

# Influence of Various Gases upon Graphitization in Cast Iron.

By

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## Contents.

Introduction.	
Chapter I.	Influence of various gases upon graphitization taking place during solidification of cast iron.
§ 1.	Sample.
§ 2.	Method of investigation.
§ 3.	Experiment.
§ 4.	Summary.
Chapter II.	Influence of various gases upon graphitization in white cast iron.
§ 1.	Specimen.
§ 2.	Method of investigation.
§ 3.	Experiment.
§ 4.	Summary.
Chapter III.	Some theoretical considerations on the influence of various gases upon graphitization.
Chapter IV.	Some practical problems concerning the present investigation.
§ 1.	So called "Umgekehrter Hartguss."
§ 2.	On the formation of the fine grained fracture surrounded by the coarse grained fracture in pig iron.
§ 3.	Summary.
Acknowledgement.	

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## Introduction.

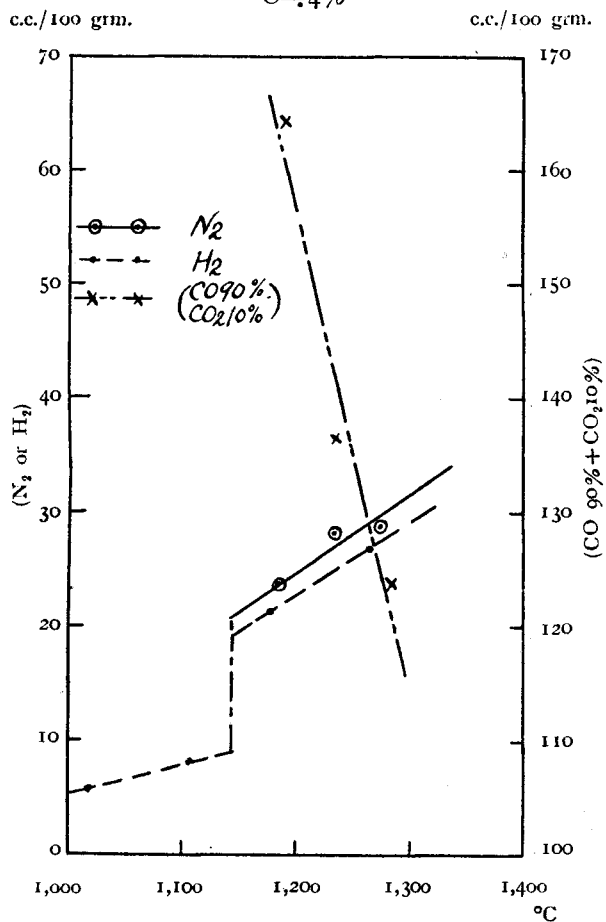
It is a well known fact that various gases are contained in cast iron in both molten and solid states. Dr. Iwase<sup>(1)</sup> measured the quantity of

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1) Sci. Rept., Tōhoku Imp. Univ.; 15, (1926), 531.

hydrogen, nitrogen and carbon oxides saturated in the cast iron having almost eutectic composition at various temperatures, and obtained the results

Fig. 1.  
(Iwase)  
Pure cast iron  
 $C \approx 4\%$



as shown in Fig. 1, which represents the following facts: (1) The quantity of hydrogen or nitrogen saturated in molten cast iron decreases as its temperature descends and a great quantity of this gas is liberated out of the iron when it solidifies. (2) The quantity of carbon oxides saturated in molten cast iron, on the contrary, increases as its temperature descends, and it is probable that they are also liberated out of the iron when it solidifies, from various phenomena met with in factory or in laboratory.

In regard to the quantitative determination of the gases contained in molten cast iron

which is melted in air by the usual manner or technically manufactured, Piwowarsky's<sup>(2)</sup> and Piwowarsky and Wuester's<sup>(3)</sup> works are to be mentioned. Table I shows the results of the former who analysed the gas liberated

2) St. E; 40, (1920), 1365.

3) St. E; 47, (1927), 698.

during solidification of pig iron manufactured in a blast furnace. The latter investigators collected the gas liberated during solidification of the molten cast iron which was melted in the Tammann furnace in air. After analysing the gases, they found in the gaseous sample methane which was considered to have been formed secondarily in the mould. Several results of their measurements are given in Table II. According to these results, the gas

**Table I**  
(Piwowarsky)

Sample. (Pig Iron)				Composition. (Vol. %)				Remarks.
Mn	P	S	Si	CO <sub>2</sub>	CO	N <sub>2</sub>	H <sub>2</sub>	
1.69	2.11	0.065	0.35	0.62	28.8	27.7	42.6	Taken at the beginning of tapping.
2.01	2.35	0.065	0.45	0.57	39.2	12.8	46.8	Taken in the middle of tapping.
1.90	2.23	0.065	0.41	0.38	42.6	10.8	45.9	Taken at the end of tapping.

**Table II**

(Piwowarsky and Wuester)

C=3.24%, Si=1.26%, Mn=0.40%, P=0.94%

Melting Temperature. (°C)	Volume of Gas. (c.c./100grms.)	Composition. (Vol. %)				
		CO <sub>2</sub>	CO	N <sub>2</sub>	H <sub>2</sub>	CH <sub>4</sub>
1,270	4.89	8.22	2.85	19.00	63.85	6.08
1,300	4.50	14.90	15.33	23.42	36.20	9.36
1,400	5.56	19.25	31.53	15.40	25.63	8.20
1,500	4.70	16.09	27.20	9.70	38.72	8.25
1,600	4.02	12.11	32.10	8.46	41.10	6.20

contained in molten cast iron consists of carbon dioxide, carbon monoxide, nitrogen and hydrogen and it is worthy of attention that the volume of hydrogen is largest among the gases contained in molten cast iron in most cases.

The principal object of the present investigation is to confirm in what degree the various gases contained in molten cast iron or in contact with white cast iron influence graphitization in these irons. Few investigators touched this problem, and it has remained fully unsolved up to the present. Profs. Honda and Murakami<sup>(4)</sup> introduced various gases into molten pure cast iron and studied the influence in question by microscopical means. They observed the fact that cast iron greatly graphitized in the atmosphere of carbon dioxide, carbon monoxide or in air, but it did not graphitize at all when it was melted in the atmosphere of nitrogen or hydrogen or in vacuo. Oberhoffer, Piwowarsky, Pfeifer-Schiessl and Stein<sup>(5)</sup> measured the quantity of carbon oxides contained in cast iron of the solid state and found the graphite flakes formed in the iron to become smaller as the quantity of oxygen contained in the iron increased, assuming that these gases were produced by the reaction between cast iron and oxygen contained in it. Piwowarsky<sup>(6)</sup> and Bardenheuer and Zeyen<sup>(7)</sup> confirmed a phenomenon that eutectic graphites are easily produced when cast iron is solidified in vacuo. Recently, T. Saitō<sup>(8)</sup> reported that eutectic graphites are also liable to be formed when cast iron solidifies in nitrogen or in hydrogen. This is an interesting phenomenon which was also observed by Kawaguchi<sup>(9)</sup> at the laboratory of Prof. D. Saitō in our university two years ago. As far as the present writer knows, only Hayes and Scott<sup>(10)</sup> and Hayes and Evans<sup>(11)</sup> are investigators who studied this problem especially on white cast iron. They confirmed the fact that the graphitization in white cast iron is favoured in the gaseous mixture consisting of carbon dioxide and carbon monoxide at 5 atmospheric pressure.

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4) Sci. Rept., Tōhoku Imp. Univ.; 10, (1921), 273.

5) St. E; 44, (1924), 115.

6) St. E; 47, (1927), 309.

7) Mit. Kaiser Wilhelm Inst. Eisenforsch; 10, (1928), 23.

8) Japanese J. I. S. I; 15, (1929), 662.

9) "Gakushi" Thesis, Dept. Min. Met., Kyōto Imp. Univ.; (1928).

10) J. Amm. Foundrymen's Assn; 33, (1926), 574.

11) Trans. Amm. Soc. St. Treat; 11, (1927), 691.

**Chapter I. Influence of various gases upon graphitization taking place during solidification of cast iron.**

§ 1. Sample.

Two kinds of materials were used in the present investigation. After these materials were melted and cast into iron mould, the ingots were crushed to pieces of the size about 2 to 8 m.m. in diameter to be taken as the sample for the present experiments. The composition of these samples is given in Table III.

**Table III**

Sample No.	Composition. (%)					Kind of Material.	Method of Preparation of Sample.
	C	Si	Mn	P	S		
A-I	4.01	0.003	0.031	0.007	0.007	Pure cast iron supplied by Kenjiho Iron Works.	After remelting in kryptol furnace, cast in iron mould.
A-II	3.80	0.004	0.029	0.008	0.007	Ditto.	Ditto.
A-III	3.95	0.005	0.034	0.009	0.007	Ditto.	After remelting in oil furnace, cast in iron mould.
B	3.54	0.70	0.56	0.53	0.13	Supplied by a factory manufacturing chilled roll.	After remelting in kryptol furnace, cast in iron mould.

§ 2. Method of investigation.

Figs. 2 and 3 show the apparatus used in the present experiments. In these figures, M represents a silit furnace used for melting of the sample, and T porcelain tube about 1,000 m.m. long and 9 m.m. in inner diameter, in which the sample was melted in the current of gas. The experiments were carried out in the following manner.

A porcelain boat containing about 25 grams of the sample was taken into the tube T at the middle of the melting furnace. After the inner space of the tube T was completely replaced by the gas wanted, the temperature of the sample was raised at a constant rate—20°C per min.—in the gaseous current of a constant flow—about 25 C. C. per min.—up to a predetermined melting temperature. As soon as the predetermined time elapsed at this temperature, the tube T was drawn in the furnace to the left direction in these figures as quickly as possible to make the molten

Fig. 2.

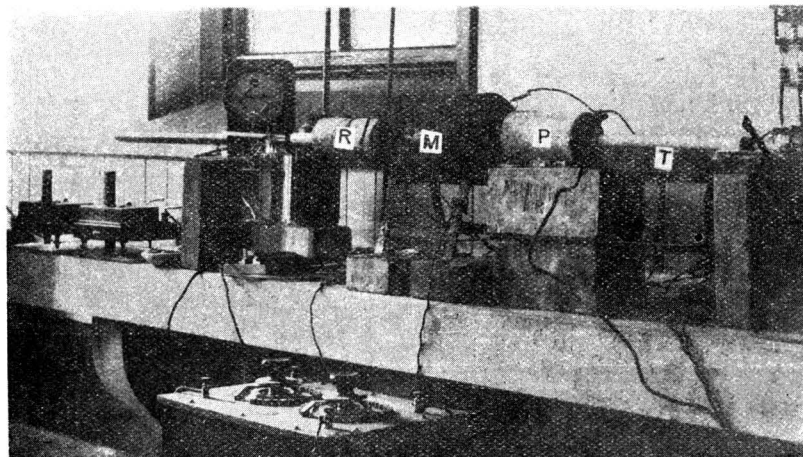
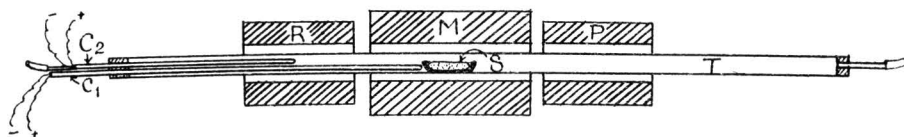


Fig. 3.



