

(2) Tungsten hinders the graphitization in the alloys, but the effect is very feeble.

§ XII. INFLUENCE OF MOLYBDENUM.

It is unknown in what form carbon in cast iron having molybdenum may exist and how the element affects the graphitization in cast iron.

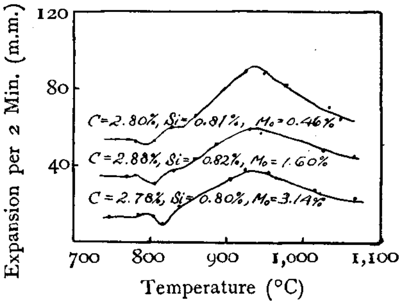
Table 16.

Specimens No.	Composition (%)			A	B	D	E	G	H
	C	Si	Mo						
1	2.80	0.81	0.46	1,070	840	930	40	4.53	0.61
2	2.82	0.79	1.07	1,070	840	940	30	4.29	0.97
3	2.88	0.82	1.60	1,070	850	930	30	3.98	1.07
4	2.79	0.81	1.99	1,070	850	930	30	4.00	1.51(?)
5	2.81	0.80	2.53	1,070	850	940	30	4.01	1.09
6	2.78	0.80	3.14	1,070	850	930	30	3.97	1.13

A. Experiment.

The compositions of the specimens are given in Table 16. Fig. 38 shows the typical graphitization curves of the alloys. Important data concerning the graphitization of the alloys are summarised in Table 16.

Fig. 38.



The relation of the beginning temperature of the graphitization of the alloys to the molybdenum content is shown in Fig. 25. The curve shows that molybdenum is practically indifferent to the temperature in question. But the amount of combined carbon in the annealed alloys gradually increases as the molybdenum content increases. The last fact has also been proved by microscopic study of the annealed alloys (Photogrs. 38 and 39).

B. Summary.

The results so far obtained may be summarised as follows:

(1) The effect of molybdenum up to about 3 per cent on the graphitization in white cast iron having 2.8 per cent of carbon, 0.8 per cent of silicon and a minute amount of other impurities has been definitely determined.

(2) Molybdenum hinders graphitization in the alloys, but the effect is very feeble.

§ XIII. INFLUENCE OF VANADIUM.

The ternary system of iron, carbon and vanadium has not yet been studied. According to Hatfield,[1] vanadium hinders the graphitization of cast iron. Oberhoffer,[2] however, doubts the unfavourable effect of the element in his work.

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[1] Cast iron in the Light of recent Research, (1918), 89.

[2] Das technische Eisen (1925), 130.

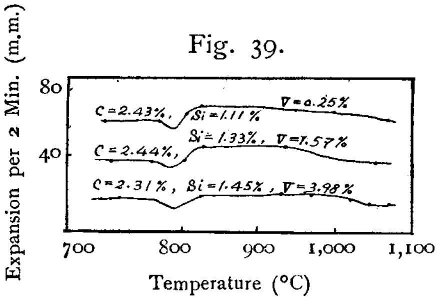
A. Experiment.

The compositions of the specimens are given in Table 17. Fig. 39 shows the typical graphitization curves of the alloys. As shown from these curves, the beginning temperatures of the graphitization of the alloys have not been definitely found. But the data concerning the graphitization of the alloys, summarised in Table 17, show that the effect of vanadium against graphitization is very remarkable up to about 0.25 per cent of the element. The above fact has also been proved by microscopic study of the alloys (Photogr. 40).

Table 17.

Specimens No.	Composition (%)			A	E	G	H
	C	Si	Va				
1	2.43	1.11	0.25	1,070	14	1.79	1.07
2	2.40	1.20	0.81	1,070	12	1.63	1.14
3	2.38	1.23	1.23	1,070	12	1.45	1.01
4	2.44	1.33	1.57	1,070	12	1.47	1.22
5	2.32	1.10	2.08	1,070	11	1.51	1.34
6	2.41	1.25	2.80	1,070	11	1.40	1.20
7	2.31	1.45	3.98	1,070	9	1.38	1.60

Fig. 39.



B. Summary.

The results so far obtained may be summarised as follows:

(1) The effect of vanadium up to about 4 per cent on the graphitization of white cast iron having 2.4 per cent of carbon, 1.2 per cent of silicon and minute amounts of other impurities has been studied.

(2) Vanadium hinders the graphitization of the alloys as found by Hatfield; its unfavourable effect becomes rapidly striking up to about 0.25 per cent of the element but afterwards increases gradually as the vanadium content increases.

§ XIV. INFLUENCE OF PHOSPHORUS.

According to many investigators,[1] combined carbon does not exist in other forms different from cementite in cast iron having phosphorus. As regards the effect of the element on the graphitization in cast iron, there is a great discrepancy in the opinions of previous investigators. According to Wüst,[2] in cast iron having a minute amount of silicon phosphorus is indifferent to graphitization up to 2.5 per cent of the element, but when beyond this content it favours graphitization and in cast iron having 0.8 per cent of silicon, the favourable effect of the element does not appear until phosphorus reaches 3 per cent. After Hamazumi,[3] on the other hand, phosphorus up to 3 per cent favours graphitization in cast iron having 1.7 per cent of silicon but when it exceeds this amount the case is reversed. Moreover, after Wüst and Schlösser,[4] phosphorus up to 0.5 per cent is practically indifferent to the graphitization of practically pure white cast iron.

A. Experiment.

The present writer first prepared several specimens having up to 4 per cent of phosphorus and a minute amount of other impurities and heated them in the usual manner. But the alloys, excepting those having lower phosphorus, showed no abnormal expansion up to 950°C at which point they suddenly contracted, as shown in Fig. 40. This contraction, of course, is due to the presence of steadite consisting of cementite, phosphide and austenite.

From this experiment it was found that the beginning temperature of the graphitization of the alloys was higher than 950°C.

Then the specimens having 0.8 per cent of silicon were prepared, their compositions being given in Table 18. Fig. 41. shows the typical graphitization curves of the alloys. These curves show that in this case

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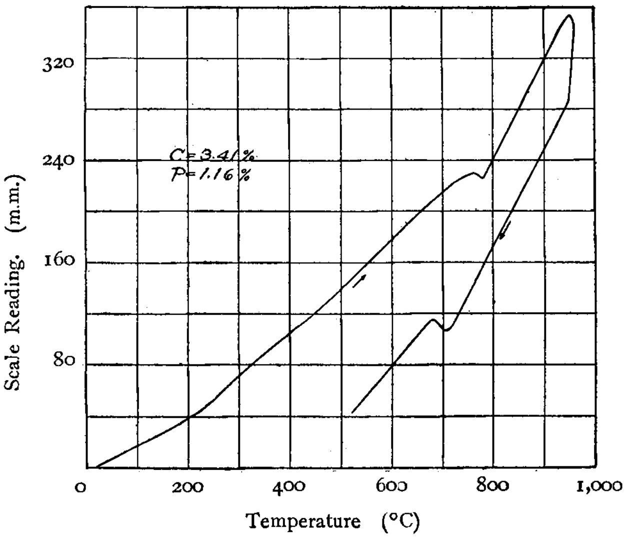
[1] Stead: Journ. Ir. St. Inst. (1900), No. II, 60; (1915), No. I, 176.
Wüst: Met. 5, (1908), 86.
Goerens u. Dobbelstein: Met. 5, (1908), 516.

[2] Met. 3, (1906), 203.

[3] Sci. Rep. Tohoku Imp. Univ. 13, (1924), 157.

[4] Stahl u. Eisen. 24, (1904), 1120.

Fig. 40.



also sudden contraction takes place at about 1,000°C on the alloys having a higher content than about 1 per cent of phosphorus.

The contraction in this case is due to the presence of the eutectic consisting of iron phosphide (Fe_3P) and austenite having phosphorus.

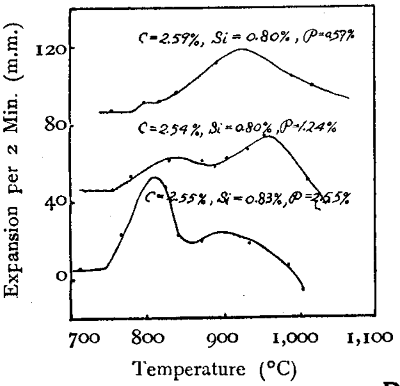
Important data concerning the graphitization of the alloys are summarised in Table 18. As the graphitization curves of the alloys having more than about 0.7 per cent of phosphorus are greatly disturbed by their A_1 transformation which takes place in the graphitization period of the alloys, it is impossible to determine data under the symbols D and E.

Table 18.

Specimens No.	Composition (%)			A	B	C	D	E	G	H
	C	Si	P							
1	2.53	0.79	0.13	1,070	870	—	950	40	4.10	0.88
2	2.74	0.80	0.38	1,070	840	—	930	40	5.21	0.52
3	2.59	0.80	0.57	1,070	820	1,070(?)	930	40	5.58	0.39
4	2.63	0.80	0.69	1,070	790	1,070(?)	—	—	5.32	0.24
5	2.76	0.81	0.88	1,070	780	1,070(?)	—	—	5.61	0.20
6	2.53	0.78	0.94	1,070	790	1,070(?)	—	—	5.35	0.31
7	2.58	0.79	1.01	1,070	780	1,070(?)	—	—	5.32	0.14
8	2.54	0.80	1.24	1,070	760	1,020(?)	—	—	5.54	0.27
9	2.48	0.81	1.88	1,070	750	1,000(?)	—	—	5.49	0.09
10	2.55	0.83	2.55	1,070	750	1,000(?)	—	—	5.52	0.11

The relation of the beginning temperature of the graphitization of the alloys to the phosphorus content is shown in Fig. 25. The relation of the amount of the combined carbon in the annealed alloys to the phosphorus content is shown in Fig. 26. These data evidently show that phosphorus favours the graphitization of the alloys to a moderate degree, and the effect reaches a maximum at about 1.2 per cent of phosphorus.

Figr 41.



The microscopic study of the alloys has proved the above conclusion. The structure of the alloys in the cast state has not shown any peculiarities except the characteristic dendritic structure (Photogr. 41). In the graphitised alloys, temper carbon exists in nodular form.

B. Summary.

The results so far obtained may be summarised as follows:

(1) The effect of phosphorus up to about 4 per cent on the graphitization in practically pure white cast iron has been studied, but the experiments have failed owing to the presence of steadite, having a melting point of 953°C. Consequently no conclusion on the effect of the element has not been reached except that the alloys have not begun to graphitise at a temperature lower than 950°C.

(2) The effect of phosphorus up to about 2.5 per cent on the graphitization in white cast iron having 2.5 per cent of carbon, 0.8 per cent of silicon and a minute amount of other impurities has been definitely determined.

(3) Phosphorus favours graphitization of the white cast iron having silicon; the effect of the element reaches a maximum at about 1.2 per cent of the element and further increase of the phosphorus content is almost indifferent to the effect.

(4) White cast iron having phosphorus has a tendency to produce nodular temper carbon.

§ XV. INFLUENCE OF SULPHUR.

Sulphur is generally believed, from the works of previous investigators,[1] to hinder the graphitization in cast iron to a great degree.

Among them, Liszner prepared white cast irons in sand moulds and determined the tempesature at which they began graphitization by thermal analysis. His results, reproduced from his paper, are given in Table 19.

As regards the theory on the effect of sulphur under discussion, Levy[2] attributed the unfavorable effect of the element to the presence of a thin film of iron sulphide between the eutectic cementite crystals which prevented the balling up of the cementite under an assumption that a balling up of the cementite was a necessary preliminary to the graphitization of the cementite. Stead[3] and Hatfield,[4] on the other hand, believed that the cementite in cast iron containing sulphur became stable because the small percentage of the element associated with the cementite crystals.

Table 19.

Specimens No.	Total C	Graphite C	Si	S	Begg. Temp. of Graphn. (°C)
A.1	3.38	0.08	0.41	0.151	765
2	3.32	0.07	0.43	0.198	807
3	3.35	0.04	0.44	0.242	865
3a	3.36	0.02	0.43	0.256	867
4	3.30	0.02	0.42	0.318	920
5	2.84	0.00	0.39	1.24	1,023

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1) Wüst: Mat. 3, (1906), 201.
Wüst u. Schlösser: Stahl u. Eisen 24, (1904), 1120.
Liszner: Ferrum 11, (1912), 44.

2) Journ. Ir. St. Inst. (1908) No. II, 45.

3) Hatfield: Cast iron in the light of recent Research, (1918), 68.

4) ditto. 197.

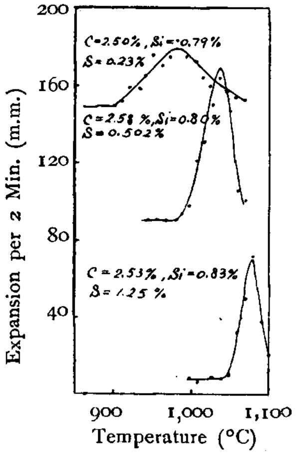
A. Experiment.

The compositions of the specimens are given in Table 20. Fig. 42 shows the typical graphitization curves of the alloys. Important data concerning the graphitization of the alloys are summarised in Table 20. The relation af the beginning temperature of the graphitization of the alloys to the sulphur content is shown in Fig. 25. The relation of the amount of the combined carbon in the annealed alloys to the sulphur content is shown in Fig. 26. These data evidently show that sulphur increasingly hinders the graphitization of the alloys as the sulphur content becomes greater.

Table 20.

Spesimens No.	Composition			A	B	D	E	G	H
	C	Si	S*						
1	2.55	0.81	0.118	1,070	900	980	40	4.00	0.69
2	2.50	0.79	0.230	1,070	900	980	40	3.98	0.79
3	2.76	0.82	0.395	1,070	960	1,020	80	3.83	0.80
4	2.58	0.80	0.502	1,070	980	1,040	100	4.20	0.82
5	2.62	0.75	0.646	1,070	1,000	1,050	80	3.34	0.94
6	2.51	0.80	0.986	1,070	1,030	1,060	80	3.62	1.26
7	2.53	0.83	1.250	1,100	1,050	1,080	70	2.74	0.69(?)
8	2.71	0.80	1.848	1,070	—	—	—	—1.22	2.24
9	2.49	0.78	2.407	1,070	—	—	—	—1.93	2.47

Fig. 42.



In this experiment, it has been found that the beginning temperature of the graphitization of the alloys was far higher than that found by Liszner in the white cast iron having composition as given in Table 19. It is also interesting to find that the alloys having higher sulphur graphitise rather more easily than the alloys having lower sulphur when they

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* Found by the evolution method.

begin to graphitise, although the former begin to graphitise at a temperature higher than the beginning temperature of the graphitization of the latter.

In the microstructure of the alloys in the cast state having higher than about 0.9 per cent of sulphur, round crystals probably, iron sulphide was observed and its amount gradually increased as the sulphur content increased (Photogr. 44). It was observed to be practically neutral to the graphitization in the alloys (Photogr. 46).

B. Summary.

The results so far obtained may be summarised as follows:

(1) The effect of sulphur up to about 2.5 per cent on the graphitization in white cast iron having 2.5 per cent of carbon, 0.8 per cent of silicon and a minute amount of other impurities has been definitely determined.

(2) Sulphur increasingly hinders graphitization of the alloys as the sulphur content increases.

(3) The alloys having higher sulphur may graphitise rather more easily than those having lower sulphur when they begin to graphitise, although the beginning temperature of the former is higher than that of the latter.

(4) A crystal, probably iron sulphide, found in the alloys having higher than about 0.9 per cent of sulphur is practically neutral to graphitization.

§ XVI. INFLUENCE OF MANGANESE.

Carbon[1] seems to exist in the form of a solid solution of cementite Fe_3C and manganese carbide Mn_3C in white cast iron having less than about 30 per cent of manganese.

According to Wüst and Schlösser,[2] manganese up to about 0.5 per

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1) Oberhoffer: Das technische Eisen, (1924), 110.
2) Stahl u. Eisen. 24, (1904), 1120.

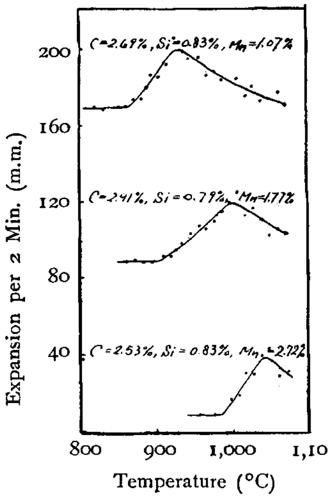
cent is practically indifferent to graphitization in pure white cast iron, but a further addition of the element hinders graphitization in an increasing degree as the manganese content increases. According to Wüst and Meiszner,[1] the effect of the element against graphitization in cast iron having 1.5 per cent of silicon does not appear until the manganese content exceeds 2.5 per cent.

A. Experiment.

Table 21.

Specimens No.	Composition			A	B	D	E	G	H
	C	Si	Mn						
1	2.71	0.80	0.42	1,070	870	940	40	4.35	0.79
2	2.58	0.78	0.65	1,070	880	940	40	4.09	0.61
3	2.69	0.83	1.07	1,070	870	930	40	3.58	0.52
4	2.80	0.80	1.43	1,070	890	960	40	3.96	0.67
5	2.91	0.79	1.77	1,070	910	1,000	40	3.98	0.84
6	2.57	0.78	2.09	1,070	950	1,000	40	3.51	1.28
7	2.63	0.83	2.45	1,070	970	1,020	40	3.21	1.16
8	2.53	0.83	2.72	1,070	990	1,040	40	2.49	1.31
9	2.67	0.80	3.69	1,070	—	—	—	1.53	2.12

Fig. 43.



The compositions of the specimens are given in Table 21. Fig. 43 shows the typical graphitization curves of the alloys. Important data concerning the graphitization of the alloys are summarised in Table 21. The relation of the beginning temperature of the graphitization of the alloys to the manganese content is shown in Fig. 25. The relation of the amount of the combined carbon in the annealed alloys to the manganese content is shown in Fig. 26. These data show that manganese is practically indifferent to the graphitization of the alloys up to about 1 per cent, but after-

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[1] Ferrum. 11, (1914), 91.

wards the effect of the element against graphitization becomes suddenly marked as the manganese content increases.

The above fact has been also proved by the microscopic study of the alloys. (Photogrs. 47 and 48)

B. Summary.

The results so far obtained may be summarised as follows:

(1) The effect of manganese up to about 3.5 per cent on the graphitization in white cast iron having 2.5 per cent of carbon, 0.8 per cent of silion and a minute amount of other impurites has been definitely determined.

(2) Manganese up to about 1 per cent is practically indifferent to the graphitization of the alloys but when it exceeds the above limit its effect against graphitization becomes marked as the manganese content increases.

§ XVII. GENERAL SUMMARY.

In this part the effect of the fifteen kinds of elements which are naturally contained or may be intentionally added in future in cast iron on the graphitization in the two kinds of white cast irons, one of which is practically pure, and the other having 0.8 per cent of silicon, has been shown with a great clearness by means of the new methods of investigation. Details of the results obtained have been summarised in each paragraph. Here only the general survey of the results are described.

(1) The elements whose effects have been studied in the present experiments are classified according to those effects as follows:

Elements which favour graphitization in white cast iron are Si, Al, Ti, Ni, P, Cu, Co, Au, and Pt.

Elements which hinder graphitization in white cast iron are Cr, S, Mn, Va, Mo, and W.

The elements are approximately arranged according to the degree of their effect in lowering the beginning temperature of graphitization of practically pure white cast iron as follows:

(Strong) → Si, Al, (Ti), Ni, Cu, Co, (P) → (Weak).

The elements are approximately arranged according to the degree of their effect in raising the beginning temperature of graphitization of white cast iron having 2.5 per cent of carbon, 0.8 per cent of silicon and a minute amount of other impurities as follows:

(Weak) → W, Mo, Mn, Va, Cr, S → (Strong).

