

A New Phenomenon concerning the Graphitization of White Cast Iron and its Application to the Manufacture of Black Heart Malleable Castings.

By

Daikichi Saito and Hiroshi Sawamura.

(Received Apr. 19th, 1927.)

CONTENTS.

- Introduction.
- Part I. Theoretical Treatment of the New Phenomenon.
- § I. Method of investigation.
- § II. Investigation of the new phenomenon by heating white cast iron at a constant rate.
- A. Method of experiment.
- B. Influence of quenching temperature.
- C. Influence of quenching medium.
- D. Influence of repeated quenches.
- § III. Investigation of the new phenomenon by heating white cast iron at a constant temperature.
- A. Method of experiment.
- B. Influence of quenching temperature.
- C. Influence of quenching medium.
- D. Influence of repeated quenches.
- § IV. Relation between the stability of quenched white cast iron and its carbon and silicon contents.
- A. Method of experiment.
- B. On white cast iron quenched in water.
- C. On white cast iron quenched in rape-seed oil.
- § V. Theoretical consideration of the new phenomenon.
- § VI. Summary.

Part II. Practical Application of the new Phenomenon.

- § I. Some experiments on the diffusion of temper carbon in γ -iron.
 - A. Method of experiment.
 - B. Experiment.
- § II. Quenching experiments on some kinds of white cast iron castings.
 - A. Sample.
 - B. Method of experiment.
 - C. Results.
- § III. Tensile strength and elongation of the black heart malleable castings manufactured by the application of the new phenomenon.
 - A. Test bar.
 - B. Method of experiment.
 - C. Results.
- § IV. Characteristics of the new method of manufacturing black heart malleable castings.
- § V. Summary.
Acknowledgment.

INTRODUCTION.

Since Reaumur disclosed a process producing malleable castings in 1722, a great number of investigators have studied this subject. But, so far as the present writers know, they all used cast iron in its condition as cast as the starting material of their investigation; no information about the influence upon this industry of the heat treatment of white cast iron before annealing, has yet been published.

The present writers have paid attention to the last point and studied this unknown problem systematically. They discovered a new phenomenon, viz., that if white cast iron be hardened it becomes very unstable. In this paper, the new phenomenon and the results of some experiments carried out with the purpose of applying it to practice are intended to be treated.

PART I.

THEORETICAL TREATMENT OF THE NEW PHENOMENON.

§I. METHOD OF INVESTIGATION.

In the experiments to be described in this part, the present writers adopted Prof. Honda's dilatometer in order to measure accurately the progress of the graphitization in white cast iron as in the previous investigation.⁽¹⁾ Microscopical study was also made as a supplementary work of the dilatometer experiment. The details will be given when occasion arises.

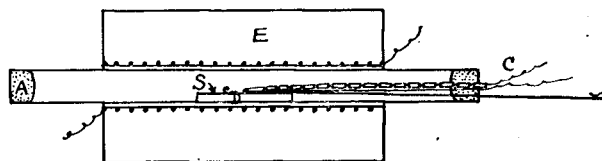
§II. INVESTIGATION OF THE NEW PHENOMENON BY HEATING WHITE CAST IRON AT A CONSTANT RATE.

A. Method of experiment.

Specimen:— White cast iron of suitable composition was cast in green sand moulds 6 m. m. thick and 200 m. m. long. The dilatometer specimens were then prepared in the form of a cylindrical rod 5 m. m. thick and 70 m. m. long by cutting and grinding the bar.

Method of quenching the specimen:— When the quenching of the specimen was required, the apparatus as shown in Fig. 1 was used. The specimen (S) laid in an electric resistance furnace (E) was heated at a constant rate, 20° C per min., and as soon as it was raised to a required temperature, it was drawn out of the furnace and thrown into a quenching medium filled in a beaker of 500 c. c. capacity as swiftly as possible.

Fig. 1.



- A: Asbestos stopper.
- C: Thermo-couple.
- E: Electric furnace.
- S: Specimen.

(1) Mem. Coll. Eng., Kyoto Imp. Univ., vol. 4 (1926), p. 159.

Method of heat treatment of the specimen during the dilatometer experiment:— In all the experiments of this kind, the specimen was heated to a required temperature at a constant rate, 10° C per min., and then immediately furnace cooled. During this heat treatment, the cover of the dilatometer was tightly closed from the open air.

B. Influence of quenching temperature.

The specimens were quenched from various temperatures in water at 15° C, and the influence of the quenching temperature on the stability of white cast iron was studied. The analysis of the specimen used in this experiment is given in Table I.