- M: Melting furnace.  
 R: Regulating furnace.  
 P: Preheating furnace.  
 T: Melting tube.  
 S: Sample.  
 C<sub>1</sub>, C<sub>2</sub>: Thermo-couples.

iron cool at the middle of the furnace R. The cooling rate of the molten sample could be finely regulated by adjusting the temperature of the furnace R. The furnace P was used to preheat the right half of the tube before it was brought to the left.

Both C<sub>1</sub> and C<sub>2</sub> are precious metals thermo-couples which were used for the measurement of the temperature of the sample and the furnace R respectively. The gases to be used in the present investigation were purified and dried with special care referring to the following publications: L. Vanino; *Handbuch d. Praeparativen Chemie* (1921), L. Moser; *Die Reindarstellung von Gasen* (1920).

After the sample had cooled to the room temperature, it was broken and its fracture was first studied. A microscopical study of the specimen was then carried out in order to examine the quantity of cementite and graphite and also the modes of formation of graphite in the specimen.

§ 3. Experiment.

(i) Experiment on the cooling rate of the specimen just necessary for making it into mottled cast iron.

(a) Result of experiment.

When the fracture of the specimen which melts in one kind of gas and solidifies under the different cooling rate in the same gas is examined, the following phenomena are observed.

The fracture will become white if the cooling rate is too great. It will be mottled with many white specks in the gray colored ground if the cooling rate is not so great. As the cooling rate is small, the whole area of the fracture begins to be tinted gray, but, in this case also, it is mottled with many specks of faint color in the deep gray colored ground. We can observe microscopically free cementite remaining undecomposed in these specks of faint color. In the present experiments, the author tried to confirm the temperature of the furnace R, just necessary for obtaining such critical cooling rate of the specimen in various gases. When cooling rate is more small, the whole area of the fracture becomes deep gray at last.

The important results are picked up among many and summarized in Table IV.

(b) Macroscopical study of fracture.

Photos. 1 to 25 show the typical fractures of the specimens. General survey of these fractures leads us to the recognition of the fact that, in all cases, the quantity of free cementite remaining undecomposed (white specks in fracture) is greater in the interior of the specimens than in their outer layer; in other words, the graphitization generally proceeded more favourably in the outer layer of the specimens than in their interior. This phenomenon, moreover, occurred more remarkably in the specimens which were melted in hydrogen or in ammonia (refer to Photos. 1, 2, 10, 12, 18, 20 to 22, 13, 24 and etc.) than those melted in air, carbon oxides or in

Table IV-1.

{Sample : A-I. Melting temperature: 1,300°C.  
 {Melting furnace: M-I. Melting time : 30 min. at 1,300°C.}

Experiment. No.	Specimen. No.	Kind of Gas.	Temp. of Furn. (R). (°C)	Fracture.	Photo. of Fracture. No.	Photo. of Structure. No.	Remarks.
1	A-I-I	Air <sup>(1)</sup>	Furnace cooling.	Gray.		37	(1) Melted in T, one of ends of which was opened to atmospheric air.
2	" 2	N <sub>2</sub>	Ditto.	Ditto.		38	
3	" 3	H <sub>2</sub>	Ditto.	Outer part: Gray; Interior: White.	1,2	39, 40	(2) Almost 0 m. m. in a common mercury manometer.
4	" 4	Vacuo <sup>(2)</sup>	Ditto.	Gray.		43	

Table IV-2.

{Sample : A-II. Melting temperature: 1,250°C.  
 {Melting furnace: M-II. Melting time : 10 min. at 1,250°C.}

Experiment. No.	Specimen. No.	Kind of Gas.	Temp. of Furn. (R). (°C)	Fracture.	Photo. of Fracture. No.	Photo. of Structure. No.	Remarks.
5	A-II-I	Air <sup>(1)</sup>	320	Mottled (with white specks).	3		(1) Melted in T, one of ends of which was opened to atmospheric air.
6	" 2	Air <sup>(1)</sup>	400	Gray.		44	
7	" 3	CO <sub>2</sub> <sup>(2)</sup>	340	Mottled (with white specks).	4		(2) Sample was heated in stagnant CO <sub>2</sub> filled up in T. After its temperature was raised to 1,250°C, the gas was passed for 10 min.
8	" 4	CO <sub>2</sub> <sup>(2)</sup>	350	Mottled (with no white specks).	5	45	
9	" 5	CO	450	Mottled (with white specks).	6		
10	" 6	CO	470	Gray (with small white specks).	7	46	
11	" 7	N <sub>2</sub>	450	Mottled (with gray outer layer 1 m.m. thick.)	8		(3) Cooled in R, in which 4 amperes passed.
12	" 8	N <sub>2</sub>	470	Mottled (with no white specks).	9	47	(4) Specimen A-II-9 was remelted.
13	" 9	H <sub>2</sub>	900	white.			
14	" 10	H <sub>2</sub>	1,050 1,130 <sup>(3)</sup>	Outer part: Gray; Interior: White.	10		
15	" 11	H <sub>2</sub>	(4 Am.)	Gray.			
16	" 12	H <sub>2</sub>	Furnace cooling	Ditto.	11	48,49	
17 <sup>(4)</sup>	" 13	Air	400	Ditto.			
18 <sup>(4)</sup>	" 14	N <sub>2</sub>	500	Ditto.			



Table IV-3

{Sample : A-III. Melting temperature: 1,250°C.  
 {Melting furnace: M-II. Melting time : 10 min. at 1,250°C.}

Experiment No.	Specimen No.	Kind of Gas.	Temp. of Furn. (R). (C°)	Fracture.	Photo. of Fracture. No.	Photo. of Structure. No.	Remarks.
19	A-III-1	H <sub>2</sub>	870	Outer part: Gray; Interior: White. White.	12	50	(1) Melted in T, one of ends of which was opened to atmospheric air. (2) Specimen A-III-1 was remelted.
20	" 2	NH <sub>3</sub>	Ditto.				
21	" 3	NH <sub>3</sub>	890	Outer part: Gray; Interior: White. Gray.	13		
22 <sup>(2)</sup>	" 4	Air <sup>(1)</sup>	300				

Table IV-4

{Sample : B. }  
 {Melting furnace: M-II. }

Experiment No.	Specimen No.	Kind of Gas.	Melting Temperature. (°C)	Melting Time. (min.)	Temp. of Furn. (R). (°C)	Fracture	Photo. of Fracture. No.	Photo. of Structure. No.	Remarks.
23	B-1	Air <sup>(1)</sup>	1,270	10	Room temperature	Mottled (with no white specks).	14	51	(1) (2) Same as before.
24	" 2	CO <sub>2</sub> <sup>(2)</sup>	Ditto.	Ditto.	Ditto.	Mottled (with white specks).	15	52	
25	" 3	CO	Ditto.	Ditto.	Ditto.	Mottled (with no white specks).	16	53	(3) Specimen B-5 was remelted.
26	" 4	N <sub>2</sub>	Ditto.	Ditto.	Ditto.	Ditto.	17	54	
27	" 5	H <sub>2</sub>	Ditto.	Ditto.	900	White.			(4) Specimen B-8 was remelted.
28	" 6	H <sub>2</sub>	Ditto.	Ditto.	930	Gray (with small white specks) in interior.	18	55	
29	" 7	H <sub>2</sub>	Ditto.	Ditto.	950	Gray.			(5) Specimen B-15 was remelted.
30 <sup>(2)</sup>	" 8	Air <sup>(1)</sup>	Ditto.	Ditto.	Room temperature	Ditto.			
31	" 9	H <sub>2</sub>	1,250	0	930	Mottled (with no white specks).	19		
32	" 10	H <sub>2</sub>	Ditto.	5	Ditto.	Gray (with small white specks) in interior.	20		
33	" 11	H <sub>2</sub>	Ditto.	30	Ditto.	Outer part: Gray; Interior: White.	21		
34	" 12	H <sub>2</sub>	Ditto.	60	Ditto.	White (with thin gray outer layer).	22		
35 <sup>(4)</sup>	" 13	H <sub>2</sub>	Ditto.	0	Ditto.	Mottled (with no white specks).	23		
36 <sup>(2)</sup>	" 14	N <sub>2</sub>	Ditto.	Ditto.	Room temperature	Ditto.			
37	" 15	NH <sub>3</sub>	Ditto.	10	900	White.			
38	" 16	NH <sub>3</sub>	Ditto.	Ditto.	920	Gray (with white specks).	24	56	
39	" 17	NH <sub>3</sub>	Ditto.	Ditto.	950	Gray.	25		
40 <sup>(2)</sup>	" 18	Air <sup>(1)</sup>	1,270	Ditto.	Room temperature	Ditto.			

nitrogen (refer to Photos. 3, 4, 6, 8, 14, 15 and etc.). It is also interesting to note that in the specimens which solidified in hydrogen at the cooling rate just necessary for the production of the specimens having deep gray colored fracture, specks of the very fine grained fracture appeared locally in their interior surrounded by the coarse grained fracture as shown in Photos. 11 and 36.

(c) Microscopical study of the structure of the specimen.

The typical structure of the specimens is shown in Photos. 37-56 in which Photos. 37 to 43, 44 to 49, 50, 51 to 56 show the structure of Specimen A-I, A-II, A-III and B respectively, and Photos. 37 to 40 and 43 show the structure of the specimens made in Experiment 1 to 4.

From these photographs, it is found that eutectic graphites will develop in the specimens melted in nitrogen or in air, and also that, in the specimen melted in vacuo, all the graphites develop in eutectic form between austenite dendrites as shown by Piwowarsky, and Bardenheuer and Zeyen. Photos. 39 and 40 show the structure of the part of gray and white fracture in Photos. 1 and 2 respectively. The former is the structure of common gray cast iron and the part of white fracture is found to consist of ledeburites.

Comparing the degree of graphitization occurring in Specimen A-I-1 to A-I-4, we can recognize the fact that it is greatest in Specimen A-I-4 (melted in vacuo) which has a moderate quantity of free ferrite instead of free cementite, and also that it is smallest in Specimen A-I-3 (melted in hydrogen) which has a large quantity of ledeburite.

Photos. 41 and 42 respectively show the structure of the part of the coarse grained and fine grained fracture in Photo. 36. The former is almost the same as the structure shown in Photo. 39, and only very fine graphites are found to develop in the latter. In the specimens made by melting Sample A-II, A-III and B, eutectic graphites also were always produced irrespective of the kind of gas used. Photos. 44 to 47 and 50 show the structure of the part of the specimens in which eutectic and large flaky graphites exist together. Photos. 48 and 49 respectively show the structure of the part of the coarse grained and fine grained fracture in Photo. 11.

(d) Conclusion.