These elements are classified according to the type of space lattice of their crystal as given in Table 22.

Table 22.[1]

Type of Lattice	Elements.
Face-centered cubic	Al Ni Co[2] Cu Au Pt
Tetrahedral cubic	Si
Hexagonal close-packed	Ti Co[2]
Body-centered cubic	Cr Va W Mo

It is interesting to find that most of the elements which favour graphitization in cast iron crystallise in face-centred cubic and most of the elements which hinder graphitization in cast iron crystallise in body-centred cubic lattice.

(2) As shown in Figs 8, 9 and 25, most of the elements which

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1) From W. H. Bragg and W. L. Bragg: X Rays and Crystal Structure. (1924), 163.

2) Masumoto: Kinzoku no Kenkyu, 2, (1925), 877.

favour graphitization in cast iron have a limit in their effect on the beginning temperature of white cast iron.

(3) White cast irons having a highr content of some element (e. g. Si, Al, Ti, P) begin to graphitise at temperatures lower than their Ac_1, or completely graphitise until their temperature reaches their Ac_1.

(4) The constitution of the white cast irons containing silicon or aluminium has been studied, and it has been found that the stability of the cementite in the cast irons changes with the contents of carbon and the elements above-mentioned and also that the cementite in some of the alloys directly decomposes at temperatures lower than their Ac_1 by annealing.

These facts will probably hold in other cases also.

(5) In white cast iron having some element, a part or all of the carbon may exist in a combined form different from cementite. The stability of the substance, of course, has a relation to the graphitization in the mother white cast iron. Such examples have been shown on the alloys having silicon or aluminium.

(6) In white cast irons which rapidly graphitise by annealing, that is, alloys having high content of silicon, aluminium, titanium or nickel, the form of the temper carbon produced is always governed by the form of the cementite and is flaky in most cases. And both number and the size of the temper carbon are also governed by those of the cementite in the alloys.

In white cast iron which slowly graphitise by annealing, that is alloys having low content of silicon, aluminium, titanium or nickel, or having cobalt, copper, phosphorus, molybdenum or other elements having an effect against graphitization in the alloys, the form of the temper carbon is indifferent to that of the cementite and always nodular. Generally speaking, the size of the nodular temper carbon is far larger and its number far smaller than expected from the structure of the alloys in the cast state.

(7) As the mechanism of the formation of temper carbon is of the same nature as that of the formation of graphite in cast iron during cooling as shown in the following part, the behavior of the elements toward the

formation of graphite in cast iron can be apploximately inferred from the results obtained in the present work.

Part II. THEORETICAL CONSIDERATION OF THE GRAPHITIZATION IN CAST IRON.

§ I. SUPPLEMENTAL EXPERIMENTS.

A. Influence of cooling velocity on the graphitization in white cast iron having silicon.

No report of systematic investigation of the subject has been published yet, although it is very important in the malleable casting industry.

(a) Experiment.

In the present experiments the raw materials No. A, B†, D and M in Table I were used for the preparation of the specimens.

The materials were melted in a cryptol furnace and the half of the melt was cast in iron moulds and the other half in green sand moulds into rods with 5 m. m. of diameter. Two kinds of specimens from the same melt were then prepared by cutting the ingots to a length of 70 m. m. each.

Table 23.

Specimens No.		Composition (%)		Heating Temp. (°C)	Begg. Temp. of Graphitization (°C)		End Temp. of Graphitization (°C)		Decrease in Specific Gravity due to Graphitization (%)	
		C	Si			(diff.)		(diff.)		(diff.)
1	a*	2.42	0.60	1,070	960	70	—	—	3.90	1.20
	b*				1,030				2.70	
2	a	2.70	0.96	1,070	880	90	1,010	—	5.16	1.05
	b				970		—		4.11	
3	a	2.87	1.41	1,070	800	110	970	90	5.31	0.89
	b				910		1,060		4.42	
4	a	2.50	1.82	1,070	750	140	930	80	5.41	0.64
	b				890		1,010		4.77	

(*) a: Chill cast specimen.
b: Sand cast specimen.

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†) Carburetted with charcoal powder and its carbon content raised to 3.4 per cent.

The modes of the graphitization of the alloys were examined in the usual way.

The results of the present experiments are shown in Figs. 44 to 47 and tabulated in Table 23.

According to the results, the chill cast specimens always graphitise

Fig. 44.

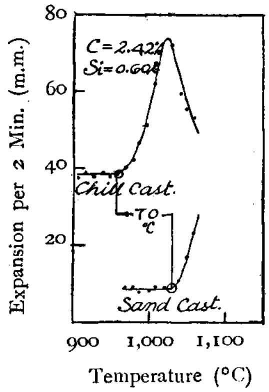


Fig. 45.

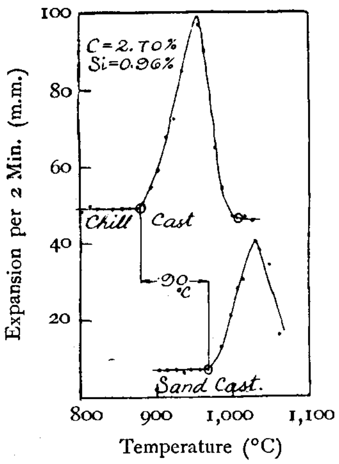


Fig. 46.

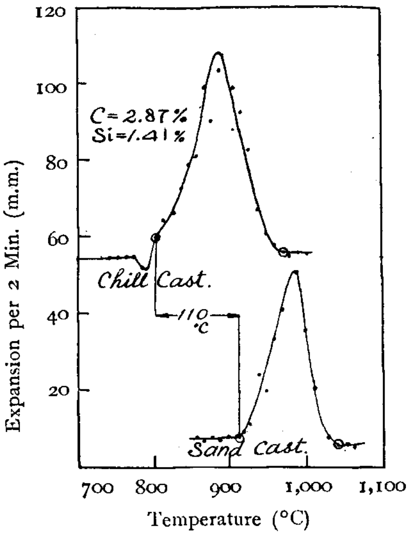
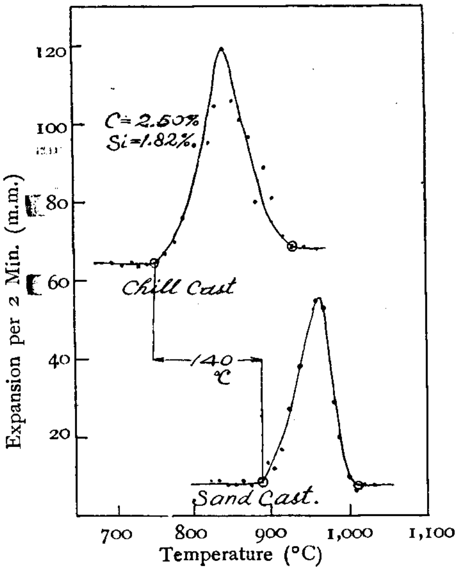


Fig. 47.



more easily than the sand cast alloys, and the higher the silicon content of the alloys the greater the difference in the beginning temperatures of the graphitization of the two kinds of specimens from the same melt. Table 23 also shows that the volume increase due to the graphitization of the chill cast alloys is always far greater than that of the sand cast alloys of the same composition as the former; in other words, the amount of the temper carbon produced in the former is far greater than that in the latter.

The effect of the cooling velocity under discussion should be considered under the following mode of cooling in three separated ranges:

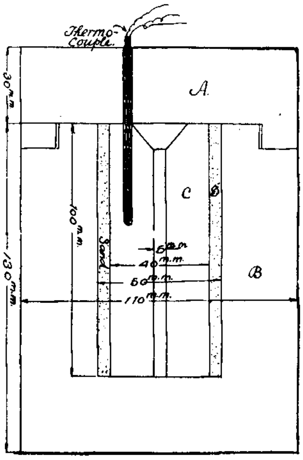
(1) Solidification velocity in solidification range.

(2) Cooling velocity in the temperature range from the temperature just below the eutectic temperature to the temperature just above the eutectoid temperature.

(3) Cooling velocity in the temperature range from the temperature just above the eutectoid temperature to room temperature.

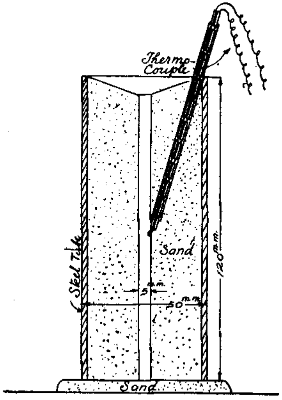
In order to find the effect of the solidification velocity of white cast iron on the graphitization in the iron, the present writer first cast the same melt in six iron moulds of the same dimensions which were heated

Fig. 48.



A=Cast iron cap.
B=Cylindrical cast iron box.
G=Cast iron mould.
D=Sand packing.

Fig. 49.



at various temperatures and a green sand mould and examined the modes of the graphitization of the specimens thus made by the usual method.

Figs. 48 and 49 show the chill mould set and the sand mould respectively used in the present experiments.

These chill mould sets were first heated in a gas furnace up to about 800° C and then taken out of the furnace and allowed to cool in the air down to the required temperature at which most of the melt was cast in them one by one and the remainder in the sand mould. These moulds were then all gradually cooled in the air after casting.

Table 24.

Specimens No.	Temperature of Mould (°C)		Composition (%)			Casting Temp. (°C)	Heating Temp. (°C)	Begg. Temp. of Graphn. (°C)	Decrease in Specific Gravity due to Graphn. (%)	Combined Carbon in annealed Specimens (%)
				C	Si					
1	Iron Mould	15	Before Tapping	3.43	0.38	1,450	1,070	960	5.51	0.82
2		125				1,430	1,070	970	5.40	—
3		280				1,420	1,070	980	5.09	—
4		390				1,410	1,070	980	3.99	—
5		595	After Tapping	3.39	0.39	1,400	1,070	980	3.81	1.64
6		760				1,410	1,070	980	3.75	1.80
7	Sand Mould	15				1,390	1,070	1,040	1.79	2.50

Table 24 and Fig. 50 show the results of the present experiments.

Examining the cooling velocity of these alloys, the velocity in question of the chill cast alloys should be far greater than that of the sand cast alloy in the temperature range up to the heating temperature of the moulds, but the case should be reversed in the temperature range below the temperature above cited.

After Newton's law of cooling, the lower the heating temperature of the moulds, the greater the cooling velocity of the chill cast alloys.

Then the results obtained show the fact that the less the cooling velocity of the alloys, the more their graphitization becomes difficult and

Fig. 50.

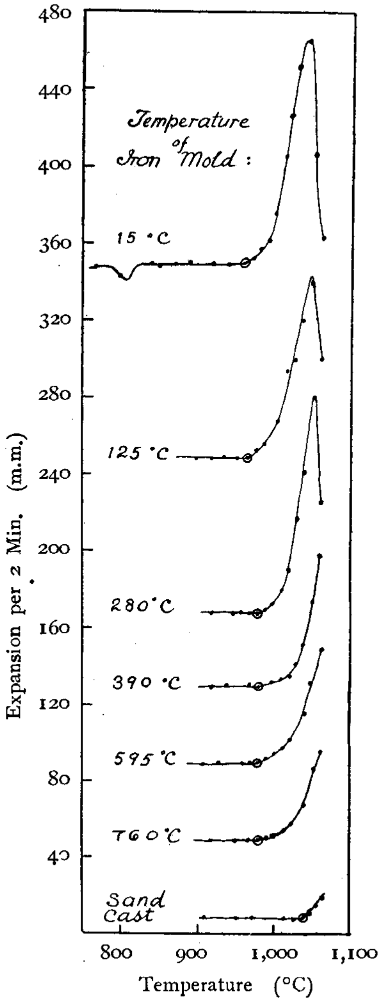
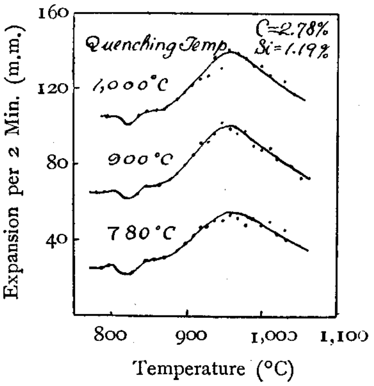


Fig. 51.



the cooling velocity in a temperature range up to the temperature just above the eutectoid temperature of the alloys has a remarkable effect on the graphitization in the alloys. Because, even the chill cast specimen No. 6, the cooling velocity of which in the temperature range below the temperature just above the eutectoid temperature of the alloys is far less than that of the sand cast alloys, far more easily graphitises than the latter.

Photogrs. 51 to 53 show the structure of the annealed alloys No. 1, 6 and 7 respectively. The amount of the cementite remaining undecomposed in the first two alloys is also here found to be far less than that in the last.

Next, in order to find the influence of the cooling velocity in a temperature range from the temperature just below the eutectic temperature to that just above the eutectoid temperature on the graphitization in white cast iron, the present writer cast the same melt at about 1,400 °C into the three green sand moulds as shown in Fig. 49. As soon as the temperature of the cast alloys descended to 1,000 °C, 900 °C and 780 °C respectively, they were forced out of the moulds into water of room temperature to be quenched. The chemical analysis as well as the graphitization curves of the specimens thus made are given in Fig. 51. These curves are all similar and consequently show that the cooling velocity in the temperature range in question has no remarkable effect on the graphitization in the alloys.

Thus the present writer believes that the solidification velocity of white cast irons has a remarkable effect on the graphitization in the irons. The explanation of the present phenomena will be discussed later.

(b) Summary.

The results so far obtained may be summarised as follows:

(1) It was found that the solidification velocity in the solidification range of cast iron has a remarkable effect on the graphitization in the solidified cast iron.

(2) The white cast iron quickly solidified more easily graphitises than that slowly solidified which has the same composition as the former.

(3) The volume increase due to the complete graphitization of the quickly solidified white cast iron is always far greater than that of the slowly solidified white cast iron having the same composition as the former.

B. Stability of isolated cementite.

Saniter(1), Honda and Murakami(2), Tammann and Ewig(3) and Ruer(4) measured the stability of the isolated cementite at high temperatures, but the results of their investigations do not coincide. The cementite employed by these investigators was all isolated from practically pure steel or white cast iron.

In the present work, the present writer has tried to find the relation of the stability of isolated cementite to the composition of the white cast iron from which the former was isolated.

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1) Journ. Ir. St. Inst. (1897), No. II, 115.
2) ditto. (1918), No. II, 385.
3) Stahl u. Eisen. 42, (1922), 772.
4) Z. an. chem. 117, (1921), 249.

(a) Experiment.

i Preparation of the sample.

About 1 kg. of white cast iron was melted in a kryptol furnace and a required amount of the raw material No. M or L given in Table I was dissolved in the melt when it was required. One half of the melt was cast in an iron mould 5 m. m. thick in bore and the other half in a green sand mould having the following dimensions: 7 m. m. x 50 m. m. x 80 m. m.. Thus the two kinds of white cast irons with varied cooling velocity were prepared from the same melt. The compositions of the alloys are given in Table 25.

Table 25.

Specimens No.	Composition (%)					
	C	Si	Mn	S*	P	Cu
1	3.23	0.18	0.13	0.18	0.13	0.15
2	3.41	0.54	0.13	0.17	0.14	0.15
3	3.28	0.21	0.14	0.71	0.13	0.15

* Found by the gravimetric method.

These alloys were next crushed to grains ½ m. m. to 1 m. m. thick, and about 100 grms. each were treated with about ½ N. hydrochloric acid in a hydrogen atmosphere in Liszner's[1] apparatus. After about 2 weeks the specimen no longer generated hydrogen bubbles when it was washed with water, alcohol and ether in order, and at last dried in dried hydrogen current.

The cementite thus obtained consisted of spongy, dark grains less than 1 m. m. thick, and easily crumbled to powder between the fingers.

In the following experiments the fine powder of cementite ground in an agate mortar was employed as the sample. The cementite isolated from the sand cast alloys was ground with special care.

The compositions of the samples are given in Table 26.

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1) Stahl u. Eisen. 45, (1925), 22.

Table 26.

Samples No.		Composition (%)						
		Total C	Graphite C	Si	Mn	S(1)	P	Cu
1′	a(*)	6.26	Trace	0.24	0.26	0.073	0.156	0.49
	b(*)	6.23	Trace	0.43	0.18	0.055	0.151	0.49
2′	a	6.47	Trace	—	—	—	—	—
	b	6.49	Trace	—	—	—	—	—
3′	a	6.03	Trace	—	—	0.219	—	—
	b	6.37	Trace	—	—	0.158	—	—

(*) a: Cementite isolated from the chill cast specimen.
b: Cementite isolated from the sand cast specimen.
(1) Found by the gravimetric method.

The above table shows that the cementite thus isolated contains a considerable amount of impurities.

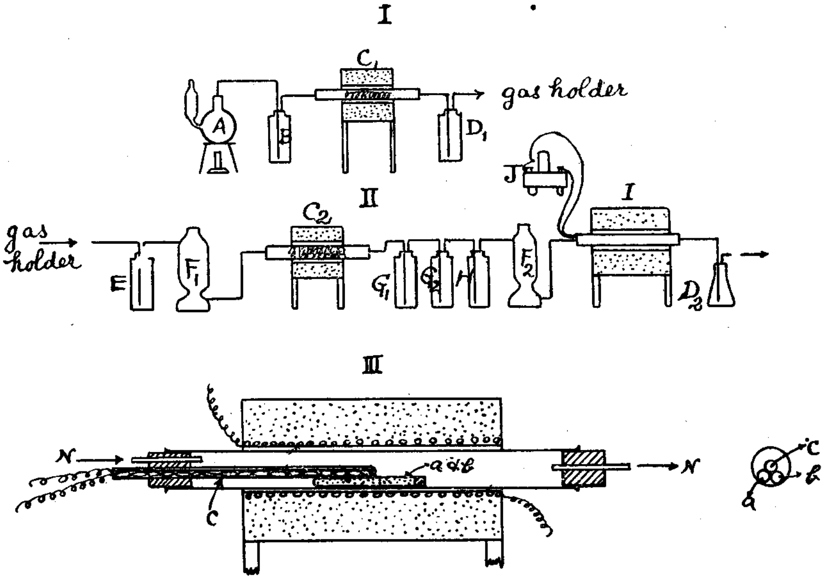
Of course, further investigation is necessary to determine definitely whether these impurities are associated with the cementite or not.

The present writer dissolved also the white cast irons having a moderate amount of phosphorus, manganese and copper respectively by the same method, and generally found that the sand cast alloys were more easily dissolved than the chill cast alloys, and also that the amount of the cementite isolated from the chill cast alloys was always greater than that from the sand cast alloys having the same composition as the former.

ii Graphitizing experiment.

Fig. 52 shows the general arrangement of the experimental apparatus. In Fig. 52–III, a and b are two silica tubes, each having one end closed, bound parallel with a nickel wire. 4 grms. each of the two kinds of samples were taken into these tubes and the open ends were stoppered with calcined asbestos. The samples were heated in the middle of an electric furnace at a constant rate of 10 °C per min. in a pure nitrogen atmosphere up to 1,100 °C, then the porcelain tube holding the silica tubes was taken out of the furnace as quick as possible and cooled in air. The samples in the silica tubes were taken out of the porcelain tube after its temperature fell to room temperature and subjected to analysis.

Fig. 52.



A = Gas Generator.
B = Washing Solution.
C = Heated Copper Gauze.
D = Conc. SO_4H_2.
E = $Na_2S_2O_4$ Sol$^{\underline{n}}$.
F = Cl_2Ca Tower.
G = SO_4Fe Sol$^{\underline{n}}$.
H = Alkaline Sol$^{\underline{n}}$ of Pyrogallol.
I = Heating Furnace
J = Galvanometer
a & b = Silica Tubes halding Sample.
c = Protecting Tube.