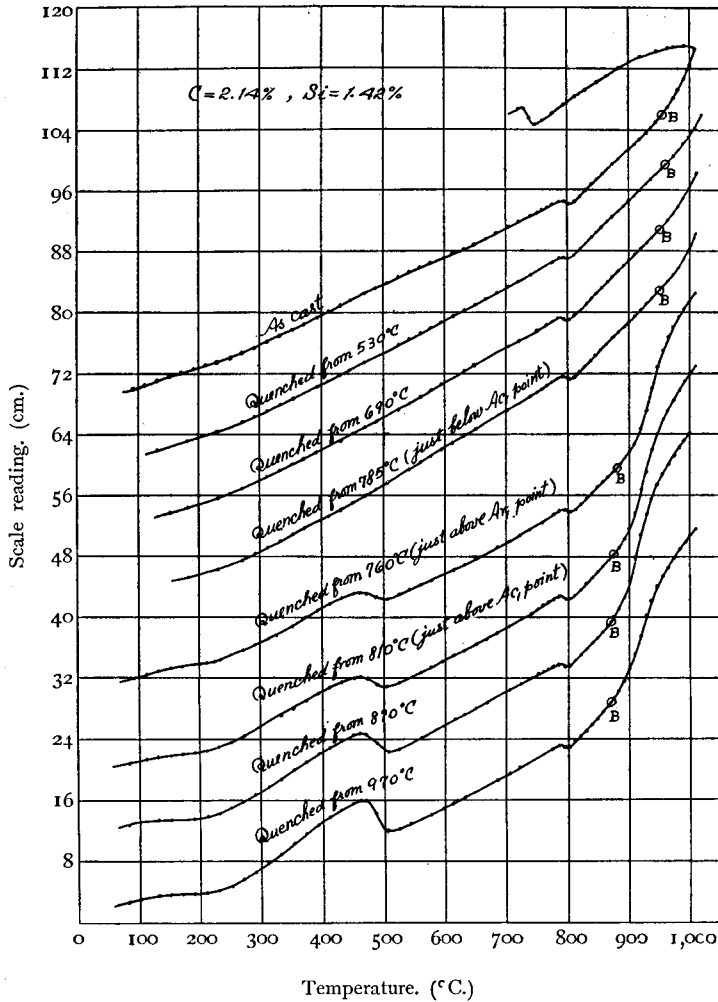
Table I.

Specimen No.	Composition (%).					
	C	Si	Mn	P	S	Cu
A	2.14	1.42	0.34	0.094	0.053	0.23

Table II.

Specimen No.	Quenching temperature. (°C.)	Method of quenching.	Beginning temperature of graphitization. (°C.)	Remarks.
A. a. 1	As cast.		955	Always quenched in water at 15°C.
„ 2	530	Usual.	960	
„ 3	690	Ditto.	950	
„ 4	785 (Just below the A_{c1} point.)	Ditto.	950	
„ 5	760 (Just above the A_{r1} point.)	Furnace cooled after heating up to 850°C by the usual method and quenched as soon as its temp. fell to 760°C.	880	
„ 6	810 (Just above the A_{c1} point.)	Usual.	875	
„ 7	870	Ditto.	870	
„ 8	970	Ditto.	870	

Fig. 2.



The quenching temperatures are summarised in Table II. Fig. 2 shows the results of the dilatometer experiment. In the figure, the abscissa represents the temperature of the specimen and the ordinate the scale reading corresponding to the expansion of it. The heating curves show that only the specimens which were quenched from the temperatures above the A_1 point contracted in two steps at about 170°C and 470°C . It is due to the tempering of α - and β - martensite as explained by Prof.

Honda.⁽¹⁾ Hence, the higher the quenching temperature, the more remarkable the contraction in question, as the higher the quenching temperature, the greater the amount of austenite concerned in the hardening.

The beginning temperatures of the graphitization of the specimens are marked with the letter *B* on the curves and as summarised in Table II.

From these results, the following new phenomena become evident :

(1) The hardening of white cast iron has a remarkable relation to its stability.

(2) Hardened white cast iron graphitizes far more easily than white cast iron in its cast state.

(3) The higher the hardening temperature of white cast iron, the easier proceeds its graphitization. But the influence in this direction is not so remarkable.