From the data obtained in the present experiments, the temperature of the furnace R necessary for obtaining the critical cooling rate of the sample at which it solidifies to mottled state having no white specks in its fracture is determined on the sample melted in various kinds of atmosphere as summarized in Table V and graphically shown in Fig. 4. In the present experiments, the graphitization in pure cast iron proceeded most favourably in vacuo, less favourably in air and carbon dioxide, and least favourably in carbon monoxide and nitrogen. In hydrogen and ammonia, it proceeded with great difficulty. The unfavourable influence of hydrogen and ammonia,

**Table V.**

{ Melting temperature: (For Sample A-II, 1,250°C)  
 : (For Sample B, 1,270°C) }  
 { Melting time : 10 min. }

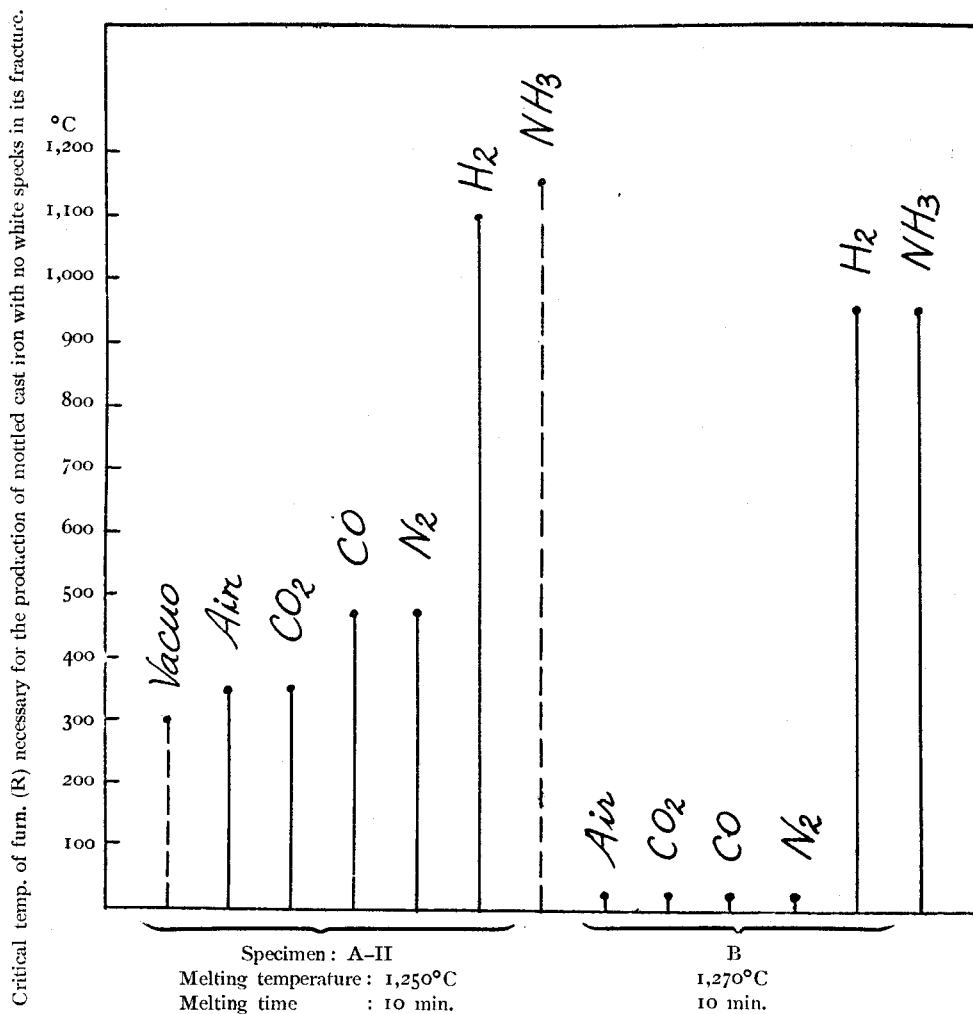
Kind of Sample.	Kind of Gas	Critical Temp. of Furn. (R) just necessary for the Production of Mottled Cast Iron with no White Specks in its Fracture. (°C)
A-II	Vacuo	300*
	Air	350
	CO <sub>2</sub>	350
	CO	470
	N <sub>2</sub>	470
	H <sub>2</sub>	1,100
	NH <sub>3</sub>	1,150(+)
B	Air	Room temperature
	CO <sub>2</sub>	Ditto.
	CO	Ditto.
	N <sub>2</sub>	Ditto.
	H <sub>2</sub>	950
	NH <sub>3</sub>	950

\* Estimated from the data given in Table IV-1.

(+) " " " " Table IV-3.

moreover, was more remarkable on Sample B having a moderate quantity of various impurities than on pure cast iron.

Fig. 4



It is also evident that the graphitization even in pure cast iron does not necessarily require the presence of carbon oxides in the iron, because the iron graphitizes even when it is melted in hydrogen, if it is slowly cooled. If the fact that pure cast iron graphitizes even in hydrogen is due to the action of carbon oxides which may be originally contained in the iron, it will be impossible to obtain the result given in Experiment 18.

(ii) Experiment on the absorption velocity of some gases in molten cast iron.

According to Sieverts<sup>(12)</sup>, the relation between the quantity of hydrogen ( $m$ ) saturated in iron at a constant temperature and its pressure ( $p$ ) is expressed by the following formula :

$$m = KV\sqrt{p}$$

where

$K$  is a constant.

If this law approximately holds on the various gases contained in cast iron, when the atmosphere of A-gas in contact with molten cast iron containing a large quantity of A-gas is changed by that of B-gas, A-gas contained in the iron will be gradually replaced by B-gas, because, in this case, the partial pressure of B-gas in the atmosphere is far greater than that of A-gas which is practically negligible. In the present experiments, after Sample B was melted in hydrogen, the atmosphere was then replaced with nitrogen or carbon monoxide, or vice versa, in order to know the influence of such treatment upon the graphitization in the iron and then to get some hint concerning the present problem. Sample B was found in the previous experiments (refer to Table IV) to become gray cast iron when it solidifies in nitrogen or in carbon monoxide in the furnace R of 300°C, but to become white cast iron when it solidifies in hydrogen at the same cooling rate. The present experiments were carried out by adopting these relations. The method of treatment of the sample and the results obtained are summarized in Table VI.

From these results, it is acceptable that molten cast iron containing a large quantity of hydrogen can easily absorb carbon monoxide, whereas nitrogen can be absorbed only with difficulty, and also that molten cast iron containing a large quantity of carbon monoxide or nitrogen can easily absorb hydrogen.

As hydrogen thus has this property of being easily absorbed in molten cast iron and as it not only hinders remarkably the graphitization in cast iron, but also often makes the structure of solidified cast iron

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12) Z. Elektrochem ; 16, (1910), 707.

Table VI.

{Sample : B. Melting temperature; 1,250°C}  
 {Melting furnace: M-II. Temp. of furn. R : 300°C}

Experiment No.	Method of Treatment.	Fracture.	Photo. of Fracture. No.
41	Melted in N <sub>2</sub> ; 15 min. in N <sub>2</sub> at 1,250°C; Cooled in N <sub>2</sub> .	Gray	26
42	" ; 75 " ; "	Ditto.	27
43	Melted in H <sub>2</sub> ; 15 min. in H <sub>2</sub> , then 30 min. in N <sub>2</sub> at 1,250°C; Cooled in N <sub>2</sub>	White	28
44	" ; " , 60 " ; "	Ditto.	29
45	" N <sub>2</sub> ; " N <sub>2</sub> , 30 " H <sub>2</sub> ; " H <sub>2</sub>	Ditto.	30
46	" ; " , 5 " ; "	Ditto.	31
47	" CO; 15 min. in CO at 1,250°C ; " CO	Gray	
48	" H <sub>2</sub> ; 15 min. in H <sub>2</sub> , then 30 min. in CO at 1,250°C; " CO	Mottled (with no white specks.)	32
49	" ; " , 90 " ; "	Ditto.	33
50	" CO; " CO, 5 " H <sub>2</sub> ; " H <sub>2</sub>	Gray	34
51	" ; " , 30 " ; "	White	35

heterogeneous, some proper means, if possible, are recommended by which molten cast iron may not be brought into direct contact with hydrogen and the gases which produce hydrogen, or to make this time of contact as short as possible during the process of the technical manufacture or melting of cast iron as in the blast furnace or in the cupola.

#### § 4 Summary.

(1) Molten cast iron was solidified at various cooling rates in different kinds of atmosphere—vacuo, air, carbon dioxide, carbon monoxide, nitrogen, hydrogen and ammonia, and the influences of these gases upon the graphitization in cast iron were compared.

(2) The graphitization in pure cast iron proceeded more favourably in vacuo than in air and carbon dioxide. It proceeded more favourably in air and carbon dioxide than in carbon monoxide and nitrogen. Hydrogen and ammonia greatly hindered the graphitization in pure cast iron.

(3) The graphitization in pure cast iron did not necessarily require the presence of carbon oxides in molten cast iron.

(4) It was observed that the above relations were almost true and valid for the case of cast iron containing a moderate quantity of various impurities.

(5) When cast iron solidifies in various gases, the graphitization proceeds more favourably in the outer layer of the iron than in its interior. This new phenomenon occurs more remarkably in the cast iron melted in hydrogen or in ammonia than in the iron melted in air, carbon dioxide, carbon monoxide, or in nitrogen.

(6) Eutectic graphites are easily produced when cast iron is melted in hydrogen or in nitrogen. In the cast iron melted in vacuo, all graphites develop in eutectic form between austenite dendrites.

(7) Molten cast iron containing a large quantity of hydrogen can easily absorb carbon monoxide but absorbs nitrogen with difficulty, and molten cast iron containing a large quantity of carbon monoxide or nitrogen can easily absorb hydrogen.

**Chapter II. Influence of various gases on graphitization in white cast iron.**

§ 1. Specimen.

The cast iron melted in a kryptol furnace was cast in 10 or more green sand moulds into rods of white cast iron about 10 m. m. thick and 200 m. m. long. The cylindrical dilatometer specimens, 7.5 m. m. thick and 80 m. m. long, were then prepared by grinding and cutting these rods. The composition of the specimens is given in Table VII.

**Table VII.**

Specimen No.	Composition. (%)						Kind of Material.
	C	Si	Mn	P	S	Cu	
C-I	2.48	1.02	0.019	0.009	0.013	0.051	(Kenjiho pure cast iron) + (armco iron) + (silicon)
C-II	2.67	1.03	0.012	0.002	0.013	0.060	Ditto.
D	2.74	1.18	0.320	0.165	0.075	0.151	Supplied by a factory manufacturing black heart malleable cast iron.

§ 2. Method of investigation.

In this investigation, a dilatometer was devised especially for this

experiment. It is shown in Figs. 5 and 6, in which T represents a silica tube 9 m. m. in inner diameter. It has a gas inlet near one end and an outlet near the other end. Both  $t_1$  and  $t_2$  are two smaller silica tubes having one end closed and an outer diameter of about 7.5 m. m. The former tube is connected with T by a thin flexible india rubber tube G, and  $t_2$  is fixed to the one end of the larger tube T by fusion as shown in the figure.

The expansion of the specimen S is transmitted to a mirror, the deflection of which is observed by means of a scale and a telescope.

Fig. 5.

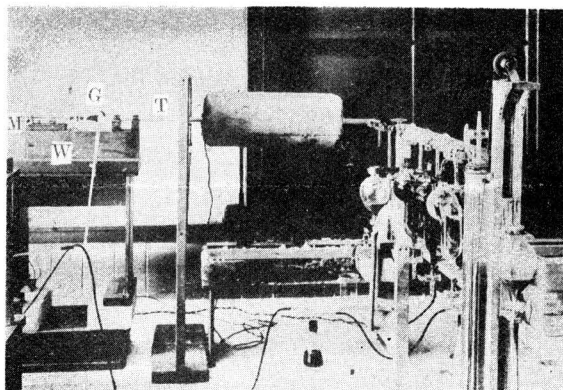
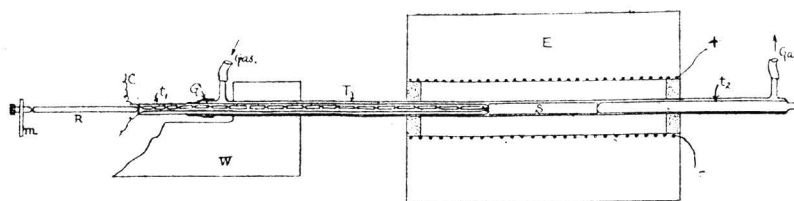


Fig. 6.



- E: Electric furnace.
- $T_1$   $t_1$  &  $t_2$ : Silica tubes:
- G: Gum tube.
- C: Thermo-couple:
- R: Rod.
- M: Millor.
- S: Specimen.
- W: Fixed stand.