The nitrogen used in the present work was chemically generated by sodium nitrite and ammonium chloride and purified in the arrangement as shown in Fig. 52–I and II.

The results of the experiments are summarised in Table 27.

The table shows that the higher the silicon content of the alloys the greater the graphitization degree of the cementite isolated from those alloys, and also that the cementite isolated from the chill cast alloys is more unstable than that from the sand cast alloys having the same composition as the former.

The fact that the graphitization degree of the cementite isolated from the alloy having a high sulphur content (Specimen No. 3) is rather greater than that of the cementite isolated from the alloy having a low sulphur

Table 27.

Samples No.		Composition (%)				Real(*) Graphite C (%)	Graphitization Degree (%)
		Original	Treated				
		Tatal C	Tatal C	Graphite C	Combined C		
		A	B	C	D	A−D=E	$\frac{E}{A}\times 100$
1′	a	6.26	5.96	0.42	5.54	0.72	11.50
	b	6.23	6.15	0.36	5.79	0.44	7.04
2′	a	6.47	5.85	4.30	1.55	4.92	76.04
	b	6.49	6.05	4.36	1.57	4.92	75.81
3′	a	6.03	5.82	1.02	4.80	1.23	20.40
	b	6.37	6.27	0.71	5.56	0.81	12.71

(*) Assumed that the loss in total carbon by the treatment is due to the oxidation of the temper carbon produced.

content (Specimen No. 1) may show that the effect of the difference in the silicon content of these alloys on the stability of the cementite which they contain is far greater than that of the difference in the sulphur content in the alloys on the stability of the cementite at such a high temperature.

(b) Summary.

The results so far obtained may be summarised as follows:

(1) The cementite was isolated chemically from the white cast iron of varied composition and cooling velocity, and its graphitization degree at high temperature was examined.

(2) The silicon content of white cast iron affects the stability of the cementite isolated from that cast iron.

(3) The cooling velocity of the white cast iron containing silicon affects the stability of the cementite isolated from that cast iron.

(4) The amount of the cementite isolated from the chill cast alloys is always greater than that of the cementite isolated from the sand cast alloys.

C. Relation between temper carbon and graphite.

Graphite is the name given to the carbon produced in cast iron in cooling. Temper carbon is the name given to a form of carbon obtained during the annealing of white cast iron.

(a) Substantial relation.

Whether these two kinds of carbons are different from each other substantially or not has long been the subject of discussion among iron metallurgists. But recently it has been solved with great clearness by the application of X-ray analysis by many investigators[1]; so called temper carbon has been found to be the same allotropic form of carbon as graphite in cast iron or natural graphite. Northcott[2] and Liszner and Horney[3] have tried also to prove the above fact from other directions. Among the results obtained by these investigators the ignition temperatures of these carbons are pretty ambigious. Hence, in the present experiment, the writer has measured the modes of oxidation of the carbons accurately to supplement the results of the previous investigators.

i Experiment.

Preparation of sample :— The kinds of samples examined and the raw materials from which the samples were produced are summarised in Table 28.

Among these samples, lampblack was prepared by treating commercial lampblack with conc. nitric acid and fluoric acid after heating it in a closed platinum crucible at 1,050 °C for 5 minutes. Charcoal, coke, sugar carbon and natural graphite were first finely powdered in an agate mortar and then purified in the same manner as above mentioned. Temper carbon and graphite in cast iron were extracted and purified by the same method as adopted by Liszner and Horney.

As raw materials for obtaining graphite samples, the present writer used the cast irons having graphite which was formed under different modes of cooling. The microscopic appearance of the graphite in the mother cast irons is shown in Photogrs. 55 to 62.

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1) Iokibe: Sci. Rep., Tohoku Imp. Univ. 9, (1920), 275.
Asahara: Sci. Paper, Inst. Phy. Chem. Research. Japan No. 3.
Wever: Mitt. Kaiser Wilhelm Inst. f. Eisen Forsch. 4, (1922), 81.

2) Journ. Ir. St. Inst. (1923), No. I, 491.

3) Stahl u. Eisen 45, (1925), 1297.

Table 28.

Samples No.	Kinds of Samples	Kinds of Materials	Modes of Cooling of Materials	Ash Content in Samples (%)	Photogr. No.	Size of Graphite Flake	Begg. Temp. of Violent Oxidation (°C)
1	Lampblack	Commercial	—	0.65	—	—	350
2	Charcoal	Cherry	—	1.09	—	—	390
3	Sugar Carbon	—	—	0.83	—	—	410
4	Coke	—	—	3.24	—	—	460
5	Temper Carbon	Malleable Casting	—	0.08	54	—	610
6	Graphite	Centrifugal Cast Iron Pipe made by the de'Lavaud's Process	Quick	0.11	55	Small	550
7	Graphite	Cast Iron cast in an Iron Mould with thin Wall	Quick	0.16	56	Small	620
8	Graphite	Cast Iron cast in Sand Mould	Slow	0.10	57	Small	650
(*) 9	Graphite	Kenjiho Coke Pig (a)	Slow	0.07	58	Small	650
(*)10	Graphite	Kenjiho Coke Pig (b)	Slow	0.09	59	Large	710
11	Graphite	Cast Iron furnace cooled	Very slow	0.13	60	Large	710
12	Graphite	Wanishi Coke Pig	Slow	0.11	61	Large	630
13	Graphite	Ogure Charcoal Pig	Slow	0.07	62	Large	640
14	Graphite	Blast Furnace Kish	—	0.05	—	Very large	740
15	Natural Graphite	From Ceylon	—	0.10	—	Very small	830

(*) a: The portion of fine fracture. b: The portion of coarse fracture in the same fracture of the pig.

The graphites corresponding to sample No. 6 and 7 (Photogrs. 55 and 56) were quickly formed and are small in size. The graphites corresponding to sample No. 8 and 9 (Photogrs. 57 and 58) are also small in size though they were slowly formed. The graphites corresponding to sample No. 10 to 13 (Photogrs. 59 to 62) were slowly formed and are large in size.

Blast furnace kish graphites were obtained by picking up one by one graphite flake of large size from the blast furnace kish. They were sized with a 2 m. m. screen and its oversize was adopted as the sample.

Oxidation experiments :— Formerly Moissan[1] determined the ignition temperatures of various kinds of carbons by heating them in an oxygen current and introducing darbon dioxide, produced by the combustion of carbon, into baryta water to form a milky precipitate· By the same method but in an air current, Northcott[2] determined the ignition temperatures of carbons as follows :

Lampblack	Natural graphite	Temper carbon
550 °C	670 °C	650 °C.

Liszner and Horney[3] heated carbons in an oxygen current and observed a glow generated in carbons with the naked eye when the temperature of the carbons reached the following ignition temperatures :

Graphite in cast iron	Temper carbon
725 °C	620 °C.

In the present experiment, the writer adopted Honda's thermobalance[4].

The general arrangement of the experimental apparatus is shown in Fig. 53. K is the thermobalance, the sensibility of which was 900 m. m. per gram at the scale distance of 2000 m. m. The water bottle a was always overflowing, so the velocity of the water stream flowing out of the bottle into the oxygen holder b through a siphon was constant. The oxygen in the holder b was then forced into the electric furnace g from two small

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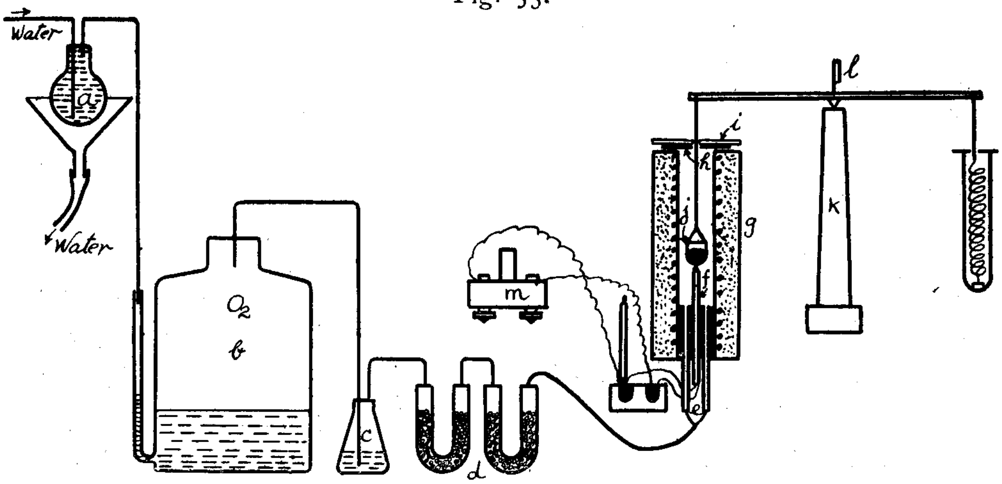
1) Moissan: The Electric furnace, (1904).

2) Loc. cit.

3) Loc. cit.

4) Sci. Rep., Tohoku Imp. Univ. 4, (1915), 97.

Fig. 53.



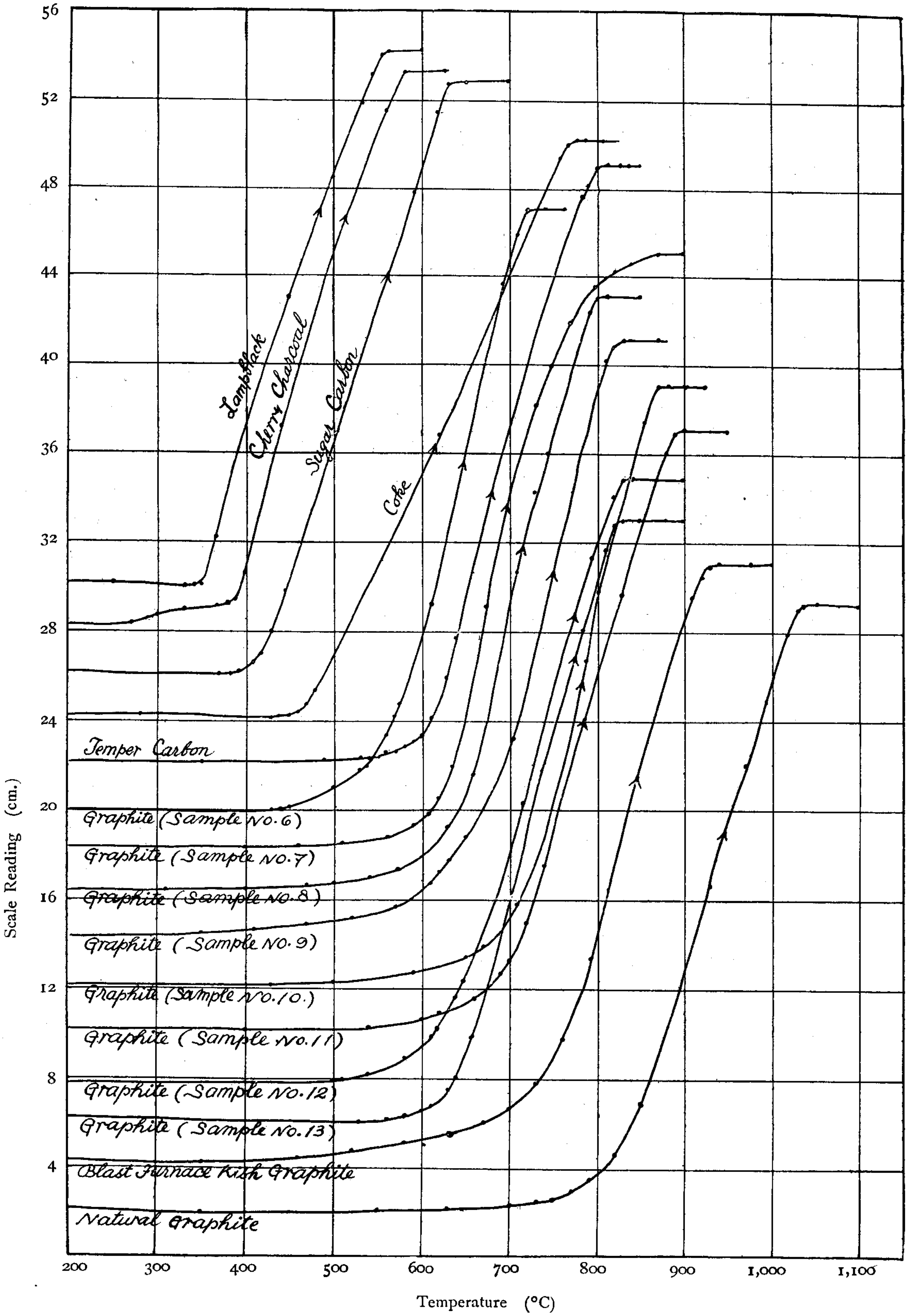
a=Water Bottle. b=Oxygen Holder. c=Sulphuric Acid Bottle. d=Soda Lime U Tubes. e=Oxygen Inlet Tubes. f=Thermocouple. g=Electric Furnace. h=Platinum Cover. i=Asbestos Cover. j=Platinum Crucible. k=Thermobalance. l=Mirror. m=Galvanometer.

inlet tubes e at a practically constant speed passing through drying apparatuses c and d. In the present experiment the amount of oxygen used was about 40. c. c. per min. In each experiment, 0.3 gram of the sample was taken and lightly packed in a small cylindrical platinum crucible j hanging by a platinum wire at one end of the balance in the middle of the furnace. The temperature was measured with a thermocouple consisting of platinum and platinum-rhodium wires, the hot junction of which was placed just below the bottom of the crucible. The heating rate was kept constant and was 5 °C per min.

The results of the experiment are graphically shown in Fig. 54. In these curves, the ordinate represents the deflection of the scale and the abscissa the temperature of the samples.

All the curves show that the gradual oxidation of the samples begins at a certain temperature and it continues to a higher temperature at which violent oxidation of the samples begins, afterwards the mass of the samples almost linearly decreases with the temperature. The beginning temperature of the violent oxidation probably corresponds to the so-called

Fig. 54.


56
52
48
44
40
36
32
28
24
20
16
12
8
4
Scale Reading (cm.)
200
300
400
500
600
700
800
900
1,000
1,100
Temperature (°C)
Lampblack
Cherry Charcoal
Sugar Carbon
Coke
Temper Carbon
Graphite (Sample No. 6)
Graphite (Sample No. 7)
Graphite (Sample No. 8)
Graphite (Sample No. 9)
Graphite (Sample No. 10.)
Graphite (Sample No. 11)
Graphite (Sample No. 12)
Graphite (Sample No. 13)
Blast Furnace Kish Graphite
Natural Graphite

ignition temperature. The temperatures of the samples under discussion are apploximately given in Table 28.

After repetition of the experiment these temperatures were found to be characteristic for the samples.

Some metallurgists believe that temper carbon is a mass consisting of minute graphite crystals, and graphite in cast iron is a well-developed graphite crystal. If this conception is true, the beginning temperature of the violent oxidation of carbons of apparently small size can not be higher than that of carbons of apparently large size. But this presumption is contrary to the facts; the beginning temperature of violent oxidation of the temper carbon is rather higher than that of the graphites expressed by sample No. 6 or almost equal to that of the graphites expressed by sample No. 7, their apparent size being far larger than that of the former as shown in Photogrs. 55 and 56; the beginning temperatures of violent oxidation of the graphites expressed by sample No. 8 and 9 (Photogrs. 57 and 58) are almost equal to those of the graphites expressed by sample No. 12 and 13 (Photogrs. 61 and 62), though the apparent size of the former is far smaller than that of the latter; and the beginning temperature of violent oxidation of the flaky graphites in cast iron or blast furnace kish graphites are far lower than that of the natural graphite sample, though the apparent size of the former is far larger than that of the latter.

Asahara[1] classified various forms of carbons into four types according to the sharpness of the intensity maxima in the X-ray interference figure of the carbons. He furthermore believed that the difference in the sharpness of the maxima was simply due to the difference in the size of the crystalline individuals.

Table 28 seems generally to show that the smaller the size of the crystalline individuals of graphites, the lower the beginning temperature of violent oxidation.

Now if we assume that a graphite in cast iron is not a single crystal but a mass consisting of a great number of submicroscopic graphite crystals

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[1] Loc. cit.

just the same as temper carbon, and also that the beginning temperature of violent oxidation of carbon is a characteristic for the size of crystalline individuals forming graphite or temper carbon, the results obtained in the present experiment can be easily explained.

That is say, the beginning temperature of violent oxidation of the graphite which was quickly formed may be low in spite of its apparent size being rather large, because the size of its crystalline individuals is small owing to the shortness of the time necessary for its development; and the beginning temperature of violent oxidation of the graphites which were slowly formed should be high in spite of its apparent size being small for the reverse reason to the above.

Indeed, the conception that the graphite in cast iron is a mass consisting of submicroscopic crystals was already expressed by Wever[1].

ii Summary.

The results so far obtained may be summarised as follows:

(1) The modes of oxidation of various forms of carbon was accurately measured by a thermobalance in an oxygen current at constant speed.

(2) The beginning temperature of violent oxidation is characteristic for the form of carbon.

(3) Graphite in cast iron is probably a mass consisting of submicroscopic graphite crystals in great number exactly similar to temper carbon.

(4) The beginning temperature of violent oxidation probably depends on the size of the submicroscopic graphite individuals making a form of carbon and not on the apparent size of that carbon. Hence the ignition temperature of temper carben is not necessarily lower than that of graphites.

(b) On the form of temper carbon and graphite.

It is generally believed that graphites are always flaky and temper carbon nodular under microscope. But it is not true; nodular graphite is easily produced and flaky temper carbon is often formed.

Photogr. 63 shows the structure of a kind of cast iron as cast in sand mould having nodular graphites just the same as temper carbon in

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[1] Loc. cit.

malleable casting. Photogr. 64 shows another example of flaky temper carbon just the same as flaky graphites in ordinary cast iron. It was produced by quickly graphitising a white cast iron having 3.43 per cent of carbon, 2.84 per cent of silicon and a minute amount of other impurities at 1,000 °C.

(c) Conditions for the formation of flaky or nodular temper carbon.

In the general summary of the previous part the subject was touched upon already. The present writer further investigated it by graphitising white cast iron having various compositions at various rates of graphitizing and obtained a conclusion almost the same as before.

Here only the conclusions somewhat modified are given, as follows:

(1) When white cast iron is graphitised at a temperature lower than its Ac_1, the form of temper carbon produced chiefly depends on that of the mother cementite; ledeburite cementite or primary cementite is always decomposed to flaky temper carbon and ferrite. Photogr. 65 shows the structure of a white cast iron as cast, and Photogr. 66 shows the structure of the same cast iron but graphitised at 730 °C in 4 hours. Comparing these structures, the above conclusion will be easily accepted.

(2) When white cast iron is graphitised at a temperature higher than its Ac_1, the form of temper carbon is sometimes flaky and at other times nodular. Generally speaking, nodular temper carbon, the form of which is quite indifferent to that of the mother cementite is formed under gradual graphitization, while flaky temper carbon, the form of which depends on that of the mother cementite, is produced under rapid graphitization of white cast iron. The composition of cast iron affects the conditions for the formation of these forms of carbon. Silicon, aluminium, nickel, etc. fovour the formation of flaky temper carbon; and cobalt, copper, etc. the formation of nodular temper carbon.

(d) Possibility of the transformation from flaky graphite or temper carbon to nodular graphite or temper carbon.

The following three kinds of cast irons were heated at the temperature of 1,000 °C to 1,100 °C for 50 hours in a vessel excluding air:

(1) Gray cast iron ($C=3.42\%$, $Si=3.83\%$, other impurities=minute) in which most of the carbon exists as flaky graphite.

(2) Cast iron ($C=3.48\%$, $Si=3.20\%$, other impurities=minute) having flaky temper carbon. It was made by graphitizing the cast iron in a chill state at 1,000 °C.

(3) Cast iron ($C=3.39\%$, $Co=4.60\%$, other impurities=minute) having nodular temper carbon. It was made by gradual annealing of the cast iron in a chill state.