The specimen in its cast state consists of pearlite and free cementite and its structure is similar to that shown in Photo. No. 5. The typical structure of the specimens in an annealed state is shown in Photos. Nos. 1 to 4. Comparing these photographs, it is evident that there is a great difference in the structures of the annealed specimens which were as cast, or quenched from temperatures below the A_1 point, and quenched from temperatures above the A_1 point before annealing. That is, in the former two, a considerable amount of free cementite remains ungraphitized in the pearlite matrix, indicating the fact that graphitization had not proceeded to any considerable extent; but in the latter, free cementite is sought for in vain and a small area of pearlite is found imbedded in the ferrite matrix, evidence that graphitization had proceeded very easily in this case. Moreover, in the former, temper carbon of round form, large in size and few in number, in the latter, of somewhat elongated form, small in size and many in number, is to be observed.

C. Influence of quenching medium.

The specimens, the analysis of which is given in Table III, were quenched always from 850° C in various quenching media as given in

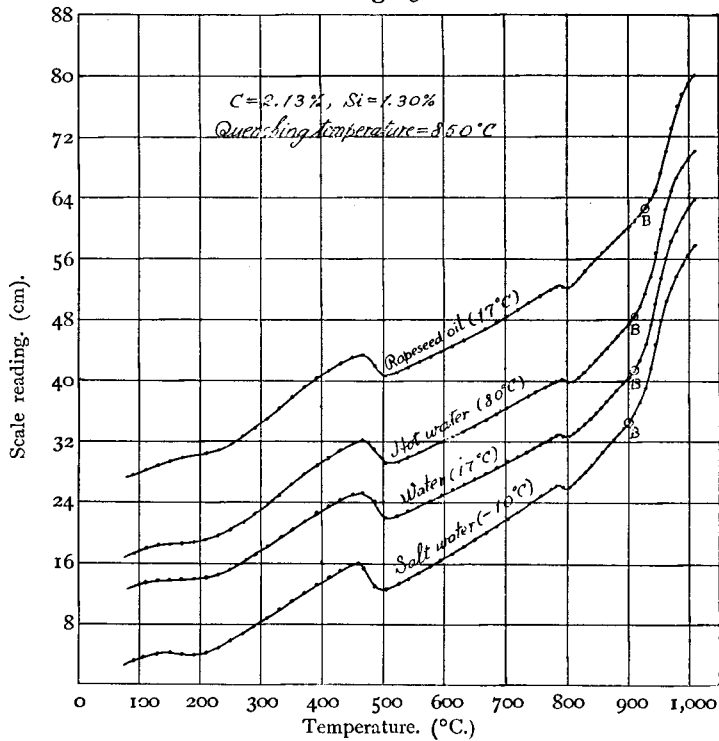
(1) Sci. Rep., Tohoku Imp. Univ., vol. 8 (1919), p. 181.

Table IV and the influence of the cooling rate on the graphitization of the specimens during quenching was measured. Fig. 3 shows the results of this experiment. The beginning temperature of the graphitization of the specimens is marked on these curves with the letter *B* and as summarised in Table IV.

Table III.

Specimen No.	Composition (%)					
	C	Si	Mn	P	S	Cu
B	2.13	1.30	0.33	0.096	0.053	0.23

Fig. 3.



The structure of the annealed specimens was quite similar to that shown in Photos. Nos. 3 and 4, but it was found that the greater the cooling rate of the specimen during quenching, the smaller the amount of pearlite in the ferrite matrix.

Table IV.

Specimen No.	Quenching medium.	Temperature of quenching medium. (°C.)	Beginning temperature of graphitization. (°C.)	Remarks.
B. 1	Salt water.	-10	900	Always quenched from 850°C.
" 2	Water.	17	910	
" 3	Water.	80	910	
" 4	Rape-seed oil.	17	930	

All these results show the tendency that the greater the cooling rate of white cast iron during quenching, the easier proceeds its graphitization.

But the variation in the cooling rate during quenching of the degree as indicated in this experiment has comparatively little effect on the result.

D. Influence of repeated quenchings.

In the previous experiments, measurements were carried out on the specimens which were quenched only once. In the present experiment, four rods of Specimen No. A were quenched repeatedly from 810° C in water at 15° C so many times as summarised in Table V and its influence on the graphitization was measured. Fig. 4 shows the results. The beginning temperature of graphitization of the specimens is shown with the mark *B* on these curves, and summarised in Table V.