The specimen was heated at a constant rate— $10^{\circ}\text{C}$  per minute—to a predetermined temperature above its  $A_1$  point, and that temperature was kept constant for a sufficient time completely to decompose free cementite. It was then furnace cooled or air cooled to room temperature. A constancy



of temperature with a maximum variation of  $2^{\circ}\text{C}$  at the annealing temperature could be obtained. The reading of the scale was taken every  $10^{\circ}\text{C}$  or  $20^{\circ}\text{C}$  during heating and cooling, and every 10 minutes during the time in which the temperature was kept constant. The gas at about 1 atmospheric pressure was passed through the tube T at a constant flow during the heat treatment. Although it was purified and perfectly dried before use with special care, it was inevitable that it should be contaminated with a minute amount of nitrogen, coming from the water always used as a confining liquid of the gas.

Chemical analysis and microscopical study were also adopted as supplementary work of the dilatometer experiments.

### § 3. Experiment.

(i) Experiment on the time required to complete the graphitization of free cementite in white cast iron.

#### (a) Experiment with Specimen C-I.

The specimens in the cast state were annealed at  $975^{\circ}\text{C}$  and those in the hardened state at  $935^{\circ}\text{C}$ . In 1927, D. Saitō and the author<sup>(13)</sup> found a new phenomenon, viz., that if white cast iron be hardened it becomes very unstable. The adoption of the hardened specimens in the present experiments is based on this fact. To prepare the hardened specimens, those in the cast state were inserted into an electric tube furnace of  $930^{\circ}\text{C}$ . As soon as the temperature of the specimens was raised to  $930^{\circ}\text{C}$ , they were dropped into water of about  $14^{\circ}\text{C}$ .

The rate of flow of gas passing through the dilatometer during the heat treatment was always about 5.2 C.C. per minute. Of course, special care was taken to replace the total vacant space in the apparatus used in this experiment with the gas to be used, wasting its large volume before the experiment was started.

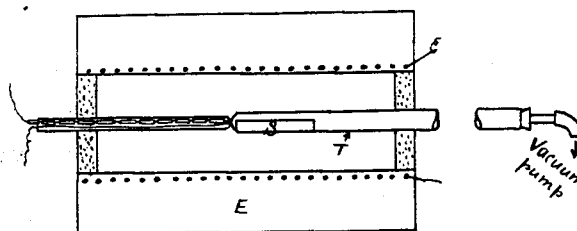
*Experiment in vacuo.* The author annealed the specimen in vacuo of high degree at  $975^{\circ}\text{C}$  and tried to find the time required to complete the graphitization of free cementite in this condition. The experiments were carried out in the apparatus as shown in Fig. 7.

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13) Mem. Coll. Eng., Kyōto Imp. Univ.; 5, (1927), 1.

After the specimens were annealed for a predetermined time at 975°C, they were air cooled in vacuo, so as to determine whether free cementite

Fig. 7.



E=Electric furnace.

T=Silica tube.

S=Specimen.

remained undecomposed or not, by microscopical study. The changes in weight of all specimens used in this experiment, and in quantity of total carbon in a specimen were determined before and after the heat treatment to check the degree of vacuo.

The results are summarized in Table VIII.

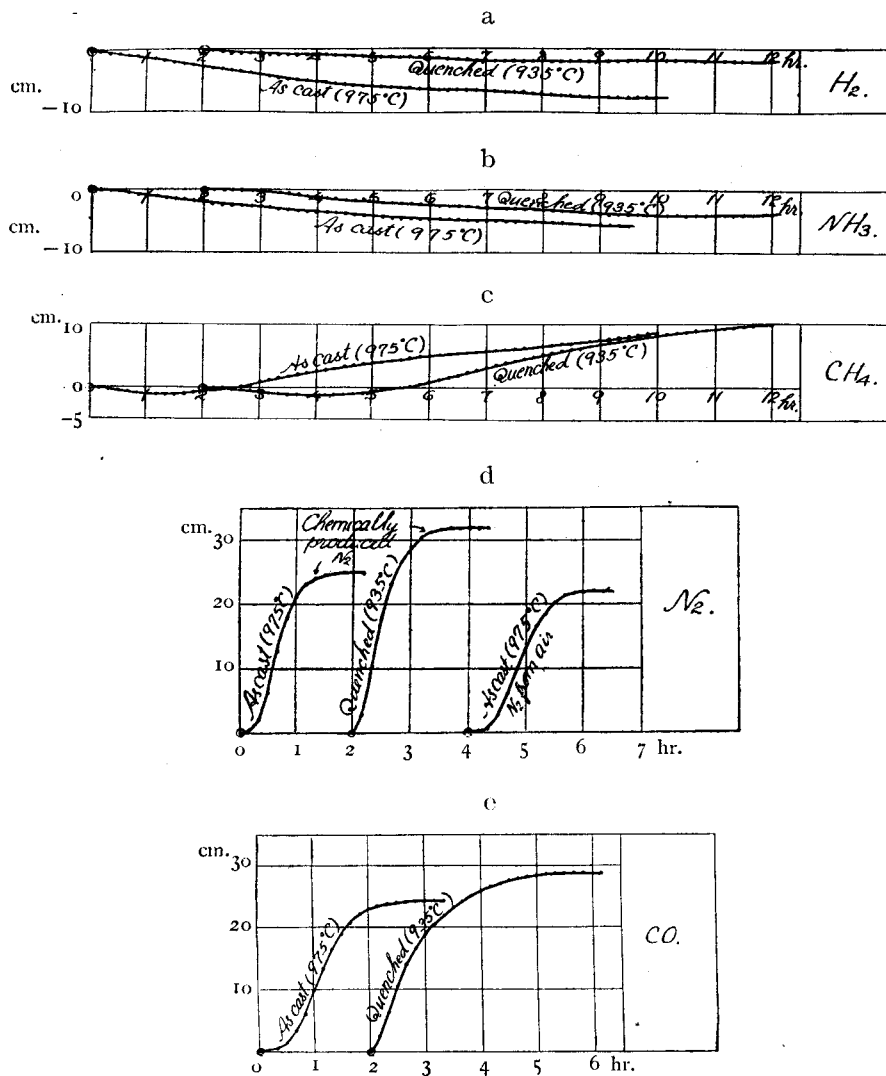
Table VIII

Experiment No.	Annealing Time kept at 975°C. (hr. min.)	Weight of Specimen. (grains.)			Total Carbon in Specimen. (%)			Remarks.
		Before Annealing	After Annealing	Difference	Before Annealing	After Annealing	Difference	
52	0 0	4.5328	4.5320	-0.0008				A minute quantity of temper carbon was produced as shown in Photo. 57.
53	1 0	5.0157	5.0154	-0.0003				A minute quantity of free cementite remained undecomposed as shown in Photo. 58.
54	1 30	33.8395	33.8393	-0.0002	2.48	2.49	0.01	Free cementite is absent as shown in Photo. 59.
55	2 0	4.6200	4.6170	-0.0030				ditto.

It was thus found that the time required to complete the graphitization of free cementite in Specimen C-I is about 1 hour and 30 minutes at 975°C in vacuo.

*Influence of hydrogen.* Fig. 8-a shows the graphitization curves of the specimen obtained in this experiment. In the figure, the abscissa represents the annealing time elapsed after the arrival of the temperature of the

Fig. 8.



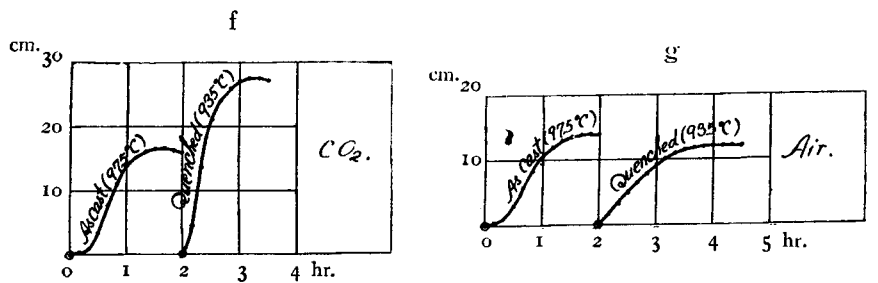
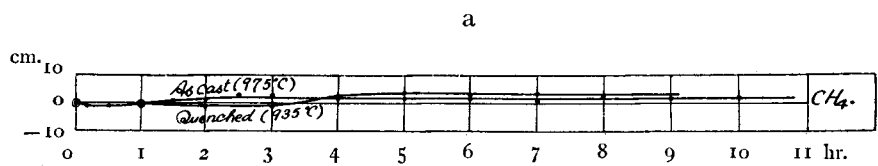
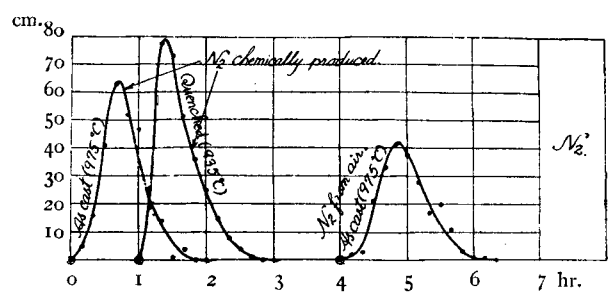


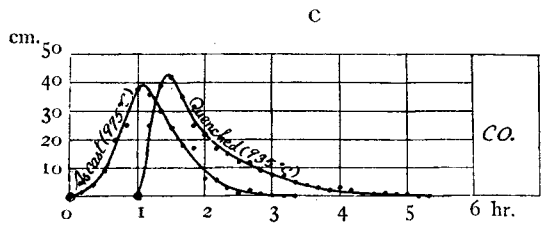
Fig. 9.



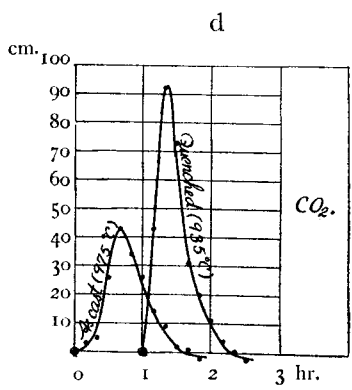
a



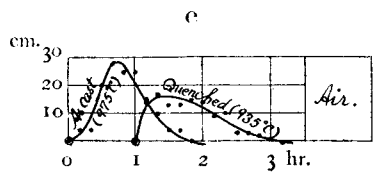
b



c



d



e

specimen to the predetermined temperature—975°C, and the ordinate the expansion of the specimen during annealing, which practically corresponds to the amount of free cementite graphitized.

In hydrogen, the specimen does not expand at all, even if it is annealed for 10 hours. The microstructure of the annealed specimens also showed that even a minute amount of temper carbon was not produced as shown in Photo. 60, and the outer layer of the specimen was somewhat decarburised.

*Influence of ammonia.* The results are shown in Fig. 8-b and given in Table IX.