The form of the graphite or temper carbon in the alloys before and after the heat treatment was microscopically studied.

But no remarkable change was observed in their form.

§ II. GRAPHITIZATION VELOCITY AND GRAPHITIZATION DEGREE OF CAST IRON.

A. Graphitization velocity of cast iron.

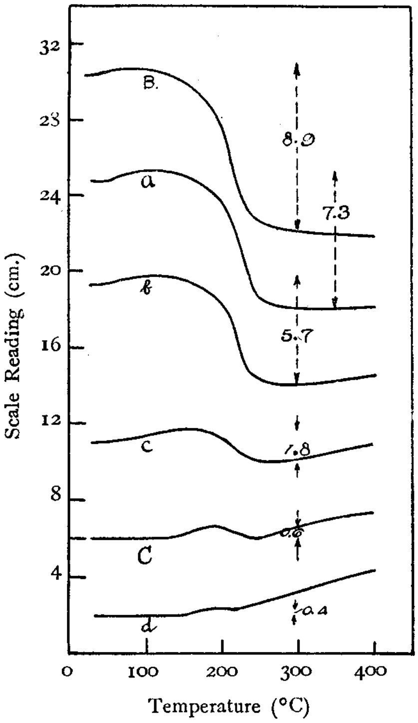
As before mentioned, Fig. 2 show the typical graphitization curve of the white cast irons having cementite as the principal constituent to be graphitised. In the figure, the ordinate corresponds to the change of the amount of the cementite to be graphitised in the graphitization period.

The present writer quenched the pieces of the same alloy, each of 12 grams weight, in water respectively from temperatures 850 °C, 890 °C,

Table 29.

Specimens No.	Quenching Temperature (°C)	Position of Quench. Temp. in Figs. 1 and 2.	A_0 (cm)	Relative Amount of Cementite
1	850	B	8.9	1.00
2	890	a	7.3	0.82
3	920	b	5.7	0.64
4	960	c	1.8	0.20
5	1,030	C	0.6(?)	0.06(?)
6	1,070	d	0.4(?)	0.04(?)

Fig. 55



920 °C, 960 °C, 1,030 °C and 1,070 °C (B, a, b, c, C and d in Figs. 1 and 2) after heating them up to these temperatures under the same conditions as adopted in the dilatometer experiment of the alloy, and found the amount of the cementite remaining undecomposed in the pieces by the usual magnetic analysis. The results are shown in Fig. 55 and Table 29.

From these date the present writer will treat on the relation between the graphitization velocity of the alloy and temperature by mathematical means in the following pages.

It is first assumed that in the alloy the constituent to be graphitised is only cementite and that the change in its amount is due only to graphitization. Now, in the present experiments,

$$t=kT$$

where

t=time

T=temperature

k=constant,

and

$$-\frac{dm}{dt}=w$$

where

m = the total amount of the cementite in the iron, and equal to 1 in the temperature range below the beginning temperature of graphitization (B),

w = the change in the amount of the cementite per unit time.

But

$$w = mv$$

where

v = the graphitization velocity, that is, the amount of the cementite to be graphitised per unit time per unit mass of the cementite.

Therefore

$$-\int \frac{dm}{m} = \int v dt$$

If the following equation be granted,

$$v = at^n \qquad \text{(1)}$$

where

a and n are positive and real numbers,

$$-\log m = a \frac{1}{n+1} t^{n+1} + k'$$

where

k' is an integral constant.

But as $k' = 0$ when t is equal to zero, that is, at the instant when the graphitization begins,

$$-\log m = a \frac{1}{n+1} t^{n+1}.$$

Therefore,

$$m = e^{-\frac{a}{n+1} t^{n+1}} \qquad \text{(2)}$$

$$w = at^n . e^{-\frac{a}{n+1} t^{n+1}} \qquad \text{(3)}$$

The asymptote of the curves (2) and (3) is the t–axis.

The maximum point of the curve (3) and the points of inflextion of these curves are as follows:

—Maximum point of the curve (3)—

$$\begin{cases} t=\left(\dfrac{n}{a}\right)^{\frac{1}{n+1}} \cdots\cdots (4) \\[2ex] w=a^{\frac{1}{n+1}}.\ n^{\frac{n}{n+1}}.\ e^{-\frac{n}{n+1}}. \cdots\cdots (5) \end{cases}$$

—Point of inflexion of the curve (2)—

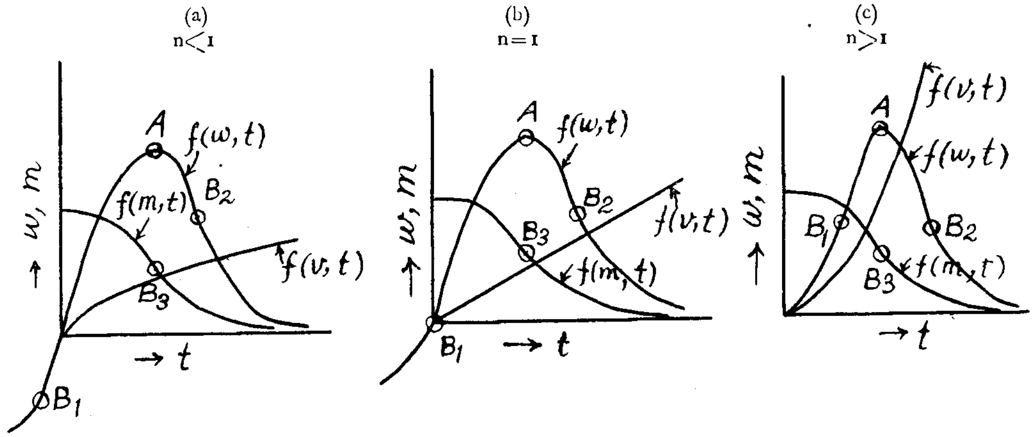
$$\begin{cases} t=\left(\dfrac{n}{a}\right)^{\frac{1}{n+1}} \cdots\cdots (6) \\[2ex] m=e^{-\frac{n}{n+1}}. \cdots\cdots (7) \end{cases}$$

—Points of inflexion of the curve (3)—

$$\begin{cases} t=\left(\dfrac{3n\pm\sqrt{5n^2+4n}}{2a}\right)^{\frac{1}{n+1}} \cdots\cdots (8) \\[2ex] w=a^{\frac{1}{n+1}}.\ n^{\frac{n}{n+1}}.\ e^{-\frac{n}{n+1}}.\ \left(\dfrac{3\pm\sqrt{5+\frac{4}{n}}}{2}\right)^{\frac{n}{n+1}}.\ \dfrac{3\pm\sqrt{5+\frac{4}{n}}}{2}\cdot \cdots\cdots (9) \end{cases}$$

From the above relations, the curves expressed by equations (1), (2) and (3) are classified into three groups as shown in Fig. 56 according to the position of the points of inflexion of the curve expressed by equation (3).

Fig. 56.



A : Maximum point.
B : Point of inflexion.

Indeed, the actual graphitization curve of the alloy (Fig. 2), for which the assumptions before given are practically applicable, has a maximum point and two points of inflexion in the first quadrant. Therefore, if equation (1) hold true, n must be greater than 1 (the case (c) in Fig. 56).

Now, taking $n=2$ and $a=4\times 10^{-3}$, the value of v, m and w at various temperatures is calculated out from the equations (1), (2) and (3) as given in Table 30.

Fig. 57 shows the relation between these values and the temperature. In the same figure, the curve representing the relation between the actual amount of cementite in the alloy and the temperature is plotted from the data given in Table 29 at the same time. Comparing Figs. 2 and 57, it is interesting to find that the empirical and mathematical curves well coincide with each other.

Therefore, the graphitization velocity of the alloy can be approximately expressed by the following equation:

$$v=4\times 10^{-3}\, t^2 \text{ or } v=4\times 10^{-3}\, T^2$$

if 2 min. be taken as the unit of time or 10 °C as the unit of temperature, that is, $k=1$.

The above equation, of course, relates to a white cast iron specially selected. Examining the graphitization curves of other white cast irons, it is readily found that the graphitization velocity of white cast iron generally varies after the equation:

$$v=a\, t^n,$$

where n is greater than 1.

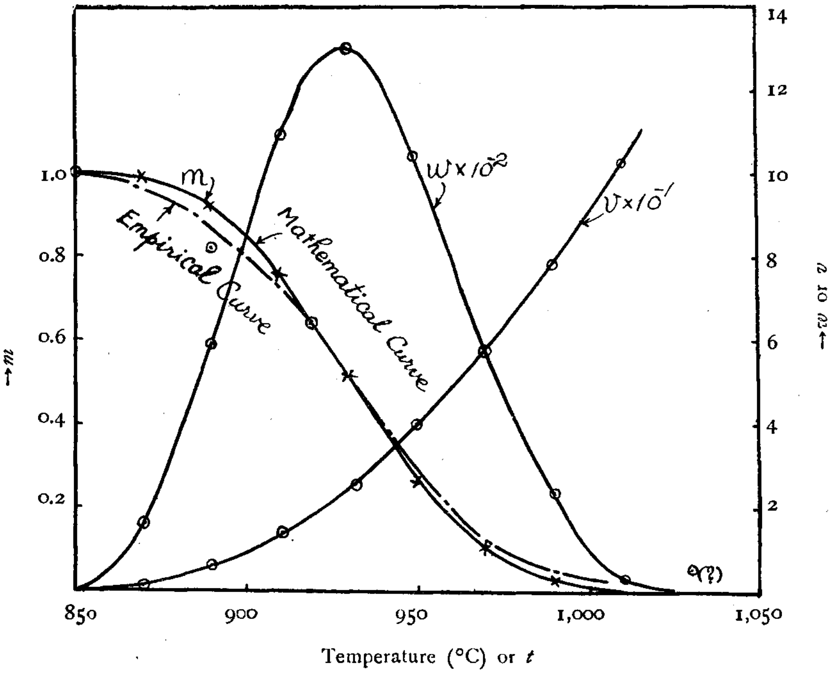
In Fig. 56—(c), let (w_1, t_1), (w_2, t_2) and (w_3, t_3) be respectively the position of the maximum point A, the positions of the points of inflexion B_1 and B_2 of the curve expressed by equation (3) and also

$$\alpha_1=\frac{w_2}{w_1},\quad \alpha_2=\frac{w_3}{w_1},\quad \beta_1=\frac{t_2}{t_1},\quad \beta_2=\frac{t_3}{t_1},\quad \text{then}$$

Table 30.

t	Temperature (°C)	v	m	w
0	850	0.000	1.00	0.000
2	870	0.016	0.99	0.016
4	890	0.064	0 92	0.059
6	910	0.144	0.76	0·109
8	930	0.256	0.51	0.131
10	950	0.400	0.26	0.104
12	970	0.576	0.10	0.058
14	990	0.784	0.03	0.024
16	1,010	1.024	4.3×10^{-3}	0.004

Fig. 57.



$$a_1=e^{-\frac{n}{n+1}\left(\frac{3-\sqrt{5+\frac{4}{n}}}{2}-1\right)}\cdot\left(\frac{3-\sqrt{5+\frac{4}{n}}}{2}\right)^{\frac{n}{n+1}}\cdot\quad\ldots\ldots\ldots\ldots\ldots(11)$$

$$\alpha_2 = e^{-\frac{n}{n+1}\left(\frac{3+\sqrt{5+\frac{4}{n}}}{2}-1\right)} \cdot \left(\frac{3+\sqrt{5+\frac{4}{n}}}{2}\right)^{\frac{n}{n+1}} \quad \ldots\ldots\ldots\ldots(12)$$

$$\beta_1 = \left(\frac{3-\sqrt{5+\frac{4}{n}}}{2}\right)^{\frac{1}{n+1}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(13)$$

$$\beta_2 = \left(\frac{3+\sqrt{5+\frac{4}{n}}}{2}\right)^{\frac{1}{n+1}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(14)$$

All these equations show that α_1, α_2, β_1 and β_2 are all independent of a, and dependent only on n; in other words, when n is constant, the greater the value of a, the smaller $t_{\text{max.}}$ and the larger $w_{\text{max.}}$ from the equations (4) and (5), that is the greater the value of a, the higher the height of the graphitization curve, and the narrower the width of the curve, but the value of α_1, α_2, β_1, and β_2 remains always invariable.

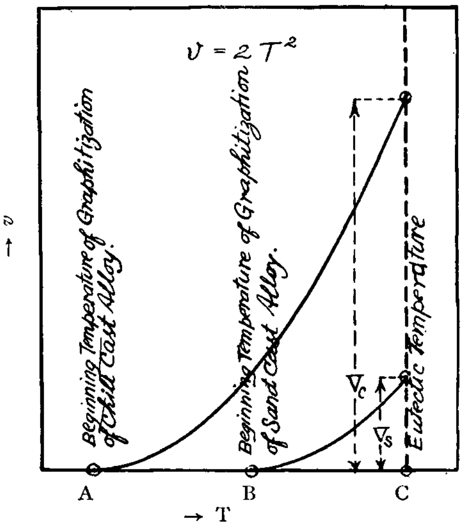
As regards the graphitization curves of white cast irons having cementite as the principal constituent to be graphitised found in the experiments mentioned in the previous part, as the values of α_1, α_2, β_1 and β_2 vary in a narrow range, the present writer believes that it will not cause a great error even if he treats their graphitization velocity considering n as constant and equal to 2 in equation (1).

Then, comparing the height of their graphitization curves given in the previous part, the relative value of a can be estimated.

Thus the present writer could obtain a general idea that the elements which favour the graphitization of white cast iron make a great, and the elements having an effect against the graphitization of white cast iron make a small.

It is also interesting to find that the solidification velocity of white cast iron having silicon has little effect on a and n, because the form of the graphitization curves of the chill cast alloys are almost similar to those of the sand cast alloys having the same composition as the former, though the height of the former is higher than that of the latter as shown in

Fig. 58.



V_C=Graphitization Velocity of Chill Cast Alloy at Eutectic Temperature.
V_S=Graphitization Velccity of Sand Gast Alloy at Eutectic Temperature.

Figs. 45 to 47, as the amount of the temper carbon produced in the chill cast alloys is greater than that of the sand cast alloys having the same composition as the former. Then it is also found that the graphitization velocity of the chill cast alloys is far greater than that of the sand cast alloys having the same composition as the former at their eutectic temperature as graphically shown in Fig. 58.

It is also evident that the difference in the graphitization velocity at eutectic temperature of these two kinds of cast irons becomes more remarkable when their silicon content is higher, since the difference in the beginning temperature of graphitization of these two kinds of cast irons becomes more remarkable when their silicon content is the higher, as shown before.

Next, the present writer will discuss the graphitization velocity of cast iron in cooling at a constant rate.

As later mentioned, the present writer believes that in most practical cases the graphite is formed under the same mechanism as in the case of the formation of temper carbon. Hence the case under discussion can be treated in the same manner as in the former case.

The graphitization velocity-temperature or the graphitization velocity–time equation in this cace is given as follows:

$$\left.\begin{array}{l} v = \dfrac{V}{b^n}\,(b-t)^n \\ v = \dfrac{V}{b^n}(b-kT)^n \end{array}\right\} \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (15)$$

where

$v =$ graphitization velocity,

$V =$ graphitization velocity at eutectic temperature,

$b =$ time required for cooling from eutectic temperature to the beginning temperature of graphitization of cementite in cast iron, or temperature difference between eutectic temperature and the beginning temperature of graphitization of cementite in cast iron,

$n =$ positive and real number,

under the following assumptions:

(1) The cooling velocity of cast iron is constant.

(2) The formula (1) exists independently of the heating rate of white cast iron.

Then the relation between the amount of cementite and cooling time or temperature is expressed by the following equation:

$$\left.\begin{aligned} m &= e^{\frac{V}{(n+1)b^n}\left\{(b-t)^{n+1}-b^{n+1}\right\}} \\ m &= e^{\frac{V}{(n+1)b^n}\left\{(b-kT)^{n+1}-b^{n+1}\right\}} \end{aligned}\right\}\quad\cdots\cdots\cdots\cdots(16)$$

under the following assumptions:

(1) Graphitization takes place immediately after complete solidification of cast iron.

(2) Only eutectic cementite is concerned in the graphitization, and the decrease in its amount is entirely due to the graphitization of it.

In the above equations, n can be approximately assumed to be constant and to be 2 in all cases as in the former case.

Fig. 59

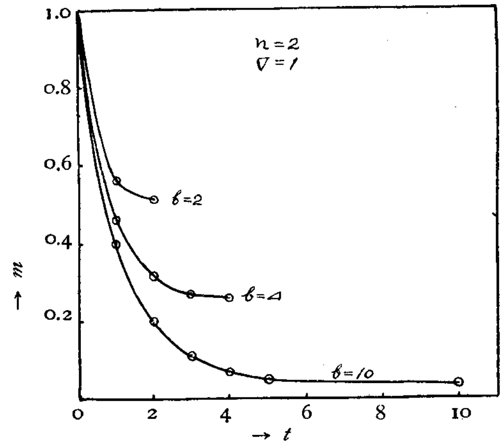


Fig. 61

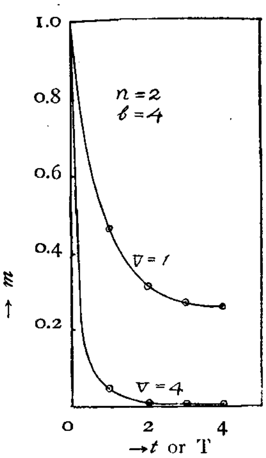
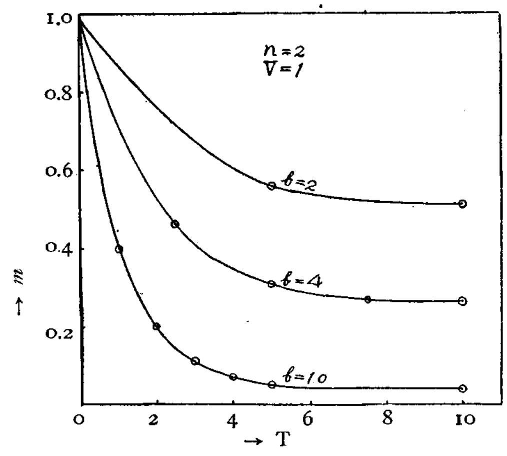


Fig. 60



Then if we assume V to be constant, the relation between m and t or T is shown in Figs. 59 and 60. If we assume b to be constant, the relation between m and t or T is shown in Fig. 61.

These curves evidently show that most of the graphites in cast iron are produced immediately after solidification, if they are formed under the probable assumptions above given.

B. Graphitization degree of cast iron.

The graphitization degree of cast iron can be generally expressed by the percentage of graphite or temper carbon for the amount of total carbon in cast iron.

As regards white cast iron, its graphitization degree greatly depends on the beginning temperature of graphitization and the graphitization velocity.

The minimum amount of cementite which remains undecomposed in cast iron cooled at a constant rate can be mathematically expressed by the following equation:

$$m_{min.} = e^{-\frac{Vb}{n+1}} \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(17)$$

If n is constant as before mentioned, we have

$$m_{min.} = e^{-k''Vb} \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(17)'$$

where

k''=constant independent of composition and of the cooling velocity of cast iron.

From the equation (17)', $m_{min.}$ depends on the product of V and b. Therefore, the form of the curve expressed by equation (16) changes as the value of V or b varies, even though $m_{min.}$ or the value of $V.b$ remains constant. Figs. 62 and 63 show the relations.

Fig. 62.

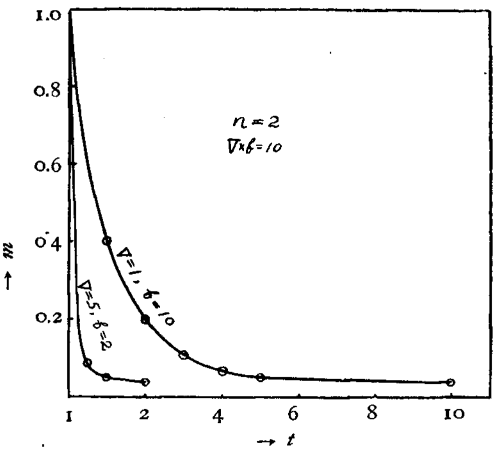
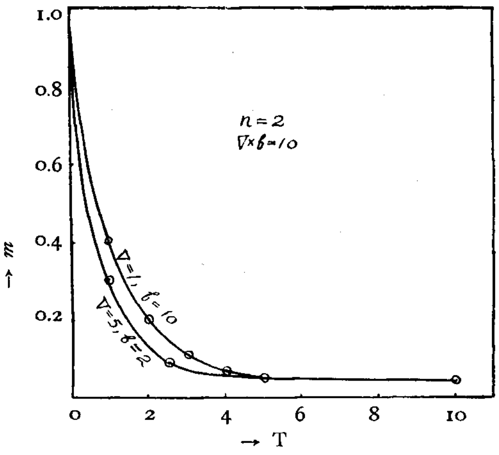


Fig. 63.



Of course, in practical cases, really the decomposition of cementite at high temperature may accompany many complex chemical changes. Hence, in order to investigate the actual phenomena of graphitization in cast iron in cooling, these chemical changes must be taken into consideration under the fundamental principles as given in formulas (16) and (17).

C. Summary.

The results so far obtained may be summarised as follows:

(1) Under the probable assumptions, the graphitization velocity of white cast irons having cementite as the principal constituent to be graphitised, which was heated at a constant rate was mathematically discussed.

(2) The graphitization velocity of these white cast irons can be expressed approximately by the following general formula:

$$v = at^n \text{ or } v = ak^n T^n$$

(3) It was found that n, in the above formula, could probably be considered as constant, which was independent of the chemical composition, and as 2, and a as variable.

(4) The solidification velocity of cast irons having silicon as the principal impurity is independent of n and a in the above formula. But the graphitization velocity at eutectic temperature of the quickly solidified cast iron is greater than that of the slowly solidified cast iron having the same composition as the former.

(5) The difference in the temperature above mentioned is more remarkable when the silicon content of the alloys is high.

(6) Under the probable assumptions, the graphitization velocity of cast iron in cooling was mathematically expressed.

(7) Under the probable assumptions, it was found that the amount of cementite remaining undecomposed in cast iron depends on the product of the graphitization velocity of cast iron at its eutectic temperature, and the time required for cooling from eutectic temperature to the beginning temperature of the graphitization of cementite in cast iron.

(8) The graphitization degree of white cast iron greatly depends on the

beginning temperature of graphitization and the graphitization velocity.

§ III. MECHANISM OF GRAPHITIZATION.

As regards the mechanism of graphitization taking place during the cooling of cast iron, many investigators maintain the view that the graphite always results from the breaking up of cementite, soon after its solidification, owing to its instability.

Recently, Honda and Murakami[1] published the same opinion. According to thir theory, however, the formation of graphite is not a direct decompositon of cementite but is due to a catalytic action of some gases.

On the other hand, other investigators believe that the graphite is a product directly separated from the melt. Especially Ruer and F. Goerens[2] experimentally found that in the pure iron and carbon system the eutectic temperature in a stable system was 7 °C higher than that in a metastable system. Tawara and Asahara[3] published an hypothesis on the direct precipitation of graphite from melt as follows:

"It is generally accepted that carbon exists as cementite in the molten iron-carbon alloys. It is probable that cementite, being a compound, may dissociate in the molten state into Fe and C, even though the amount of the dissociation may be small. The free carbon atoms may serve as the kernels for the graphitization when the condition is favorable for it. .... The deposition of the dissociated carbon out of the molten system will bring the further dissociation of the molten cementite, as a general rule, in order to secure the equilibrium. This process is repeated and graphite crystals are developed."

As regards the mechanism of the formation of temper carbon, there are also two theories just the same as in the above case. Most investigators, considering temper carbon as a product directly separated from austenite,

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[1] Sci. Rep. Tohoku Imp. Univ. 10, (1921), 273.

[2] Ferrum. (1916/17), 161.

[3] Journ. College Engg. Tokyo Imp. Univ. 9, (1918), 196.

explain the mechanism of its formation by Howe's solid sublimation theory.[1]

The solubility of austenite for carbon in pure iron-carbon alloy was investigated already in 1911 by Ruer and Iljin[2] and afterwards Ruer and Biren[3] found that in pure iron-carbon alloy the eutectoid temperature in a stable system is 12 °C higher than that in a metastable system. Recently Schwartz and his associates[4] studied the stable equilibrium diagram for iron-carbon alloy having 1.2 per cent of silicon, and furthermore investigated the effect of silicon on stable eutectoid in the iron-carbon-silicon alloy. They considered the solid solution of the stable system as a different phase from that of the metastable system and proposed the name "boydenite" for it. They suggested that boydenite is a solid solution of carbon, and austenite a solution of cementite. Thus from this new point of view, they explained the mechanism of graphitization as follows:

"The process is initiated by the separation of a graphite nucleus possibly due to carbon precipitated out by some local conversion of austenite into boydenite and excess carbon. The bulk of the solid solution, however, remains austenitic and maintains its carbon concentration by dissolving cementite.

More carbon precipitates and more cementite dissolves until the latter is used up.................... ."

But it seems to need further proofs for the conclusive determination of the existence of boydenite.

The present writer will treat on this subject from the results hitherto mentioned.

A. Mechanism of the formation of temper carbon.

Here, the mechanism of the transformation from carbon in cementite to temper carbon will be discussed.

The stability of cementite in cast iron or in an isolated state was

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1) Howe: The Metallography of Iron and Steel. (1916), 196.
2) Met. 8,(1911), 97.
3) Z. an. Chem. 113,(1920), 98.
4) Trans. amer. Inst. Min. Met. Eng. 68,(1923), 916.
Ditto. 69,(1923), 791.

experimentally confirmed to vary with the composition, and the solidification velocity, of cast iron. Unstable cementite in cast iron decomposes until the temperature of cast iron reaches its Ac_1, according to the chemical formula:

$$Fe_3C = 3Fe + C.$$

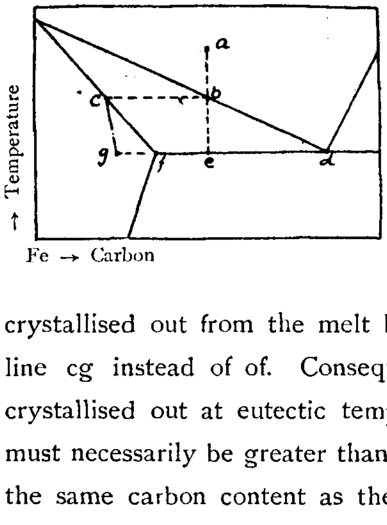
Therefore, the cementite in cast iron should also decompose at a temperature higher than the Ac_1 of the cast iron independently of austenite.

The present writer will prove the possibility of this case from various directions.

(1) Figs. 46 and 47 and Table 23 evidently show that the amount of temper carbon produced in the completly graphitised chill cast alloys is far greater than that in the completely graphitised sand cast alloys having the same composition as the former.

Fig. 64 shows the metastable equilibrium diagram of pure iron-carbon alloy. When the melt having the composition a is slowly cooled, austenite having the composition c is crystallised out of the melt at temperature b. Further slow cooling of the alloy results in more precipitation of austenite, the mean composition of which changes along the line c f. But if the melt be quickly cooled, the mean composition of the austenite crystallised out from the melt below temperature b will change along the line cg instead of of. Consequently, the amount of the eutectic cementite crystallised out at eutectic temperature in quickly cooled white cast iron must necessarily be greater than that in slowly cooled white cast iron having the same carbon content as the former.

Fig. 64.



Now if we assume that the total free cementite or a part of it in such cast irons decomposes by annealing, the amount of the resulting temper carbon in the completely graphitised chill cast alloy should be greater than that in the completely graphitised sand cast alloy. On the contrary, if temper carbon is produced after the solid sublimation theory, the amount of temper carbon in both kinds of alloys completely graphitised must be practically equal, because in this case it is the instant at which the equilibrium state is secured between austenite and carbon in the alloy when it is completely graphitised, and also the carbon content of austenite in equilibrium with carbon in cast iron having the same composition is constant at a definite temperature.

The results of the present writer evidently show the correctness of the first assumption.

(2) Chill cast white cast irons having the compositions given in Table 31 were heated in vacuo at a constant heating rate 5 °C per min. up to the end temperature of graphitization and then quenched in water.

Table 31.

Specimens No.	Composition (%)			Quenching Temperature (°C)	Combined C. in annealed Specimen (%)
	C	Si	Other Impurities		
1	3.48	1.34	Minute	1,000	0.30
2	3.43	1.36	Minute	1,000	0.24
3	3.46	1.59	Minute	950	0.21
4	3.41	1.71	Minute	950	0.08
5	3.45	2.00	Minute	900	0.01
6	3.41	2.45	Minute	860	0.06
7	3.42	2.72	Minute	840	0.02
8	3.42	2.73	Minute	800	0.01

The amount of the combined carbon in the graphitised alloys was found as given in the same table.

The results show that the amount of the combined carbon in question is far less than that of the stable eutectoid found by Schwartz.[1] Assuming that his results are reliable, the fact evidently leads to the conclusion that the total temper carbon or a part of it was produced by decomposition of cementite. Because, if the total temper carbon was precipitated from austenite, the carbon content of austenite in equilibrium with carbon at a temperature far higher than the stable eutectoid temperature must be greater than that of the stable eutectoid, but the fact shows the reverse.

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[1] Loc. cit.

(3) We often observe under the microscope cementite partly graphitised. An example has already been shown in Photogr. 5. Photogr. 67, another example, show the crumbled ledeburite cementites.

When cementite decomposes in cast iron, the form of the resulting temper carbon necessarily depends on that of the mother cementite, and in most cases becomes flaky. Consequently, the size and the number of temper carbon produced by the decomposition of cementite should depend on those of the latter, as before shown.

Now, the question arises whether nodular temper carbon is also a decomposition product of cementite or not.

The form of nodular temper carbon is evidently independent of that of cementite, and its size is generally far greater and its number is far less than those expected from the size and the number of cementite crystals as before shown. In order to allow an hypothesis that cementites are first decomposed to flaky temper carbons of smaller size and greater number, and in the second stage submicroscopic graphite crystals forming these flaky temper carbons accumulate to larger nodular temper carbon of few number, it must be formed under the fact that at relatively low temperature solid graphite crystal can easily migrate a relatively long distance through austenite in the solid state. But such migration of graphite crystals was found to be very difficult even at a very high temperature, in the present experiment.

Moreover, referring to other phenomena concerning graphitization, the present writer is compelled to believe that the genesis of nodular temper carbon is altogether different from that of the flaky temper carbon and also that the formation of the former is entirely due to the solubility difference between graphite and cementite in austenite.

Examining the mechanism of the transformation of metastable epuilibrium to the stable equilibrium of cast iron at a temperature lower than its A_1 only one process can be found, that is, the transformation is accomplished by the complete decomposition of cementite. But at a temperature higher than its A_1 the following three processes are found:

(1) Cementite is first decomposed to iron and temper carbon, and

in the second stage the former absorbs the latter to secure stable equilibrium.

(2) Cementite is first dissolved in austenite, and then the excess carbon in austenite is precipitated as temper carbon to secure stable equilibrium.

(3) The processes described under (1) and (2) proceed simultaneously.

For convenience, the present writer proposes the name "decomposition graphitization" for the mechanism of graphitization taking place under process (1) and "precipitation graphitization" for that taking place under process (2).

The precipitation of carbon from austenite should be stimulated by the presence of carbon nuclei.

The present writer believes that the graphite crystals produced by decomposition graphitization act as kernels, because the composition of white cast iron has a relation to the stability of cementite in cast iron and the readiness of the precipitation graphitization changes parallel with the stability of cementite. Therefore, theoretically speaking, decomposition graphitization should always accompany precipitation graphitization. Thus, the form of the resulting temper carbon should be defined by the relative relation between the graphitization velocity of these two kinds of graphitization. When the velocity of decomposition graphitization is greater than that of precipitation graphitization, the resulting temper carbon becomes flaky, and in the reverse case nodular temper carbon is produced. When the velocity of both forms is almost equal partly flaky and partly nodular temper carbon as shown in Photogr. 25 should be produced.

The relative relation between the velocity of these two kinds of graphitization depends on various factors - composition of cast iron, temperature, etc.

Next, the present writer will briefly touch on the mechanism of the formation of graphite from the results hitherto obtained in the present experiments.

When molten cast iron (hypoeutectic alloy) supercools to a temperature between the stable eutectic temperature F' and metastable eutectic temperature F, carbon may be precipitated out from the melt as graphite crystals. When the melt furthermore supercools under F, both cementite and carbon may be crystallised out of the melt simultaneously. In this case the velocity of the crystallization of cementite is very great, and cementite should begin to decompose as soon as it crystallises out of the melt.

The precipitation of carbon from the supercooled melt, on the contrary, between F and F′ is very difficult, and it seems to begin to proceed making graphite crystals, probably produced by decomposition of cementite as kernel when the melt supercools under F. Thus precipitation graphitization may proceed owing to solubility difference between graphite and cementite in the melt.

After complete solidification, of course, the mechanism of graphitization in the solid state should be just the same as in the case of the formation of temper carbon. The form of graphite depends on the mechanism of graphite formation. When the velocity of decomposition graphitization is greater than that of precipitation graphitization flaky graphite should be formed, and in the reverse case nodular graphite, as shown in Photogr. 63, should be produced. Since the most graphite crystals are produced at high temperature, neighbouring the eutectic temperature as before mentioned, they can collect themselves together into a well defined flaky mass under the strong action of the surface tension of austenite.

The graphite crystals which may be precipitated from the melt or those which should be produced in the melt by the decomposition of cementite probably also accumulate at last in the grain boundary of austenite, resulting in a flaky mass of graphite.

Though, theoretically speaking, graphite may be produced (1) primarily from the melt, (2) by solid sublimation of carbon, (3) by the decomposition of cementite, or (4) by the combined action of these processes, the mechanism of the formation of flaky graphites in most of the practical cases can be satisfactorily explained by the mechanism of decomposition graphitization.

B. Explanation of the effect of elements on the graphitization in cast iron.

The chief effect of elements on the graphitization in cast iron are considered as follows:

(1) The stability of cementite in cast iron or in the isolated state depends on the composition of cast iron and its solidification velocity as before shown. The theory of this phenomena has not yet been definitely shown. But if we assume that cementite may contain elements as a solid solution, various phenomena of graphitization can be simply explained. Indeed, cementite dissolving various elements has been found by other investigators in ternary alloys based on the iron-carbon system e. g. iron-carbon-tungsten alloy,[1] iron-carbon-manganese[2] alloy.

Under the above assumption, it is probable that the amount of the element dissolved in cementite increases up to the solubility limit of cementite as its content in cast iron increases. Therefore, some elements should show a limited effect on the beginning temperature of the graphitization of cementite, that is, of cast iron as experimentally shown in the previous part.

(2) In cast iron containing some element, total carbon or a part of it may appear in a combined state different from cementite. Some element may also affect the amount of cementite and the carbon containing substance different from cementite, if it is formed. Owing to the existence of the latter, graphitization in cast iron may be favoured or hindered.

Such examples have been shown already in cast iron having silicon or aluminium.

C. Explanation of the effect of cooling rate on the graphitization in cast iron containing silicon.

In the previous paragraph, the present writer has experimentally shown the fact that the solidification velocity of cast iron has a remarkable effect on the stability of the cementite in it. If the conception that cementite

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1) Loc. Cit.
2) Loc. Cit.

in cast iron contains other element is true, the phenomena above given may be explained as follows:

In pure hypoeutectic iron–carbon alloy, the amount of eutectic increases up to a certain limit as the solidification velocity of cast iron increases, but the composition of the eutectic does not depend on the solidification velocity. On the contrary, in cast iron having another element the composition of the eutectic generally varies with the variation of the amount of the eutectic. Accordingly, the amount of the element dissolved in eutectic cementite, and consequently the stability of eutectic cementite, should generally vary with the solidification velocity of cast iron.

The structure of the cast iron solidified with a greater solidification velocity is, of course, finer than that of the cast iron solidified with a less solidification velocity, as shown in Photogrs. 49 and 50. But such degree of difference in the apparent fineness of structure produced by the variation of the solidification velocity of cast iron probably does not have a remarkable relation to the above phenomena.

Next, the present writer will discuss the combined effect of the solidification velocity and the cooling velocity after the solicification of cast iron on its graphitization.

Photogr. 68 shows the fracture of a cast iron pipe in the cast state made by the de' Lavaud's centrifugal casting process. The chilled portion (a) is white, the next portion (c) black and the inner portions (d) and (e) have gray fractures. The distribution of the various elements in the outer portions, (a) and (c), and the inner portions, (d) and (e), is shown in Table 32.

Table 32.

Position	Composition (%)							
	Total C	Graphite C	Combined C	Si	Mn	P	S	Cu
Outer Parts (a)+(b)+(c)	3.75	3.45	0.30	2.43	0.29	0.160	0.075	0.160
Inner Parts (d)+(e)	3.79	3.15	0.64	2.46	0.29	0.139	0.071	0.170

Photogrs. 69 to 73 show the structure of various portions. The above table and these photographs evidently show that in (a), the cooling velocity of which is geatest, most of the carbon exists in a combined form, and in (e), the cooling velocity of which is least, most of the carbon exists as large flaky graphites. It is interesting to find that most of the carbon exists as minute graphite flakes in (c), the cooling velocity of which is intermediate between those of (a) and (d), in which even the minute islets of free cementite remains undecomposed in a pearlitic matrix.

The last fact is contrary to our general conception that graphitization takes place more completely as the cooling velocity of cast iron is less.

Recently Schüz[1] and Hamazumi[2] investigated the same phenomena. Schüz considered that graphites as shown in Photogr. 71 were produced directly from the melt as eutectic graphites. Hamazumi explained the above phenomena by Honda and Murakami's theory of graphitization before referred to, and considered that the graphites as shown in Photogr. 71 were produced by the decomposition of cementite under the catalytic action of the gases contained in cast iron.

The above phenomena is evidently due to the difference in the cooling velocity of each portion along the thickness of the pipe, since the method of manufacture of the pipe has no effect on the distribution of other elements along the thickness of the pipe, as given in Table 32. The present writer will try to explain it from the results hitherto obtained in the present experiments.

Now, if we assume that graphites in cast iron are produced after equation (16), then the time required for cooling from the eutectic temperature of the alloy to the beginning temperature of graphitization of the cementite in the alloy b decreases almost linearly with the increase of v, and the solidification velocity of the alloy increases as v increases, consequently the graphitization velocity of the cast iron at eutectic temperature V decreases as v decreases, probably approaching its minimum value asymptotically. These relations are shown graphically in Fig. 65.

From formula (17)′, we know that the amount of eutectic cementite

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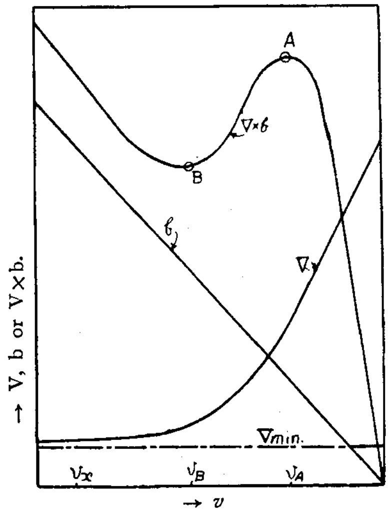
[1] Stahl u. Eisen, 45,(1925), 144.

[2] Loc. Cit.