**Table IX**

Experiment No.	Kind of Atmosphere in Dilatometer.	Condition of Specimen before Annealing.	Annealing Temperature. (°C)	Total Carbon in Specimen (%)			Time required to complete the Graphitization of Free Cementite. (hr. min.)	Photo. of Structure No.
				Before Annealing.	After Annealing.	Difference		
56'	Vacuo.	As cast.	975	2.48	2.49	+0.01	1 30	60
57	H <sub>2</sub>	As cast.	975	2.48	2.17	-0.31	10+α	
58	H <sub>2</sub>	Quenched.	935				10+α	61
59	NH <sub>3</sub>	As cast.	975	2.48	2.29	-0.19	9+α	
60	NH <sub>3</sub>	Quenched.	935				10+α	62
61	CH <sub>4</sub>	As cast.	975	2.48	2.32	-0.16	10+α	
62	CH <sub>4</sub>	Quenched.	935				10+α	63
63	N <sub>2</sub> (Chemically produced.)	As cast.	975	2.48	2.39	-0.09	1 50	
64	N <sub>2</sub> (Chemically produced.)	Quenched.	935				1 50	65
65	N <sub>2</sub> (From air.)	As cast.	975				2 0	
66'	O <sub>2</sub>	As cast.	975				2+α	67
67	CO	As cast.	975	2.48	2.37	-0.11(?)	3 10	
68	CO	Quenched.	935				4 0	68
69	CO <sub>2</sub>	As cast.	975	2.48	2.04	-0.44	1 30	
70	CO <sub>2</sub>	Quenched.	935				1 10	69
71	Air.	As cast.	975	2.48	2.06	-0.42	1 50	
72	Air.	Quenched.	935				2 10	

The influence of this gas is almost similar to that of hydrogen.

*Influence of methane.* The results are shown in Figs. 8-c and 9-a

and given in Table IX. In Fig. 9, the abscissa represents the annealing time and the ordinate the expansion of the specimen per 10 minutes which practically corresponds to the amount of free cementite graphitized in this time.

The specimen graphitizes very slowly in methane.

*Influence of nitrogen.* A specimen was annealed in nitrogen chemically produced, and another specimen in this gas obtained from air. The results are shown in Figs. 8-d and 9-b, and given in Table IX.

The graphitization in the specimen proceeds easily in this gas whatever the genesis of the gas may be.

*Influence of oxygen.* In this experiment, the author adopted an apparatus of similar construction to the dilatometer, for fear of the damage done to the dilatometer due to the action of iron oxide produced during the heat treatment of the specimen. After the specimen was annealed for a predetermined time in the current of oxygen in this apparatus at 975°C, it was air cooled and its structure was studied by the microscope. The results are summarized in Table X.

Table X

Experiment No.	Annealing Time kept at 975°C. (hr. min.)	Remarks.
73	1 0	A large quantity of free cementite remained undecomposed.
74	1 30	A moderate quantity of free cementite remained undecomposed as shown in Photo. 64.
75	2 0	A minute quantity of free cementite remained undecomposed in the interior as shown in Photos. 65 and 66.

The time required to complete the graphitization of free cementite was then decided to be about 2 hours in oxygen.

*Influence of carbon monoxide.* The results are shown in Figs. 8-e and 9-c, and given in Table IX.

The graphitization of the specimen proceeds with moderate ease in this gas. But in this gas, it takes a longer time than in vacuo and in nitrogen.

*Influence of carbon dioxide.* The results are shown in Figs. 8-f and 9-d, and given in Table IX.

The specimen graphitizes very easily in this gas.

*Influence of air.* The results are shown in Fig. 8-g and 9-e, and given in Table IX.

The specimen also graphitizes very easily in air. It was, of course, distinctly oxidised and decarburised.

(b) Experiment with Specimen No. D.

The method of this experiment is the same as above mentioned. Specimens in the cast state only were annealed at various temperatures.

*Experiments in vacuo.* From the results summarized in Table XI,

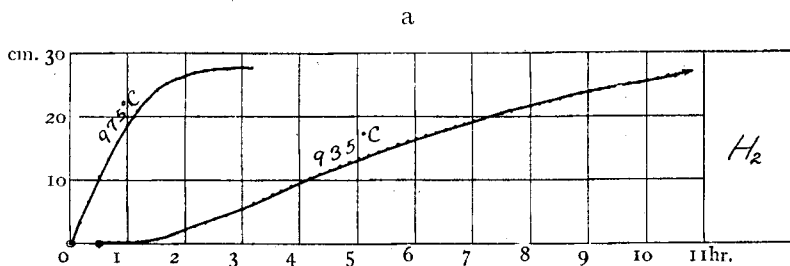
**Table XI**

Experiment No.	Annealing Time kept at 975°C. (hr. min.)	Remarks.
76	0 30	A moderate quantity of free cementite remained undecomposed.
77	1 0	A minute quantity of free cementite remained undecomposed.
78	1 30	Free cementite is absent.

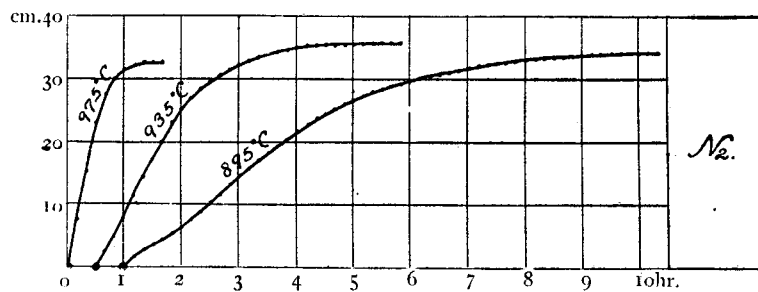
it was confirmed that the graphitization of free cementite at 975°C was completed in about 1 hour and 30 minutes in vacuo.

The specimen was, moreover, annealed at 935°C in the Honda's dilatometer, keeping the degree of vacuo at 3 m.m. of mercury column. The result of this experiment is shown in Figs. 10-e and 11, and given in Table XII.

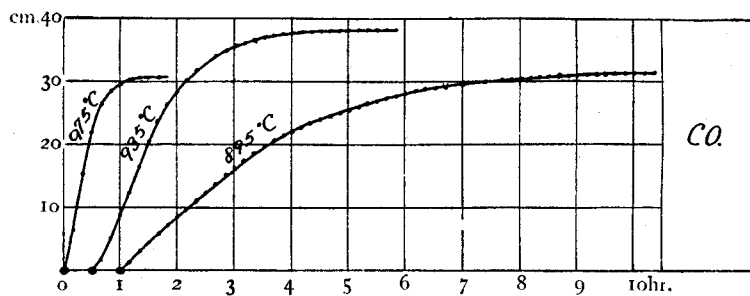
Fig. 10.



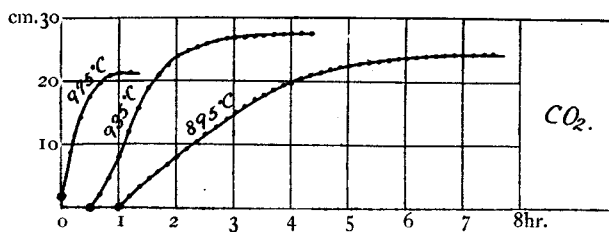
b



c



d



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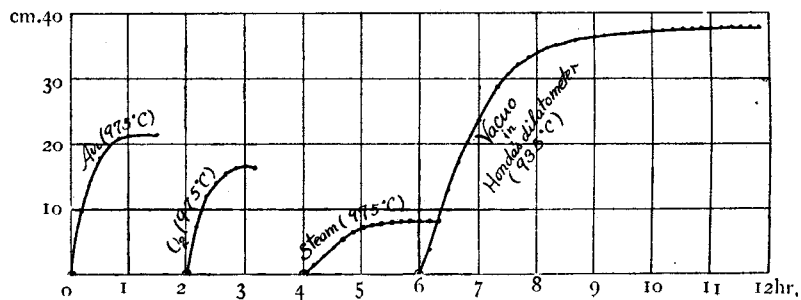




Table. XII

Experiment No.	Kind of Atmosphere in Dilatometer.	Annealing Temperature. (°C)	Time required to complete the Graphitization of Free Cementite. (hr. min.)	
			hr.	min.
79'	Vacuo. (In a silica tube)	975	1 + α	
80	Vacuo. In the Honda's dilatometer	935	5	20
81	H <sub>2</sub>	975	2	50
82	H <sub>2</sub>	935	10 + α	
83	N <sub>2</sub>	975	1	30
84	N <sub>2</sub>	935	5	0
85	N <sub>2</sub>	895	9	0
86	CO	975	1	30
87	CO	935	4	50
88	CO	895	9	0
89	CO <sub>2</sub>	975	1	0
90	CO <sub>2</sub>	935	3	30
91	CO <sub>2</sub>	895	6	30
92	O <sub>2</sub>	975	1	0
93	Air	975	1	10
94	Steam	975	1	50

*Influence of hydrogen.* The specimen was annealed at 975°C and 935°C. The results are shown in Figs. 10-a and 11 and given in Table XII.

*Influence of nitrogen.* The results are shown in Figs. 10-b and 11, and given in Table XII.

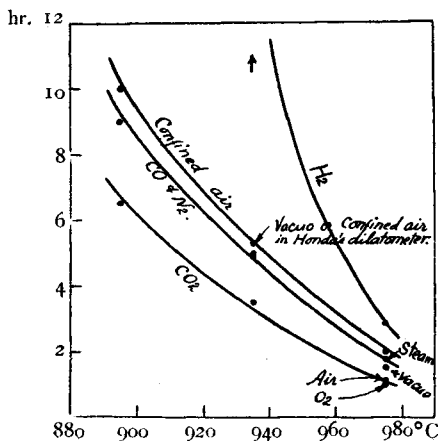
*Influence of carbon monoxide.* The results are shown in Figs. 10-c and 11, and given in Table XII.

*Influence of carbon dioxide.* The results are shown in Figs. 10-d and 11, and given in Table XII.

*Influence of oxygen, air and steam.* The results are shown in Figs. 10-e and 11, and given in Table XII.

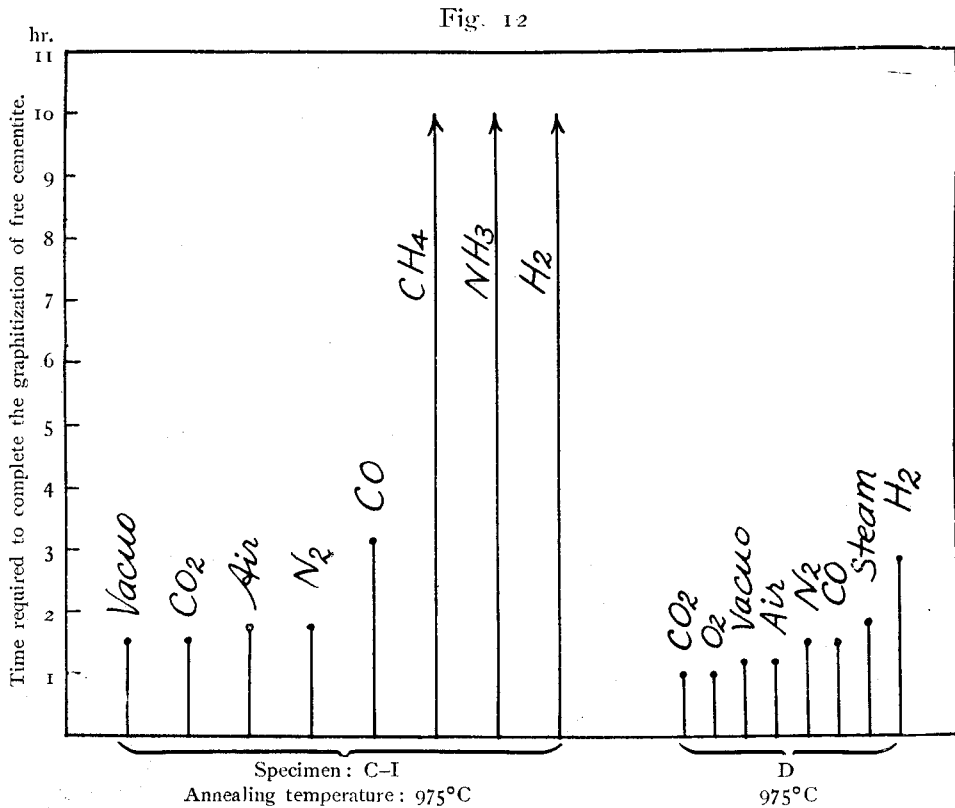
Fig. 11.