Fig. 65.



remaining undecomposed in cast iron depends on the product of V and *b*. The relation between v and V.b can also be graphically shown in the same figure. The v–V.b curve evidently shows that it has a maximum point A at v_A and a minimum point B at v_B. In other words, as the cooling velocity of the cast iron increases, the amount of eutectic cementite remaining undecomposed decreases up to minimum, and then increases up to maximum, and afterwards again gradually decreases.

Fig. 65 shows the ideal relation between the graphitization degree of the cast iron and its cooling velocity. But when it is applied to practical cases, it should be somewhat modified since in those cases graphitization accompanies various chemical changes as summarised in Table 33 in cast iron at the same time, and the cooling velocity of cast iron also greatly affects the process of these chemical changes.

Table 33.

No.	Kinds of Change	Velocity of Change
1	$\boxed{\text{Fe}_3\text{C}}$ → [Fe] + [Graphite] Graphitization	Variable
2	$\boxed{\text{Austenite}}$ + [Fe] → [Unsaturated Austenite]	Rapid
3	$\boxed{\text{Fe}_3\text{C}}$ + [Fe] → [Saturated Austenite]	Rapid
4	$\boxed{\text{Fe}_3\text{C}}$ + [Unsaturated Austenite] → [Saturated Austenite]	Rapid
5	[Fe] + [Graphite] → [Saturated Austenite]	Slow
6	[Unsaturated Austenite] + [Graphite] → [Saturated Austenite]	Slow

☐ : Constituents originally contained.
[ ] : Resulting constituents.

As shown in Fig. 62 when the value of V.b is constant, the more rapidly graphites are produced, the more quickly cast iron is cooled.

If the value of V.b is large, in the quickly cooled cast iron, most of the eutectic cementite rapidly decomposes and afterwards only chemical reaction (2) predominates, resulting in small graphites in a ferrite matrix accompanying small amount of cementite. The carbon content of the resulting steel matrix is, moreover, diminished by the following causes:

(1) When the solidification velocity of cast iron having a hypoeutectic composition is great, a less amount of austenite having a lower carbon content and a greater amount of eutectic cementite are produced.

(2) Silicon diminishes the solubility of carbon in austenite.

In the slowly cooled cast iron, as cementite gradually decomposes, chemical changes (2), (3) and (4) proceed without reserve, resulting after all in large graphite flakes in a eutectoid matrix.

But if the cooling velocity of cast iron is far less, cast iron having large graphite flakes in a ferrite matrix accompanying a small amount of cementite may also be formed, because, as shown in Figs. 59 and 60, the less the cooling velocity, the more rapidly the graphitization occurs, if V is constant.

In short, cast iron which cools under the cooling velocity of v_A or v_X, in Fig. 65 may consist of graphites and ferrite accompanying a smaller amounf of cementite, if the value of V.b is great; cast iron which cools under the cooling velocity of v_B may consist of graphites and a steel matrix having a greater amount of cementite even in such a case.

The present writer considers the structure as shown in Photogr. 71 as produced under the cooling velocity v_A in Fig. 65, the structure as shown in Photogr. 72 as produced under the cooling velocity v_B, and the structure as shown in Photogr. 73 as produced under the cooling velocity v_X.

The phenomena under discussion should become more remarkable if the silicon content of cast iron be higher, since the difference between $V_{max.}$ and $V_{min.}$ becomes more remarkable when the silicon content of the cast iron is higher, as betore found experimentally.

The graphites as shown in Photogr. 71 are very small and intimately mixed with ferrite accompanying a small amount of cementite, so it is natural that the doubt should arise whether they are eutectic graphites separated out from the melt.

But the present writer believes that they are decomposition products of cementite from his conception of graphitization before mentioned. The fineness of their size is due to the rapid decomposition of the fine cementite crystals produced by their quick crystallization.

When chill cast white cast iron having silicon are rapidly graphitized at high temperature, a structure similar to that under disscussion can be easily obtained. Photogr. 64 shows an example.

§ IV. GENERAL SUMMARY.

The general survey of the investigation described in this part may be summarised in the following words:

(1) It has been found that the solidification velocity of cast iron having silicon has a remarkable effect on the stability of the cementite in the cast iron.

(2) It was found that the silicon content of cast iron has a remarkable effect on the stability of the cementite isolated from the cast iron. The fact that the stability of the cementite in cast iron varies with the composition of the cast iron is probably due to the stability of the cementite itself.

(3) The cementite in cast iron probably always contains an other element however small and its stability depends on the kind and the amount of the element contained in it. Thus the effect of the element and the solidification velocity on the graphitization in cast iron can be clearly explained.

(4) Temper carbon is produced by two different kinds of mechanism; that is decomposition graphitization and precipitation graphitization. The latter probably starts making carbon produced by the decomposition of cementite as kernel.

(5) The form of the temper carbon is determined by the relative

relation between the velocity of decomposition graphitization and that of precipitation graphitization. If the former is greater than the latter, the flaky temper carbon is produced, and in the reverse case the nodular temper carbon is produced.

(6) From the results obtained in the present investigation the mechanism of the formation of graphite has been briefly discussed. In practical cases, flaky graphite is the decomposition product of cementite. If graphite is produced from austenite it must be nodular.

(7) The relation between temper carbon and graphite has been studied from various directions. It is impossible to distinguish graphite clearly from temper carbon. Apparently large flaky graphite is also a mass consisting of submicroscopic graphite crystals.

(8) From the graphitization curves of white cast iron the relation between the graphitization velocity of white cast iron and the temperature has been mathematically discussed.

(9) Applying the results obtained in (8) to the graphitization of cast iron during cooling, the relation of the amount of cementite and cooling time has been found under some probable assumptions.

(10) The combined effect of the solidification velocity and the cooling velocity on the graphitization in cast iron has been discussed touching on the mechanism of the formation of the so-called eutectic graphite.

Eutectic graphite is a decomposition product of small cementite crystals which quickly crystallise out of the melt.

Acknowledgment.

In conclusion the present writer expresses his hearty thanks to Professor D. Saito under whose guidance the present work has been carried out. My thanks are also due to Dr. S. Iguchi and other gentlemen for their kindness in supplying raw materials used in the present experiments.

Fig. 8.

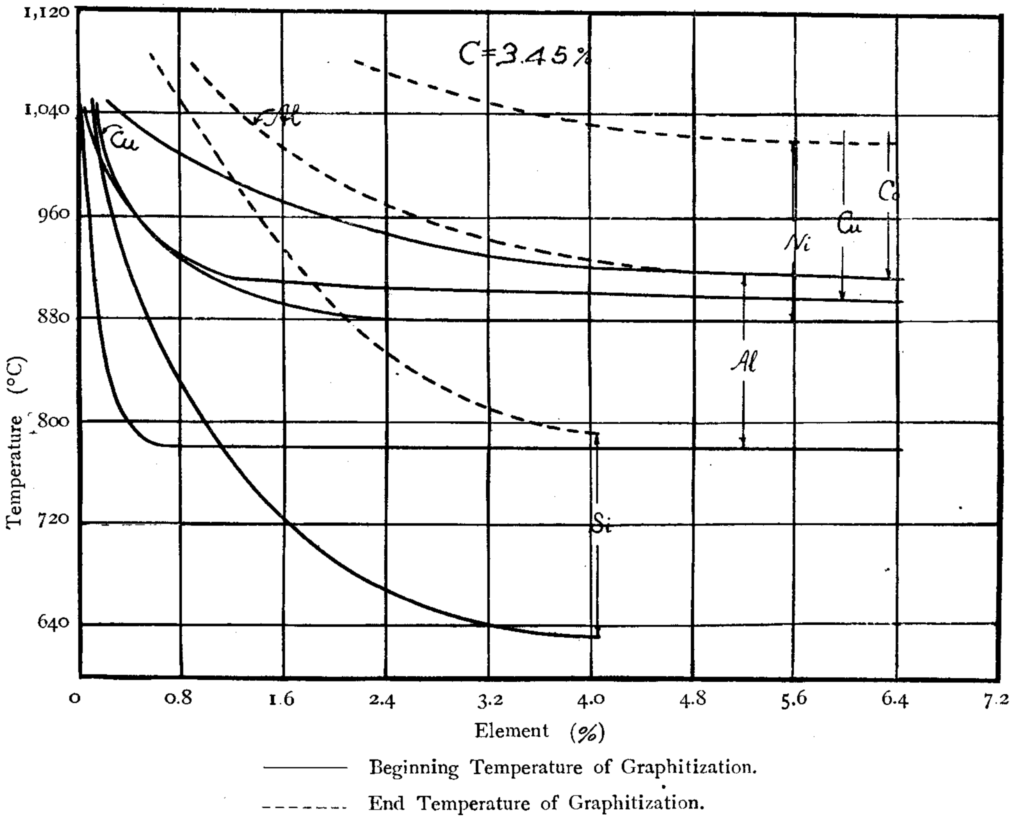

C=3.45%
Al
Cu
Ni
Cu
Co
Al
Si
1,120
1,040
960
880
800
720
640
Temperature (°C)
0
0.8
1.6
2.4
3.2
4.0
4.8
5.6
6.4
7.2
Element (%)
Beginning Temperature of Graphitization.
End Temperature of Graphitization.

Fig. 9.

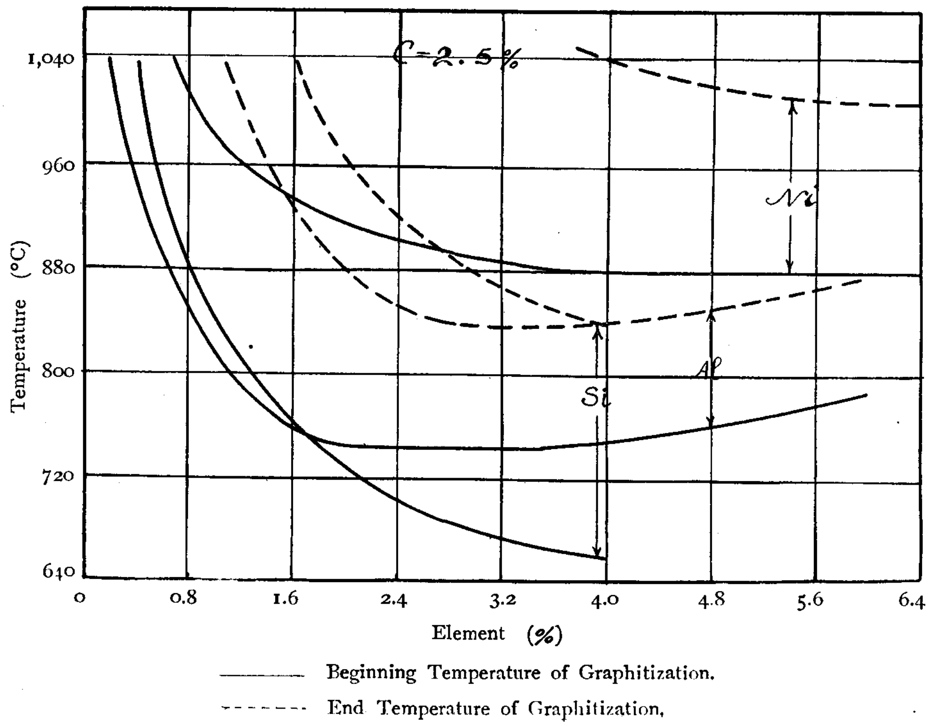
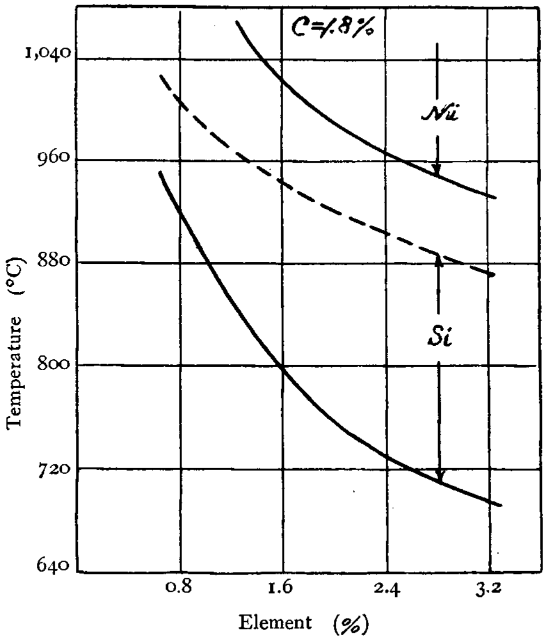

C=2.5%
Ni
Al
Si
1,040
960
880
800
720
640
Temperature (°C)
0
0.8
1.6
2.4
3.2
4.0
4.8
5.6
6.4
Element (%)
Beginning Temperature of Graphitization.
End Temperature of Graphitization.

Fig. 10.



——— Beginning Temperature of Graphitization.

- - - - - - End Temperature of Graphitization.

Fig. 11.

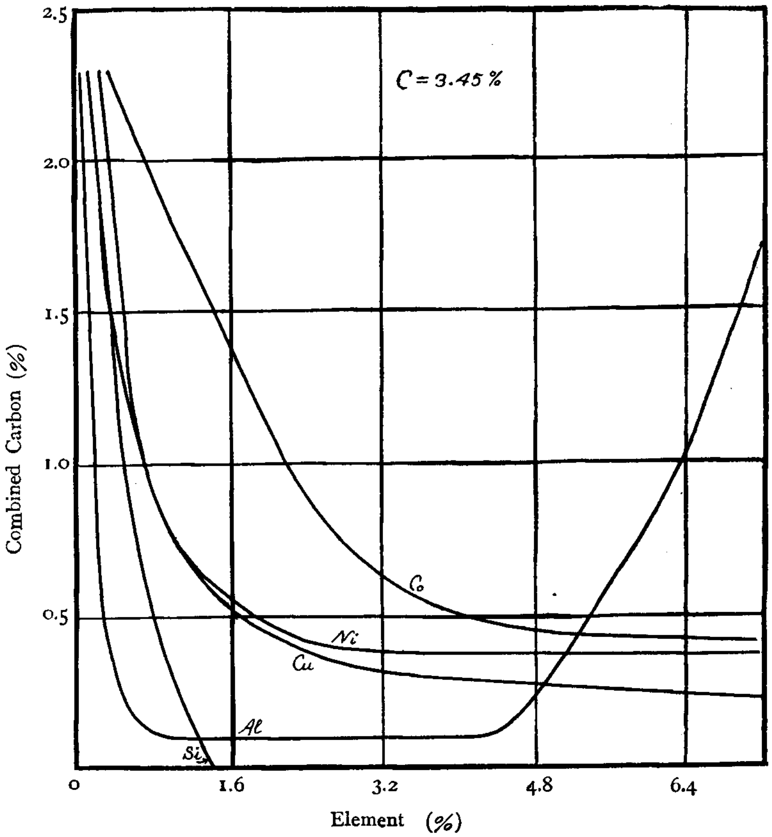


Fig. 12.

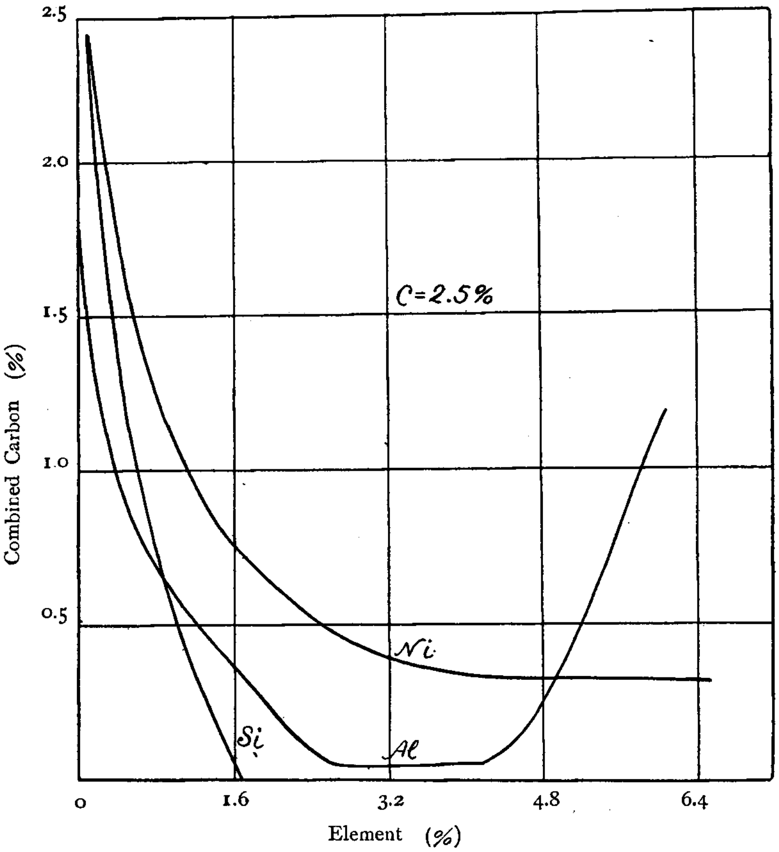

2.5
2.0
1.5
1.0
0.5
Combined Carbon (%)
C=2.5%
Ni
Si
Al
0
1.6
3.2
4.8
6.4
Element (%)

Fig. 13.

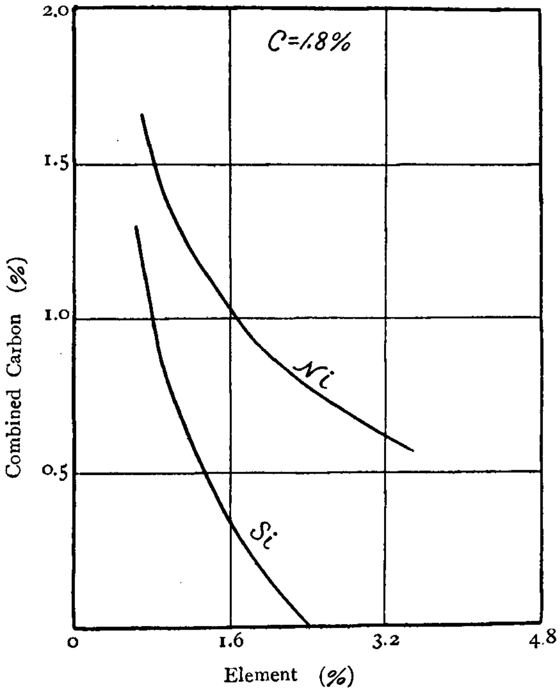

2.0
1.5
1.0
0.5
Combined Carbon (%)
C=1.8%
Ni
Si
0
1.6
3.2
4.8
Element (%)

Fig. 25

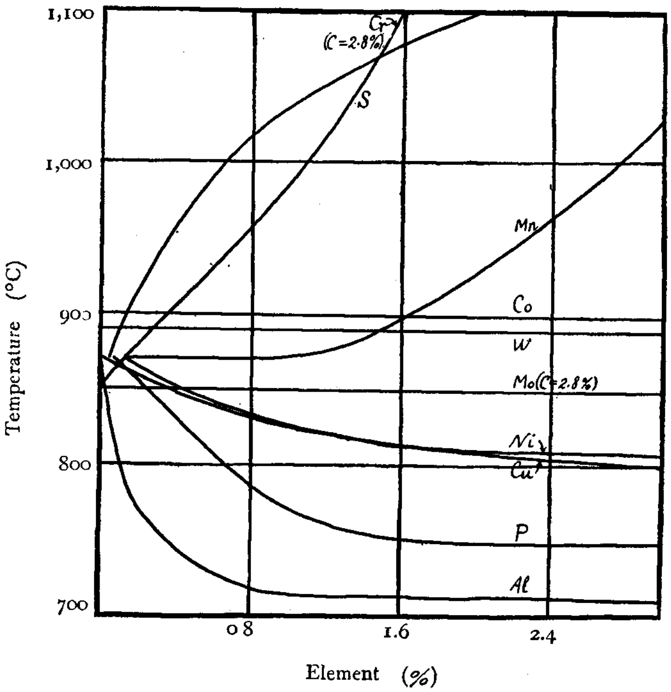
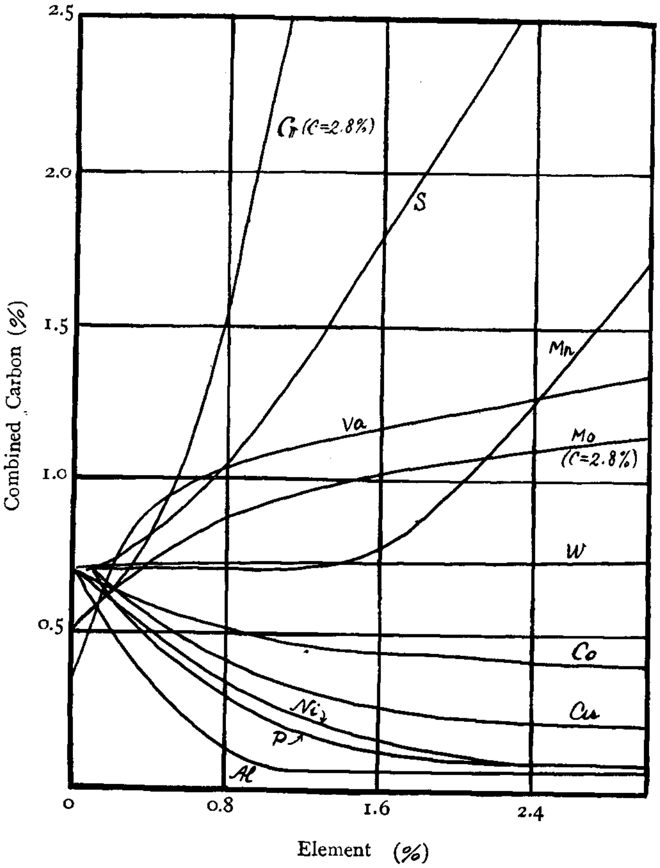
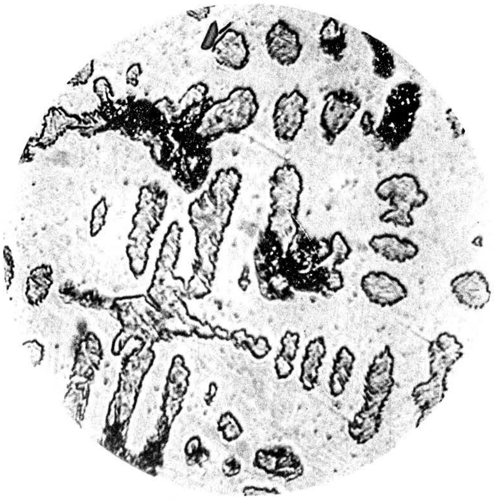

1,100
1,000
900
800
700
Temperature (°C)
G (C=2.8%)
S
Mn
Co
W
Mo(C=2.8%)
Ni
Cu
P
Al
0.8
1.6
2.4
Element (%)

Fig. 26.

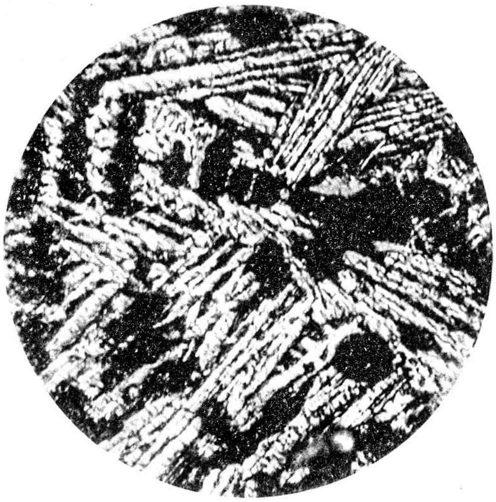

2.5
2.0
1.5
1.0
0.5
Combined Carbon (%)
G (C=2.8%)
S
Mn
Va
Mo (C=2.8%)
W
Co
Cu
Ni
P
Al
0
0.8
1.6
2.4
Element (%)

All specimens were etched with dilute nitric acid, if not specially remarked.

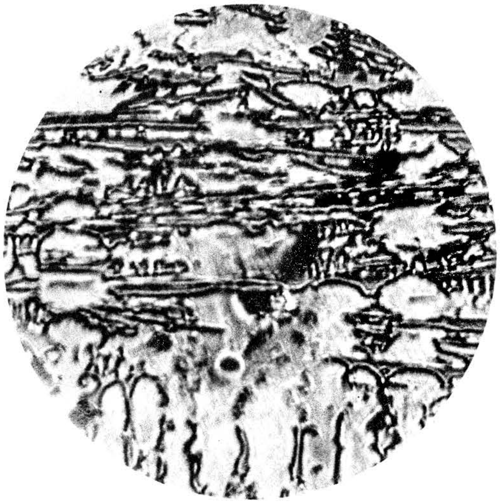
Photogr. No. 1. × 900
C=3.47%, Si=1.74%



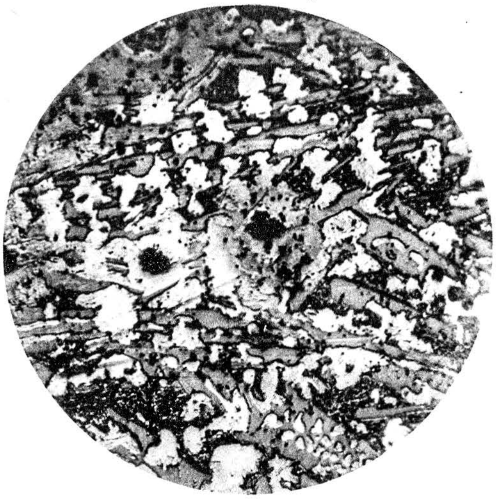
Photogr. No. 2. × 900
C=3.45%, Si=5.80%



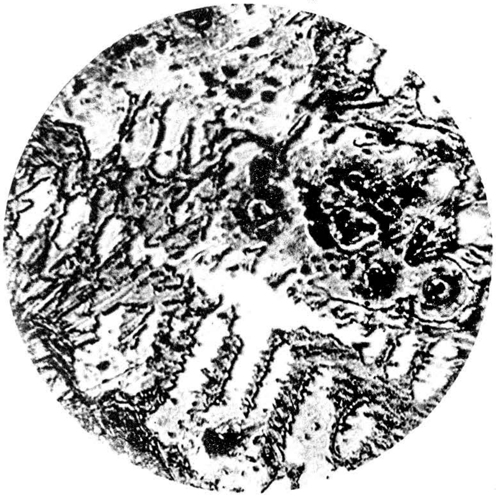
Photogr. No. 3. × 900
C=3.47%, Si=1.74%
Etched with sodium picrate



Photogr. No. 4. × 900
C=3.43%, Si=2.3%
Etched with sodium picrate

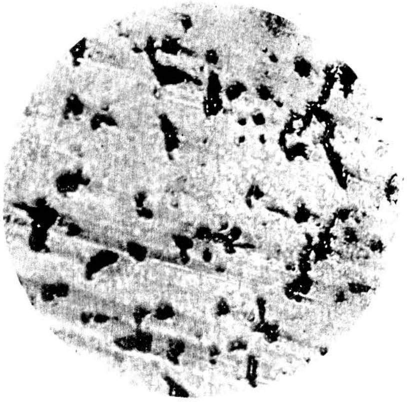


Photogr. No. 5. × 900
C=3.45%, Si=3.93%
Etched with sodium picrate



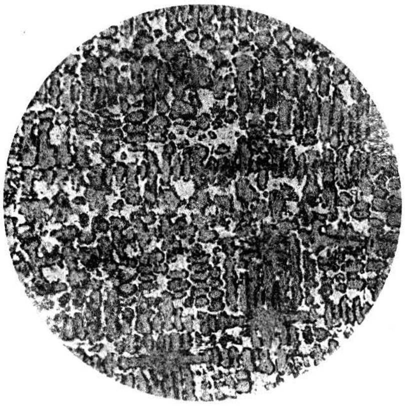
Photogr. No. 6. × 900
C=3.45%, Si=5.80%
Etched with sodium picrate

Pl. VI.



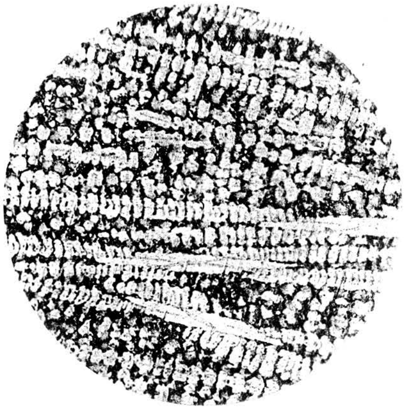
Photogr. No. 7. × 450
C=3.49%, Si=1.05%

Photogr. No. 8. × 300
C=3.69%, Al=2.90%



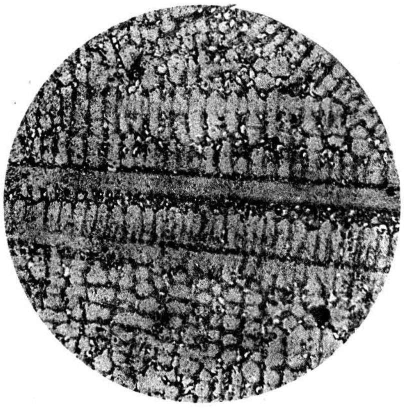
Photogr. No. 9. × 300
C=3.54%, Al=4.22%

Photogr. No. 10. × 300
C=3.48%, Al=6.89%

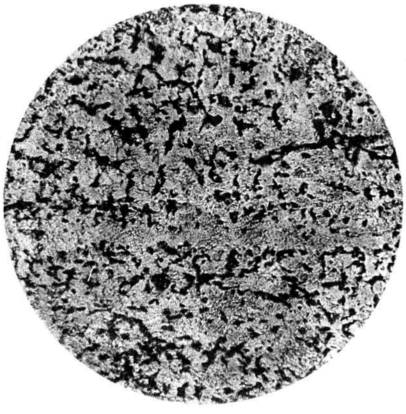


Photogr. No. 11. × 300
C=3.43%, Al=8.82%

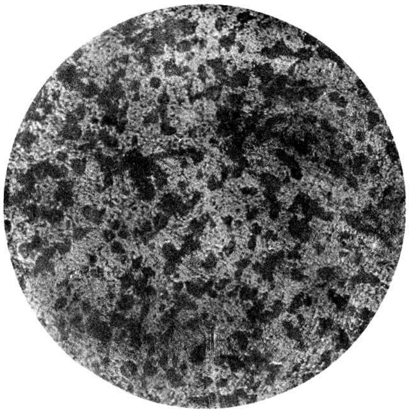
Photogr. No. 12. × 300
C=2.83%, Al=10.09%



Photogr. No. 13. × 300
C=2.34%, Al=9.68%



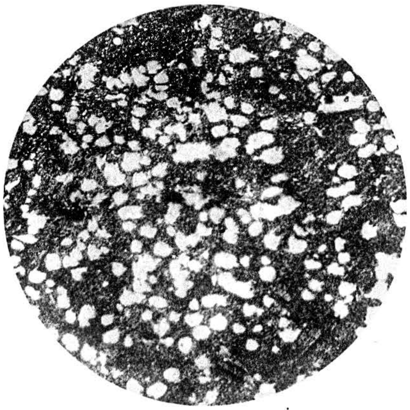
Photogr. No. 14. × 300
C=3.43%, Al=1.23%



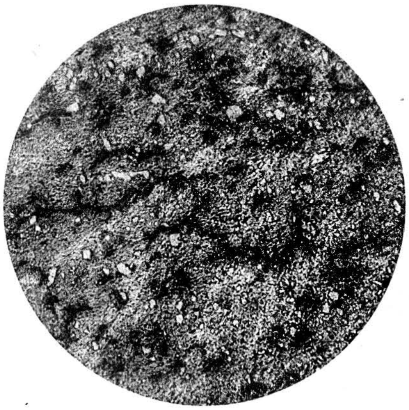
Photogr. No. 15. × 300
C=3.54%, Al=4.22%

Pl. VII.

Photogr. No. 16. ×300
C=3.49%, Ni=6.44%

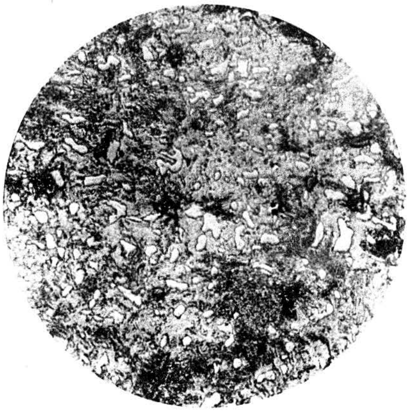


Photogr. No. 17. ×300
C=3.43%, Ni=0.49%

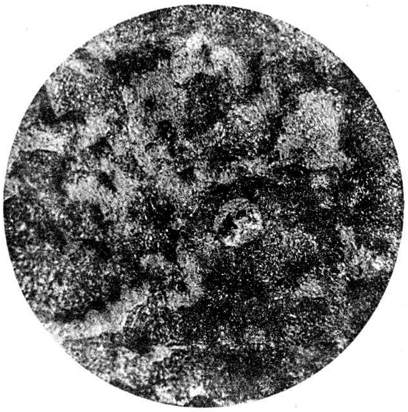


Photogr. No. 18. ×300
C=2.50%, Ni=2.90%

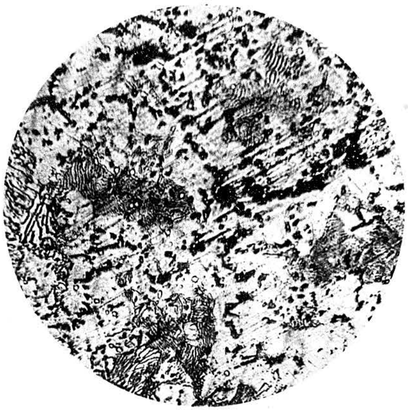
Photogr. No. 19. ×450
C=3.45%, Cu=2.09%



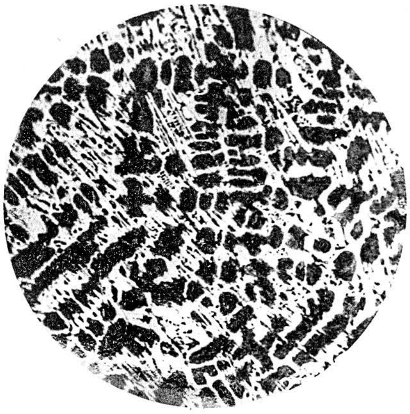
Photogr. No. 20. ×300
C=3.43%, Cu=0.60%



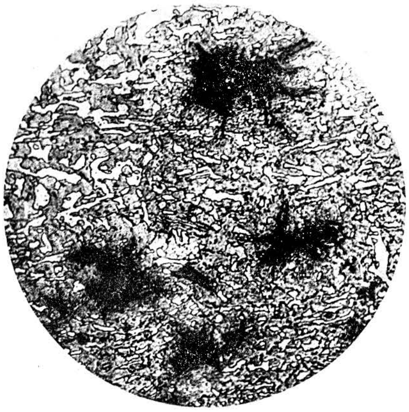
Photogr. No. 21. ×300
C=3.41%, Cu=2.67%



Photogr. No. 22. ×300
C=2.50%, Si=0.82%, Cu=1.78%



Photogr. No. 23. ×300
C=3.28%, Co=7.46%

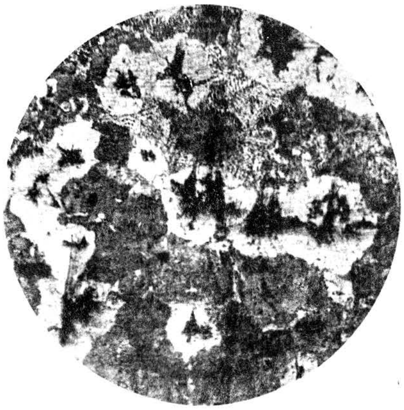


Photogr. No. 24. ×300
C=3.45%, Co=1.33%

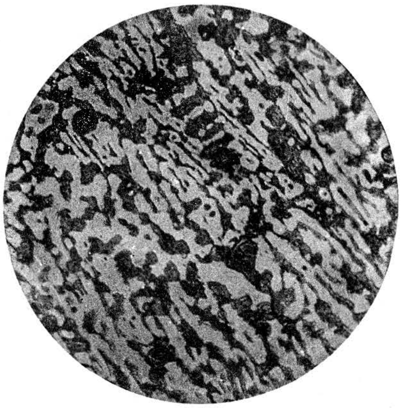
Pl. VIII.

Photogr. No. 25. ×150
C=3.28%, Co=7.46%

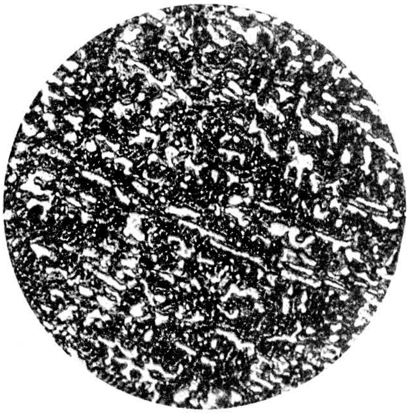
Photogr. No. 26. ×300
C=2.48%, Si=0.94%, Co=0.05%



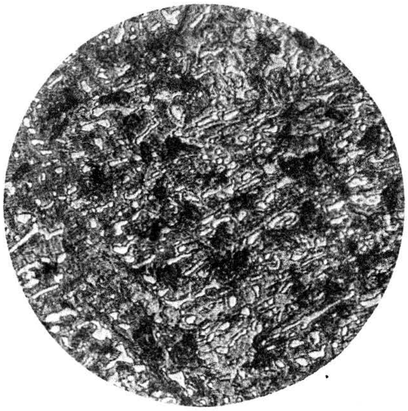
Photogr. No. 27. ×150
C=2.33%, Si=0.77%, Co=3.37%



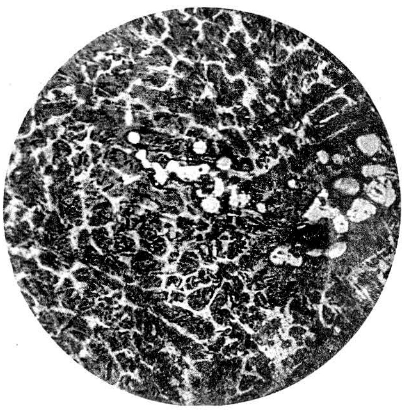
Photogr. No. 28. ×300
C=3.45%, Si=0.12%



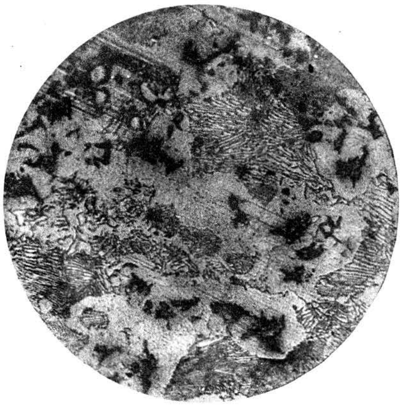
Photogr. No. 29. ×300
C=3.43%, Si=0.10%, Pt=1.03%



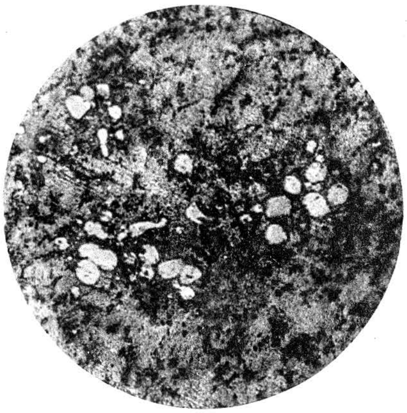
Photogr. No. 30. ×300
C=3.45%, Si=0.12%, Au=2.19%