C=2.74%, Si=1.18%.



## (c) Conclusion.

Considering the time required to complete the graphitization of free cementite in Specimen C-I annealed in the various kinds of atmosphere, we can recognize the fact that it proceeds most favourably in vacuo and carbon dioxide, in vacuo it proceeds a little more favourably than in nitrogen and far more favourably than in carbon monoxide, and also that it is remarkably retarded by hydrogen, ammonia and methane. These relations to the specimens in the cast state are also shown in Fig. 12.



In regard to the time in question in the various gases, it is shortest in carbon dioxide and becomes longer in the following order: in air, nitrogen, carbon monoxide, methane, ammonia and in hydrogen.

We see in the graphitization curves shown in Fig. 8 that the height of the curves of the specimens annealed in nitrogen and carbon monoxide

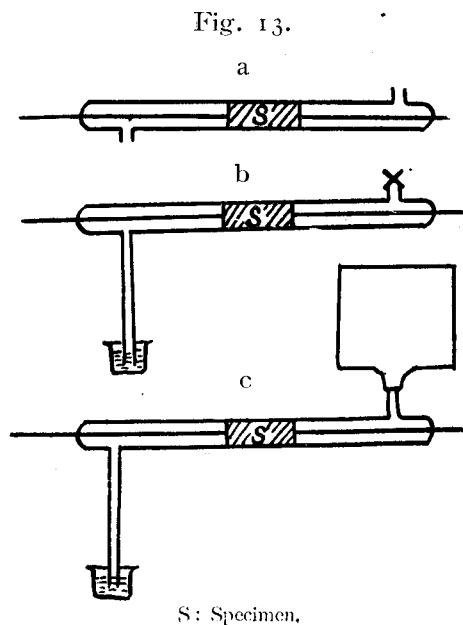
is higher than those of the specimens annealed in the oxidizing gases such as carbon dioxide and air. This is probably due to the fact that a part of free cementite was oxidized by these gases before its graphitization begins.

In the experiments with Specimen D, we have almost the same results as in those with Specimen C-I as shown in Fig. 12. The graphitization in this specimen was also completed in the shortest time in carbon dioxide and in oxygen, in a very short time in vacuo and air. It is distinctly interfered with by hydrogen. It is an interesting phenomenon that the unfavourable influence of hydrogen is far more distinct in Specimen C-I than in Specimen D.

The influence of some gaseous mixtures consisting of carbon dioxide and carbon monoxide, carbon dioxide and nitrogen, carbon dioxide, nitrogen and water vapour, or nitrogen and water vapour was also investigated, but important data were not obtained.

(ii) Influence of the quantity of air in contact with white cast iron upon the time required to complete the graphitization of free cementite in it.

(a) Experiment with Specimen C-II.



In order to determine the influence of the quantity of air in contact with Specimen C-II upon its graphitization, the specimen was annealed in the manner as shown in Fig. 13. In Fig. 13-a, both the gas inlet and the outlet of the dilatometer devised by the present writer are opened to atmospheric air in order to make the quantity of air to be in contact with the specimen infinitive. In Fig. 13-b, the gas inlet is closed and the gas outlet is connected to a gum tube, about 500 m.m. long and about 3 m.m. in diameter, the other

end of which is immersed in conc. sulphuric acid. The quantity of air to be in contact with the specimen in the dilatometer is greatly limited in this condition. In Fig. 13-c, in the place of the closed gas inlet in Fig. 13-b, a glass bottle is connected to it in an inverted position and the capacity of the bottle is changed as required. The graphitization curves of the specimen annealed in these conditions are shown in Fig. 14 and the time in question is obtained as given in Table XIII.

Fig. 14.

(Annealing temperature: 965°C.)

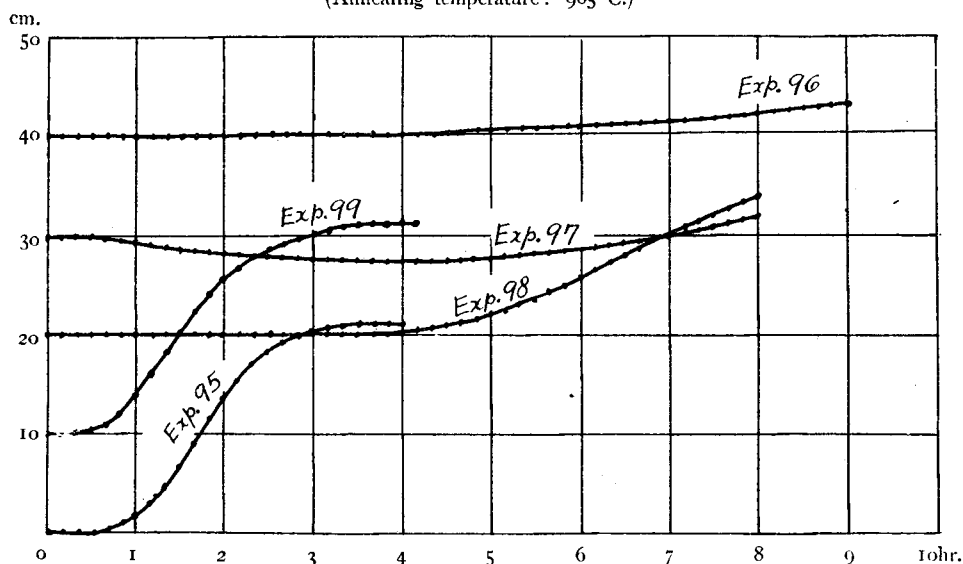


Table XIII.

{Specimen : C-II }  
 {Annealing temperature: 965°C}

Experiment No.	Method of Annealing.	Capacity of Glass Bottle. (c.c.)	Time required to complete the Graphitization of Free Cementite.	
			(hr.)	(min.)
95	Fig. 13-a.	0	3	50
96	" b.	0	9+α	
97	" c.	1,100	8+α	
98	Ditto.	3,600	8+α	
99	Ditto.	8,100	4	0

From these results, the quantity of air in contact with Specimen C-II is found to greatly affect its graphitization; viz, it hardly graphitizes even in 8 hours when it is annealed in a minute quantity of air notwithstanding that its graphitization is completed in only 4 hours when it is annealed in a sufficient quantity of air. It is interesting to note also here that the specimen graphitizes very easily in vacuo (refer to Table IX).

(b) Experiment with Specimen D.

Specimen D was annealed in the manner as shown in Fig. 13-b and in air confined in the Honda's dilatometer which was sealed by conc. sulphuric acid. The results obtained are shown in Figs. 15 and 11, and summarized in Table XIV.

Fig. 15-a.

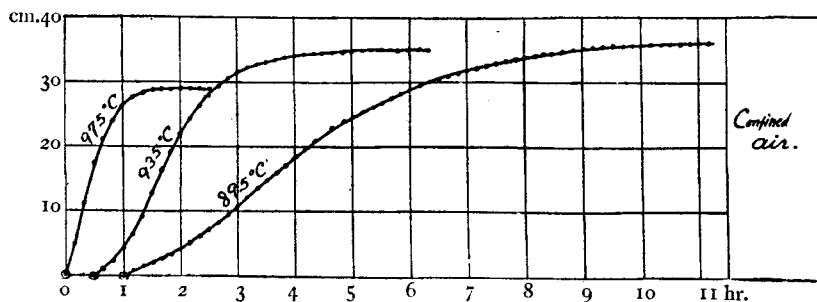
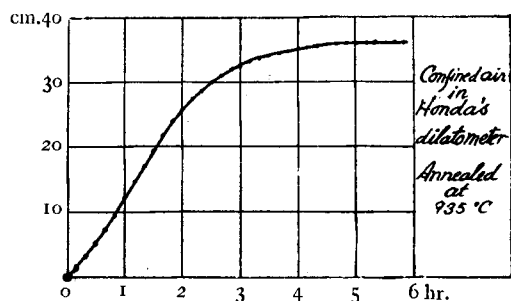


Fig. 15-b.



Comparing these results with those in Table XII, the quantity of air in contact with Specimen D has almost a negligible effect upon its graphitization.

(c) Conclusion.

Table XIV.

(Specimen: D)

Experiment No.	Method of Annealing.	Annealing Temperature. (°C)	Time required to complete the Graphitization of Free Cementite.	
			(hr.)	(min.)
100	Fig. 13-b.	975	2	0
101	Ditto.	935	5	20
102	Ditto.	895	10	0
103	Confined air in the Honda's dilatometer.	935	5	20

From the results obtained in the present experiments, a new phenomenon is found in the fact that the influence of the quantity of air in contact with white cast iron upon its graphitization is greatly dependent upon its composition; viz., the influence is very great on white cast iron containing a minute quantity of impurities excepting silicon, but almost negligible on white cast iron containing a moderate quantity of various impurities.

#### §4. Summary.

(1) A dilatometer was newly devised for the present investigation in which the specimen can be annealed in any gaseous atmosphere.

(2) The influence of various gases upon the time required to complete the graphitization of free cementite in white cast iron containing a minute quantity of impurities excepting silicon was measured at a constant temperature.

The graphitization in the specimen is completed in the shortest time in vacuo and carbon dioxide. It is completed in a somewhat longer time in air, nitrogen or in carbon monoxide than in vacuo or in carbon dioxide and it is remarkably retarded by hydrogen, ammonia or by methane. These relations are similar to those obtained in the graphitization in pure cast iron taking place during its solidification in various kinds of atmosphere (compare Fig. 4 and Fig. 12).

(3) The influence of various gases upon the graphitization in white cast iron having the composition as adopted in the manufacture of black

heart malleable cast iron was also measured and the results obtained were almost the same as those obtained on white cast iron containing a minute quantity of impurities excepting silicon.

(4) The influence of the quantity of air in contact with white cast iron upon its graphitization was measured and an interesting new phenomenon was found in the fact that it greatly depends upon the composition of white cast iron.

### **Chapter III. Some theoretical considerations on the influence of various gases upon graphitization.**

In regard to the theory on the mechanism of graphitization in cast iron, it has not yet been thoroughly propounded, although works have been devoted to it up to the present. The present writer, however, believes<sup>(14)</sup> that a great part of graphites in cast iron is produced by decomposition of cementite. If this be so, the graphitization in cast iron depends upon the stability of cementite. Profs. Honda and Murakami<sup>(15)</sup> published an opinion that graphites in pure cast iron are not produced by direct decomposition of cementite, but by its decomposition under the catalytic action of carbon oxides. According to them, the graphitization did not occur in pure cast iron which was melted in vacuo, hydrogen and nitrogen. This fact is one of the strong grounds supporting their theory. But the results obtained in the present investigation differ greatly from those obtained by them and can not be explained by their theory; viz, the graphitization in pure cast iron proceeds very favourably in vacuo; it proceeds also in nitrogen with almost same ease as in carbon monoxide; it, moreover, does not necessarily require the presence of carbon oxides in cast iron.

Now, the present writer puts forth the following hypothesis in order to explain the results obtained in the present investigation:

(1) Various gases are contained in cementite produced during the solidification of pure cast iron as long as it is not melted in vacuo.

(2) Cementite containing no gas is more unstable than that containing carbon dioxide, carbon monoxide, nitrogen or hydrogen.

14) Mem. Coll. Eng., Kyōto Imp. Univ.; 4, (1926), 159.

15) Sci. Rept., Tōhoku Imp. Univ.; 10, (1921), 273.

(3) The stability of cementite containing gases depends on the quantity and the kind of the gases which it contains; viz., as the quantity of the contained gases increases in cementite, its stability increases and reaches a maximum when it is saturated with these gases; the stability of cementite saturated with carbon dioxide, carbon monoxide or nitrogen is a little greater, and that saturated with hydrogen is far greater than that of cementite containing no gas.

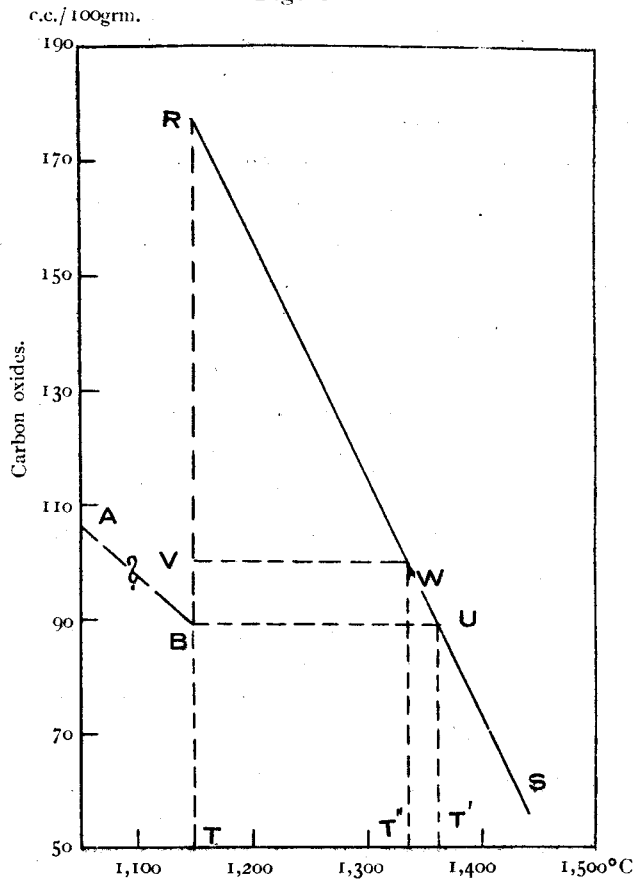
The results shown in Fig. 4 can be easily understood by the above hypothesis. The results of Experiment 31 to 34 are considered to be due to the fact that it requires a rather long time before molten cast iron is saturated by hydrogen. The present writer further proceeds to explain the phenomenon that the graphitization in cast iron containing gas occurs more remarkably in the outer part of the iron than in its interior.

It is a known fact that the excess of the gas contained in cast iron is liberated out of the iron when it solidifies and also that the solidification of cast iron proceeds from its outer surface into its interior. Then, when cast iron begins to solidify, the excess of the gas existing in the outer part of the iron is first liberated out and the excess of gas existing in its interior remains until last. In this case, the gas existing in the outer part of cast iron can be easily liberated out of the iron, but the escape of the gas from its interior, on the other hand, is difficult, because the interior is enveloped by the crust of solid or viscous mixture consisting of solid and melt when it begins to solidify. The interior thus solidifies under the pressure of the gas greater than atmospheric pressure. Then, the quantity of the gas contained in cementite produced during solidification of cast iron is greater in the interior than in the outer part which solidifies under about 1 atmospheric pressure of the gas. Consequently, cementite produced in the interior of cast iron is more stable than that produced in its outer part. The fact that this phenomenon occurs more remarkably in cast iron melted in hydrogen or in ammonia than in the iron melted in air, carbon dioxide, carbon monoxide or in nitrogen is probably due to the difference of the effect of these gases upon the stability of cementite.

The solubility of carbon oxides in molten cast iron decreases as the



Fig. 16.



temperature rises as shown in Fig. 1. Now, in Fig. 16, assume that curves AB and RS show the relation between the temperature and the solubility of these gases in pure cast iron having eutectic composition in solid and molten state respectively and also that RB is the quantity of these gases to be absorbed in the iron during melting or to be liberated out of the iron during solidification. If cast iron saturated with these gases at any temperature  $T''$  lower than  $T'$  cools at too quick a rate to absorb these gases, the total quantity of these gases in the iron remains almost practically constant until the temperature drops to its solidifying temperature when the quantity of these gases corresponding to BV is liberated out of the iron giving the above mentioned phenomenon. As readily seen from Fig.

16, the lower the temperature  $T''$ , the greater the quantity of these gases to be liberated from the iron during solidification. Then, as  $T''$  is low, the difference between the quantity of these gases contained in cementite produced in the outer part of cast iron and that in its interior becomes greater. Hence, it is acceptable that the lower the melting temperature of cast iron, the more remarkably occurs the phenomenon in question.

The cast iron containing various impurities, of course, can not be treated as pure cast iron. In this case, the stability of cementite probably depends greatly upon the quantity and also the kind of the element contained in it<sup>(16)</sup>. According to the results shown in Fig. 4, however, the influence of various gases upon the stability of cementite produced in Specimen B may be almost similar to the case of Specimen A.

Various gases are also contained in cementite in white cast iron, as long as it does not solidify in vacuo. When white cast iron is annealed in vacuo, it has to graphitize easily, because all gases are aspirated out of cementite. When white cast iron is annealed in a special gas, this gas will replace the gases contained in cementite and the quantity and the kind of gas absorbed in cementite shall greatly affect its graphitization.

The present writer wishes to confirm his consideration above mentioned and also to make it more complete by further investigation.

#### Chapter IV. Some practical problems concerning the present investigation.

##### § 1. So called "Umgekehrter Hartguss."

According to the experiences in German foundry practice, so called "Umgekehrter Hartguss" is liable to be produced in the following cases :

- (1) When scrap with much rust is used as a charge.
- (2) When charge with much sulphur is used.
- (3) When melting temperature is low.
- (4) When molten bath of the first tap is used.
- (5) When thin casting is made.

It is certain that this kind of casting is not produced owing to the

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16) Mem. Coll. Eng., Kyōto Imp. Univ., 4, (1926), 159.

17) St. E; 41, (1921), 569, 719.

segregation of the impurities contained in it. After Bardenheuer<sup>(17)</sup>, when cast iron having so called "critical composition" is cast, only the outer part of the casting is often converted to gray cast iron under the impinging action of some material in the mould in contact with the casting.

The author found in the present investigation that the gas contained in cast iron plays a principal role in the production of "Umgekehrter Hartguss". It is also readily recognized from the results of the present investigation that when cast iron having so called "critical composition" is melted at low temperature, or when molten cast iron contains a great quantity of carbon oxides owing to the use of rusty scrap as a charge, "Umgekehrter Hartguss" is liable to be produced. When molten cast iron contains a great quantity of hydrogen, the tendency for the production of this kind of casting is, of course, to be enlarged.

As casting is thick, the difference between the cooling rate of its outer part and that of its interior becomes greater when it is cast. In other words, the thicker the casting, the greater is the tendency that the graphitization proceeds more favourably in the interior than in the outer part of the casting. Hence, it is evident that "Umgekehrter Hartguss" is liable to be produced in thin casting.

§ 2. On the formation of the fine grained fracture surrounded by the coarse grained fracture in pig iron.

In the fracture of pig iron, we often observe<sup>(18)</sup> the fine grained part surrounded by the coarse grained part. This phenomenon also has not been fully explained. It was found by the present writer that molten cast iron containing a great quantity of hydrogen often produces such fracture after solidification. Hence, the present writer believes that the influence of hydrogen absorbed in molten cast iron in blast furnace is one of the principal causes producing pig iron giving such a fracture.

§ 3. Summary.

(1) From the results of the present investigation, it is concluded that so called "Umgekehrter Hartguss" is produced under the action of the gases contained in it.

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18) Taguma: Japanese J. I. S. I; 11, (1925), 697.

(2) The formation of the fine grained fracture in pig iron is probably due in some cases to the influence of the hydrogen absorbed in molten cast iron.

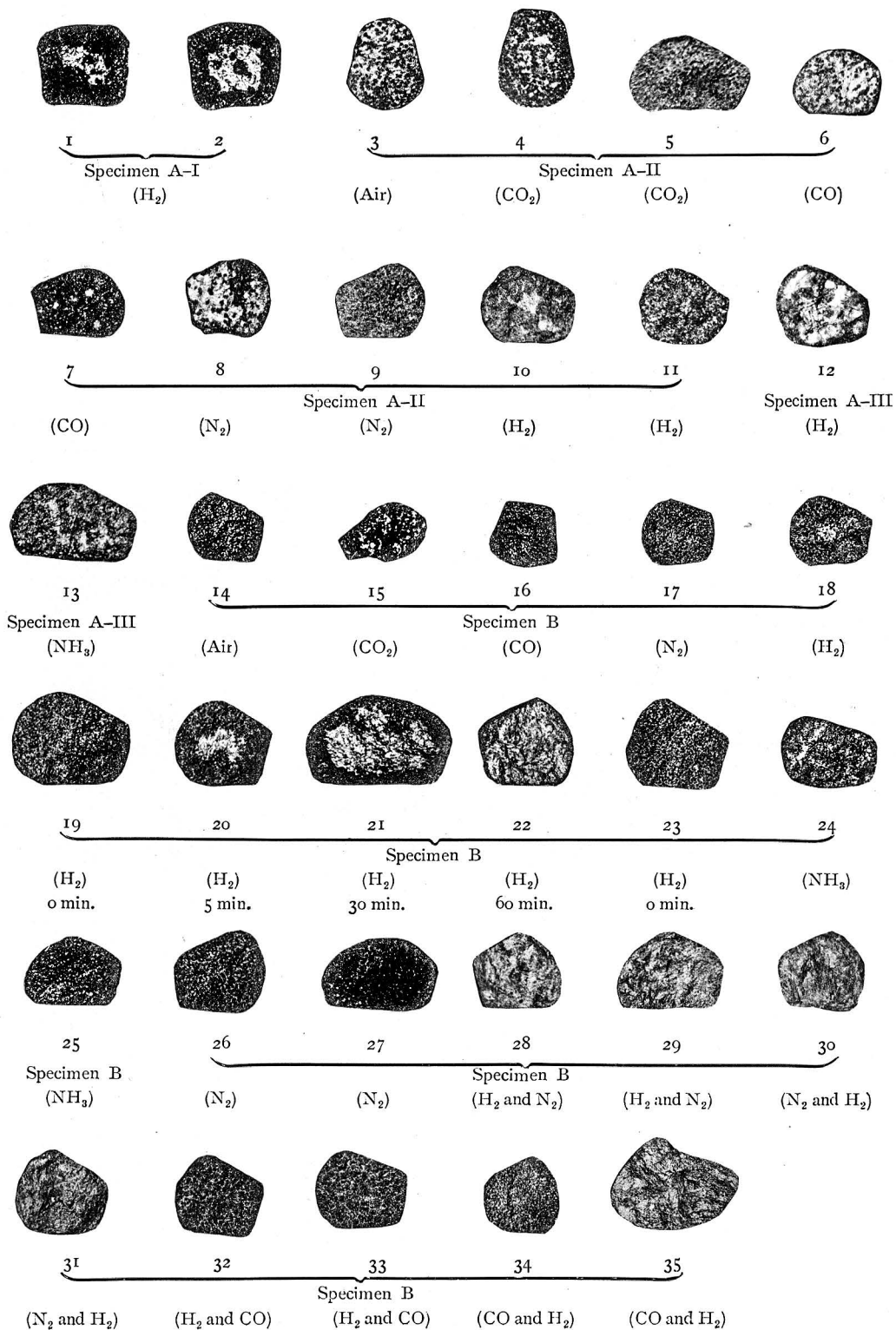
**Acknowledgement.**

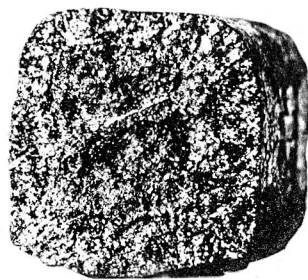
In conclusion, the present writer expresses h's cordial thanks to Prof. D. Saitō, under whose guidance the present investigation has been carried out.