Photogr. No. 31. ×300
C=2.56%, Si=1.32%, Ti=1.71%

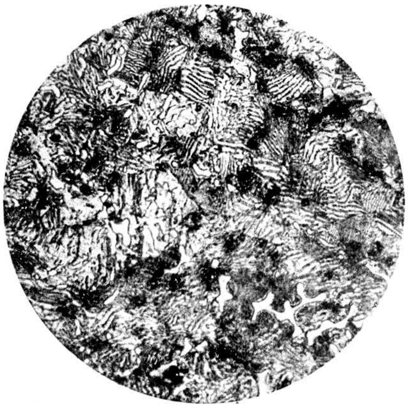


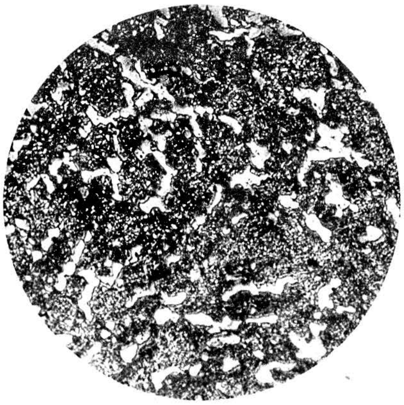
Photogr. No. 32. ×300
C=2.46%, Si=0.95%, Ti=0.44%

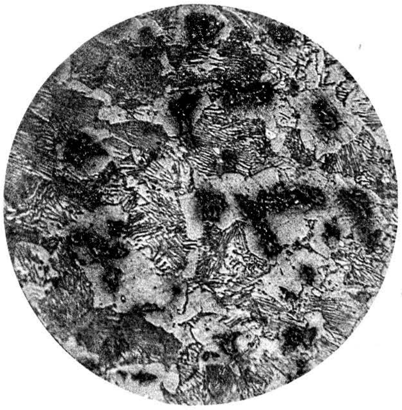


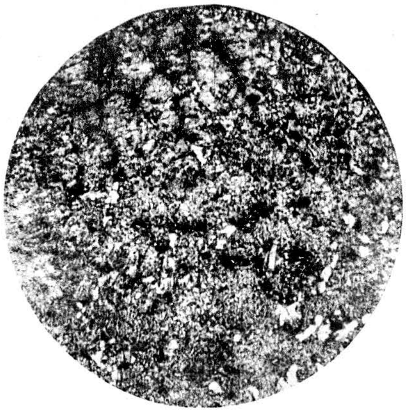
Photogr. No. 33. ×300
C=2.56%, Si=1.32%, Ti=1.71%

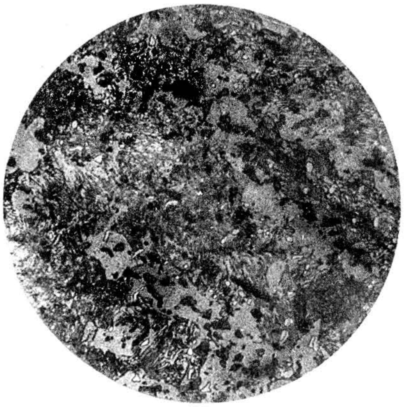
Pl. IX.

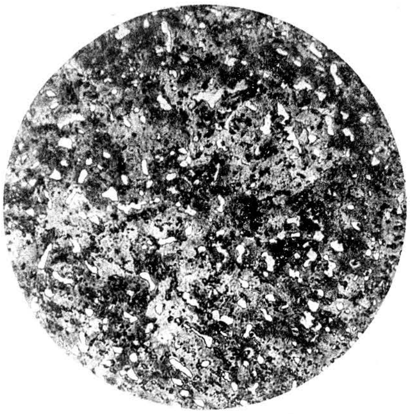

Photogr. No. 34. ×400
C=2.37%, Si=0.88%, Cr=0.26%


Photogr. No. 35. ×400
C=2.41%, Si=0.89%, Cr=0.70%

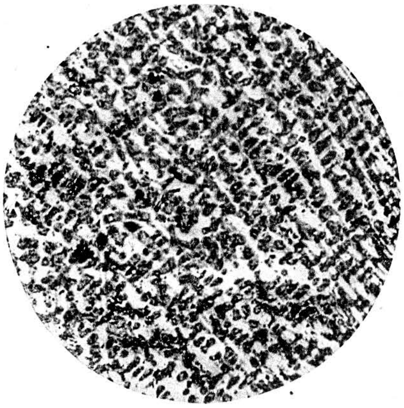

Photogr. No. 36. ×300
C=2.31%, Si=0.74%, W=0.01%


Photogr. No. 37. ×300
C=2.31%, Si=0.73%, W=3.65%


Photogr. No. 38. ×300
C=2.80%, Si=0.81%, Mo=0.46%

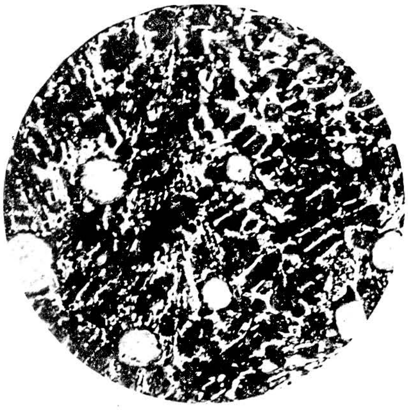

Photogr. No. 39. ×300
C=2.78%, Si=0.80%, Mo=3.14%


Photogr. No. 40. ×300
C=2.31%, Si=1.45%, Va=3.98%


Photogr. No. 41. ×300
C=2.55%, Si=0.83%, P=2.55%

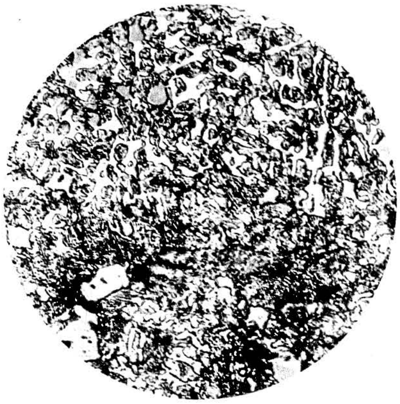

Photogr. No. 42. ×300
C=2.63%, Si=0.80%, P=0.69%

Photogr. No. 43. × 300
C = 2.55%, Si = 0.83%, P = 2.55%



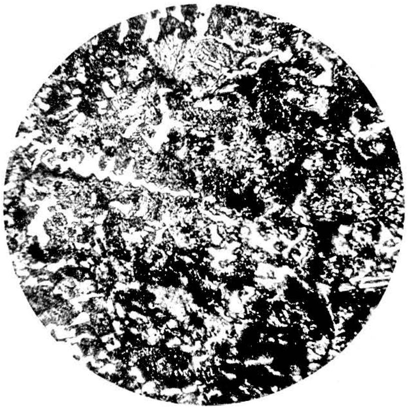
Photogr. No. 44. × 300
C = 2.49%, Si = 0.78%, S = 2.41%

Photogr. No. 45. × 300
C = 2.58%, Si = 0.80%, S = 0.50%

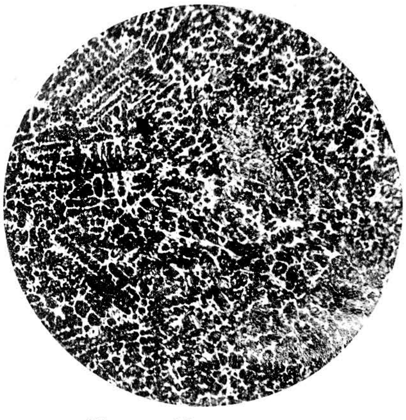


Photogr. No. 46. × 300
C = 2.71%, Si = 0.80%, S = 1.85%

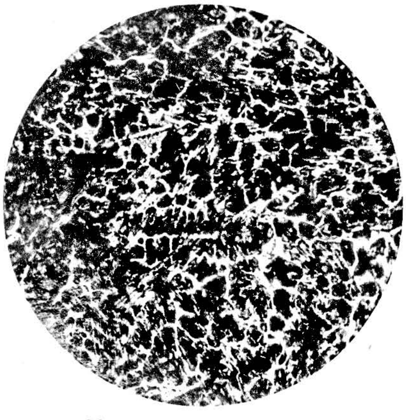
Photogr. No. 47. × 300
C = 2.91%, Si = 0.79%, Mn = 1.77%



Photogr. No. 48. × 300
C = 2.53%, Si = 0.83%, Mn = 2.72%

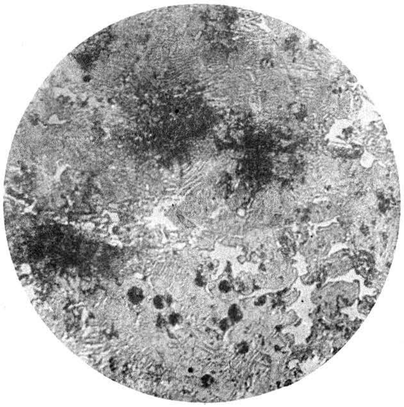


Photogr. No. 49. × 130
C = 2.29%, Si = 1.10%
Chill cast.

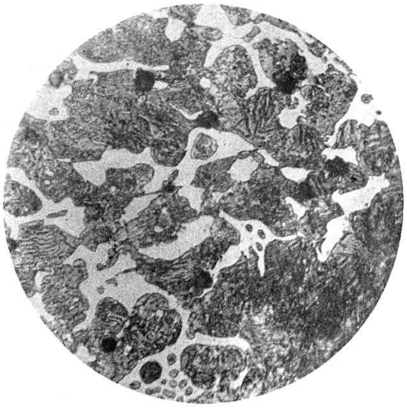


Photogr. No. 50. × 130
C = 2.29%, Si = 1.10%
Sand cast.

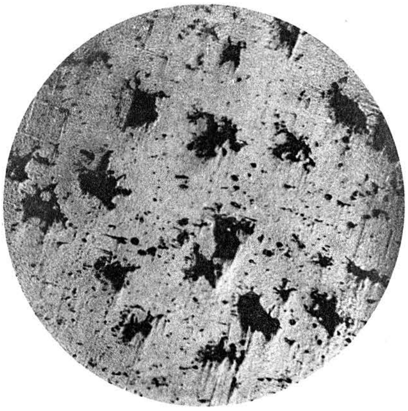
Photogr. No. 51. × 300
C = 3.39%, Si = 0.39%



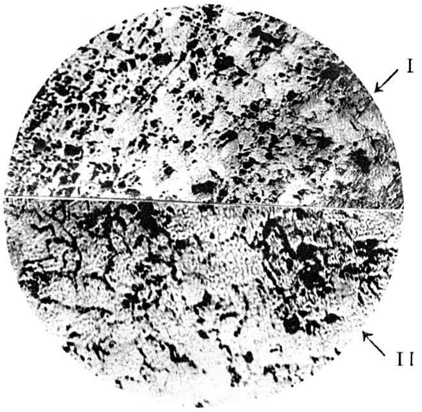
Photogr. No. 52. ×300
C=3.39%, Si=0.39%

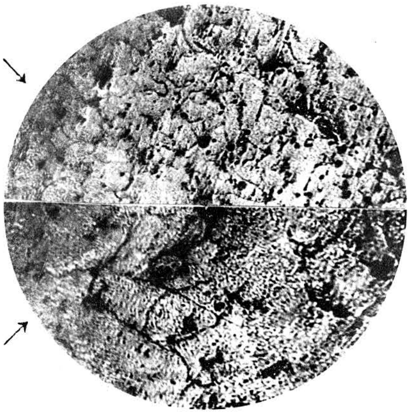


Photogr. No. 53. ×300
C=3.39%, Si=0.39%

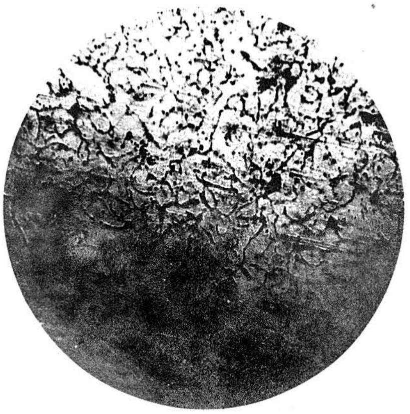


Photogr. No. 54. ×150
Malleable casting.

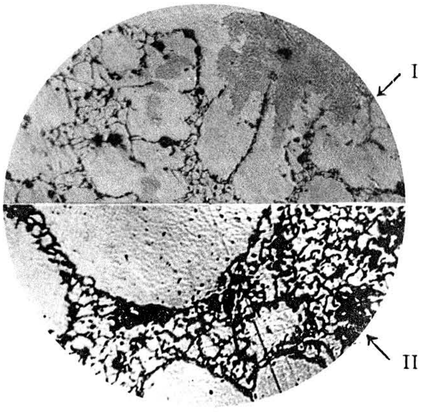




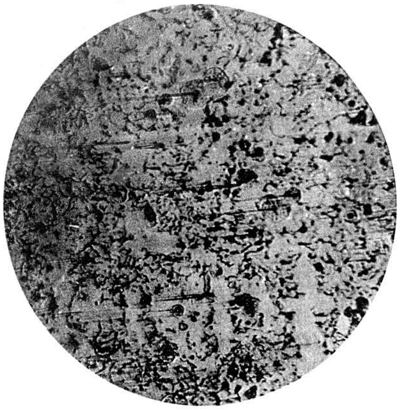
Photogr. No. 55—A. Photogr. No. 55—B.
Centrifugal cast iron made by the de' Lavaud's process.
(Outer portion) (Inner portion)
I : × 150 II : × 300



Photogr. No. 56. ×150
Cast iron cast in an iron
mould with thin wall.



Photogr. No. 57.
I : ×150, II : ×300.
Cast iron cast in sand mould.

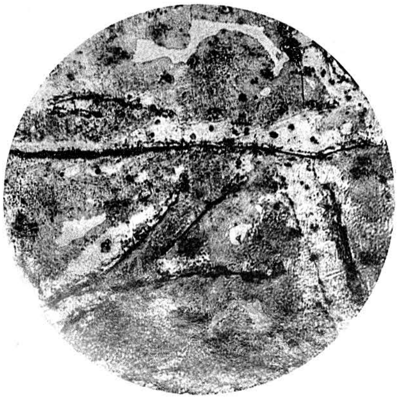


Photogr. No. 58. ×150
Pig. (Kenjiho)

Photogr. No. 59 ×150
Pig. (Kenjiho)

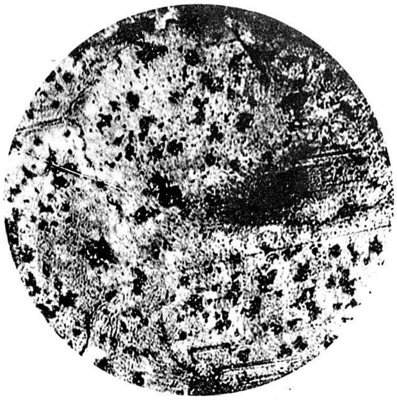
Pl. XII.

Photogr. No. 60. ×150
Cast iron furnace cooled.

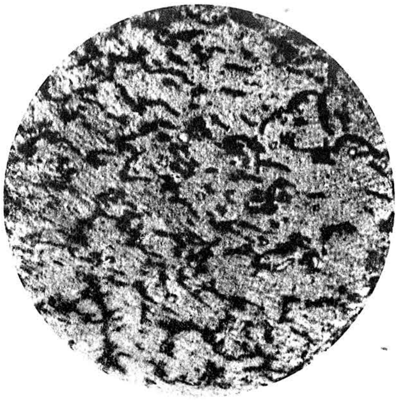


Photogr. No. 61. ×150
Pig. (Wanishi)

Photogr. No. 62. ×150
Pig. (Ogure)

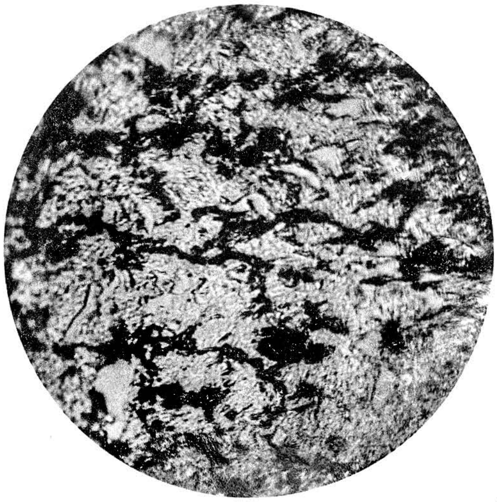


Photogr. No. 63. ×300
Cast iron as cast in sand mould.

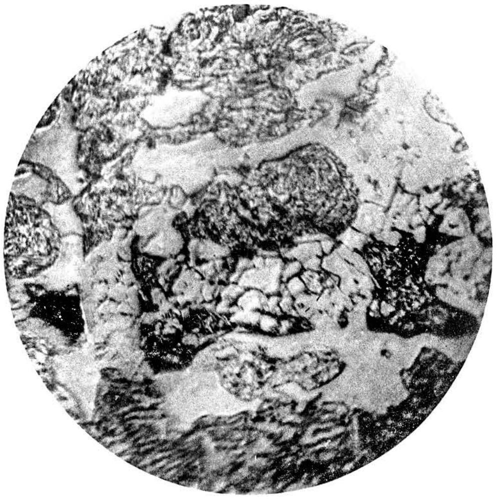


Photogr. No. 64. ×750
C=3.43%, Si=2.84%

Photogr. No. 65. ×300
C=3.45%, Si=1.74%



Photogr. No. 66. ×750
C=3.45%, Si=1.74%



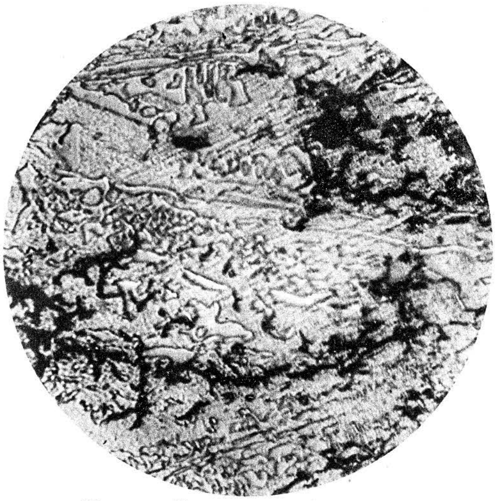
Photogr. No. 67. ×600
C=3.43%, Si=0.39%
The same specimen as No. 53.

Pl. XIII.

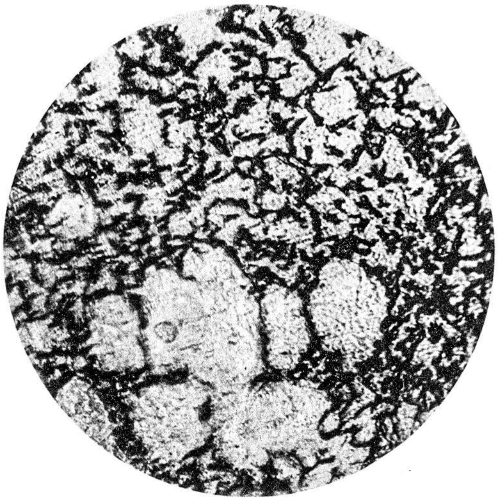
Structures of a centrifugal cast iron pipe made by the de' Lavaud's process.

Photogr. No. 68. × 1
Fracture

Photogr. No. 69. × 600
Portion (a)



Photogr. No. 70. × 600
Portion (b)



Photogr. No. 71. × 600
Portion (c)

Photogr. No. 72. × 600
Portion (d)

Photogr. No. 73. × 600
Portion (e)