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Fracture

× 2





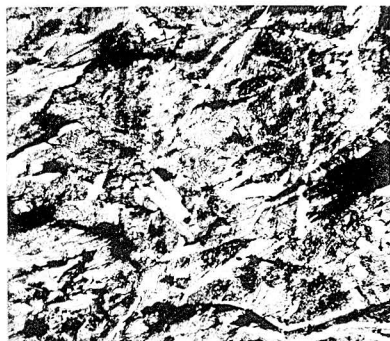
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Specimen A-I-3'  
(Exp. 3')  
(H<sub>2</sub>)



37 × 100  
Specimen A-I-1  
(Exp. 1)  
(Air)



38 × 100  
Specimen A-I-2  
(Exp. 2)  
(N<sub>2</sub>)



39 × 100  
Specimen A-I-3  
(Exp. 3)  
(H<sub>2</sub>)  
Outer part



40 × 100  
Specimen A-I-3  
(Exp. 3)  
(H<sub>2</sub>)  
Interior



41 × 100  
Specimen A-I-3'  
(Exp. 3')  
(H<sub>2</sub>)  
Outer part.



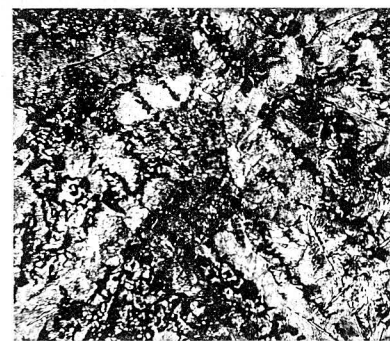
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(H<sub>2</sub>)  
Interior



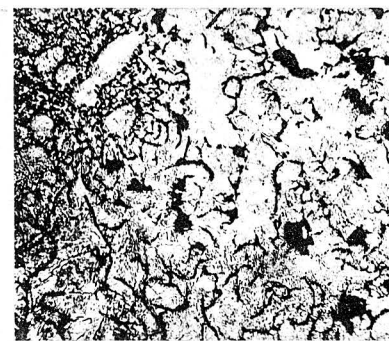
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Specimen A-I-4  
(Exp. 4)  
(Vacuo)



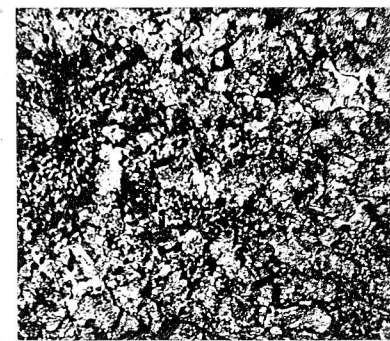
44 × 100  
Specimen A-II-2  
(Exp. 6)  
(Air)



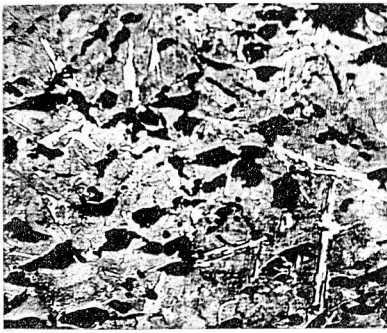
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(Exp. 8)  
(CO<sub>2</sub>)



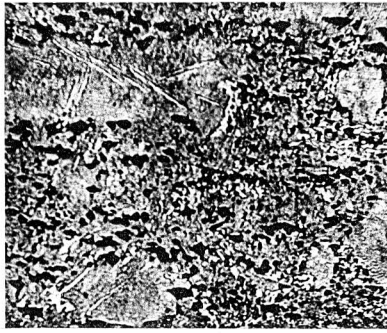
46 × 100  
Specimen A-II-6  
(Exp. 10)  
(CO)



47 × 100  
Specimen A-II-8  
(Exp. 12)  
(N<sub>2</sub>)



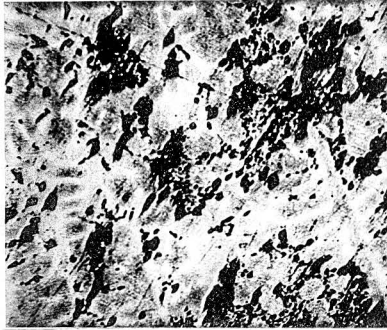
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Outer part



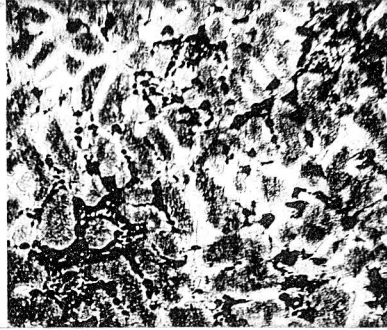
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Interior



50 X100  
Specimen A-III-3  
(Exp. 21)  
(NH<sub>3</sub>)



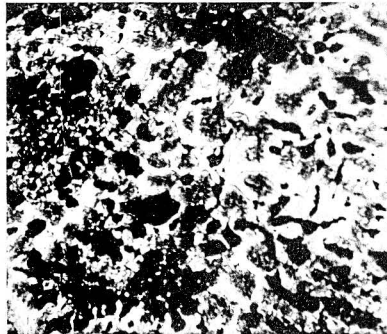
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Specimen B-1  
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(Air)



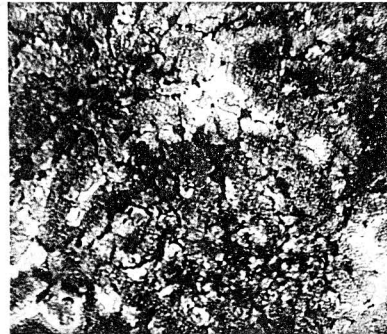
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(Exp. 24)  
(CO<sub>2</sub>)



53 X100  
Specimen B-3  
(Exp. 25)  
(CO)



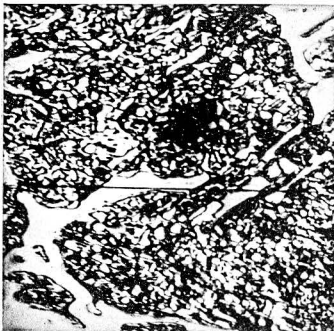
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(Exp. 26)  
(N<sub>2</sub>)



55 X100  
Specimen B-6  
(Exp. 28)  
(H<sub>2</sub>)



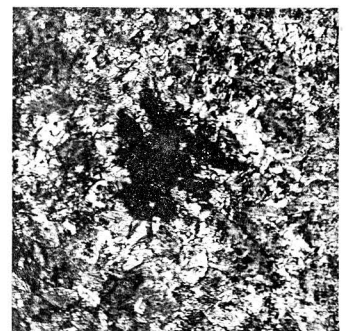
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(NH<sub>3</sub>)



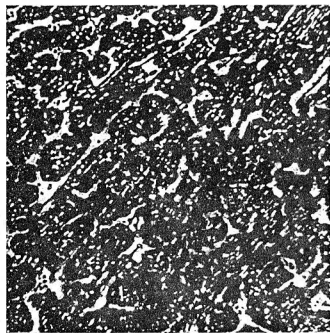
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(Vacuo)



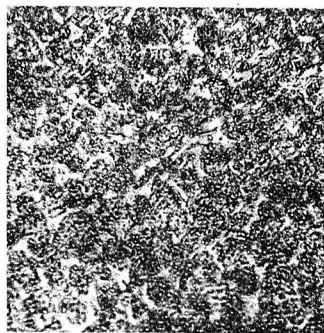
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Specimen C-I.  
(Exp. 53)  
(Vacuo)



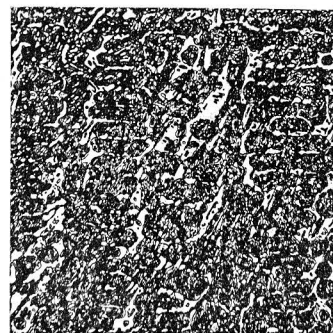
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(Exp. 54)  
(Vacuo)



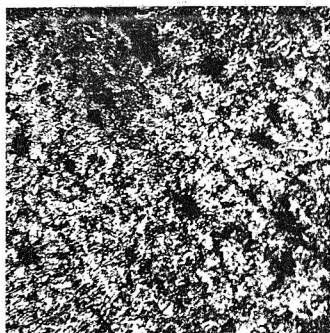
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(Exp. 57)  
(H<sub>2</sub>)



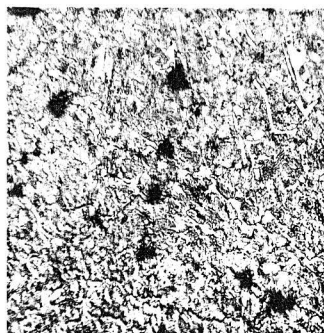
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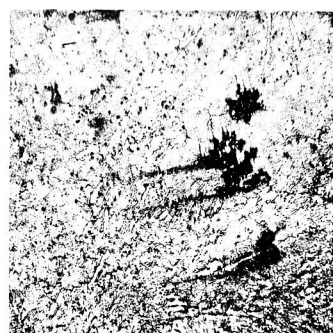
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Specimen C-I  
(Exp. 61)  
(CH<sub>4</sub>)



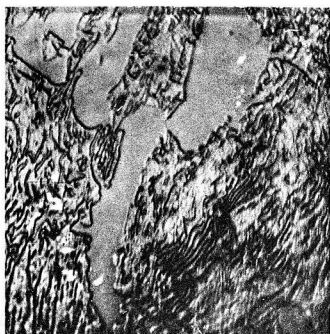
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(Exp. 63)  
(N<sub>2</sub>)



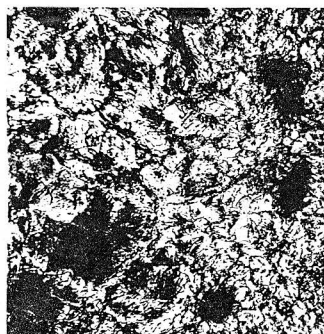
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(O<sub>2</sub>)



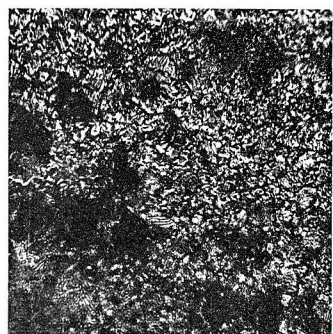
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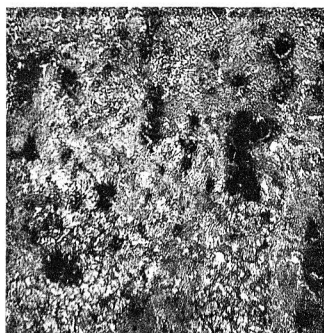
66 X600  
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(Exp. 75)  
(O<sub>2</sub>)



67 X100  
Specimen C-I  
(Exp. 67)  
(CO)



68 X100  
Specimen C-I  
(Exp. 69)  
(CO<sub>2</sub>)



69 X100  
Specimen C-I  
(Exp. 71)  
(Air)