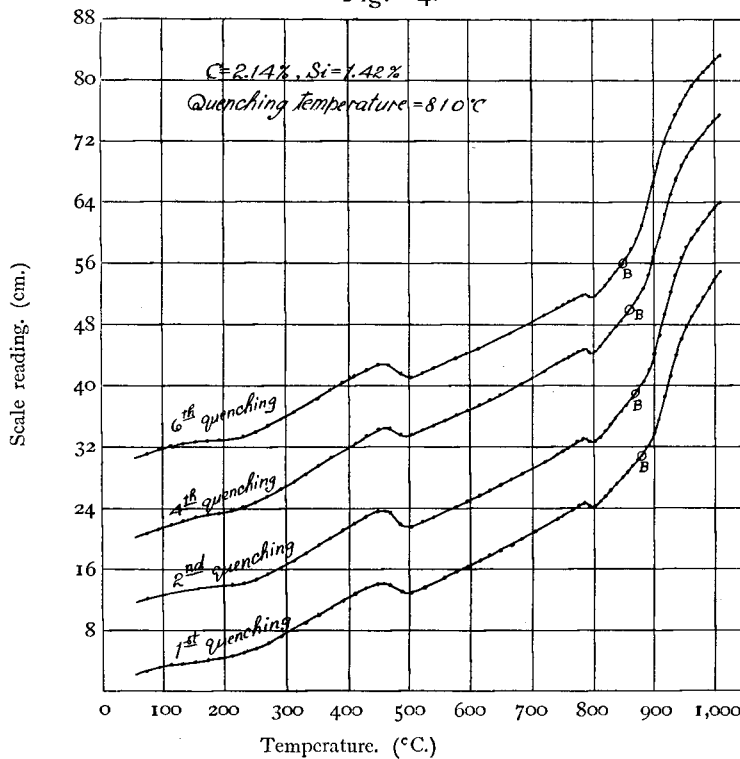
Table V.

Specimen No.	Number of times of quenching.	Beginning temperature of graphitization. (°C.)	Remarks.
A. b. 1	1	880	Always quenched in water at 15°C from 810°C.
" 2	2	870	
" 3	4	860	
" 4	6	850	

The structure of the annealed specimens was all similar to that shown in Photos. Nos. 3 and 4, but it was found that the greater the

number of repetitions of quenching, the smaller the amount of pearlite in the ferrite matrix.

Fig. 4.



These results show the fact that the greater the number of repetitions of quenching of white cast iron, the easier proceeds its graphitization. But the influence of quenching more than twice is not so remarkable as the first quenching.

§ III. INVESTIGATION OF THE NEW PHENOMENON BY HEATING WHITE CAST IRON AT A CONSTANT TEMPERATURE.

A. Method of experiment.

As the experiments to be described in this and the succeeding paragraphs have an intimate relation to the industry of black heart malleable castings, care was taken in every respect to carry them out under as nearly like actual conditions as possible.

Specimen:— Metal of suitable composition melted in a kryptol furnace was cast in 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 them.

The fineness of the structure of the specimens is shown in Photo No. 5. It is almost the same as that of the white cast iron casting which is cast for the manufacture of black heart malleable casting in practice.

Method of quenching:— As required, the specimens were quenched in exactly the same manner as described in the preceding paragraph.

Method of heat treatment of the specimens in dilatometer experiments:— The specimens were first kept at a predetermined temperature above the A_1 point for a sufficient time completely to decompose the free cementite, and then furnace cooled to room temperature or, in some cases, cooled at a constant rate to a temperature below the A_1 point and kept again at a definite temperature below the A_1 point in order to find a sufficient time to decompose the eutectoid cementite and hypereutectoid cementite if present. For convenience, the present writers call the graphitization of free cementite taking place above the A_1 point "the graphitization in the first stage," and that of the eutectoid cementite and hypereutectoid cementite, if present, taking place below the same point, "the graphitization in the second stage," following the proposal of Dr. Kikuta.⁽¹⁾

The rate of heating and cooling of the specimens were as follows:

(1)

Heating,

Room temperature \leftarrow 10° C per min. \rightarrow the annealing temperature for the graphitization in the first stage (kept).

Cooling,

The annealing temperature for the graphitization in the first stage \leftarrow furnace cooling \rightarrow room temperature.

(1) Sci. Rep. Tohoku Imp. Univ., Vol. 15 (1926), p. 120.

or

(2)

Heating,

Room temperature $\leftarrow 10^{\circ}\text{C}$ per min. \rightarrow the annealing temperature for the graphitization in the first stage (kept).

Cooling,

The annealing temperature for the graphitization in the first stage $\leftarrow 10^{\circ}\text{C}$ per min. $\rightarrow 700^{\circ}\text{C} \leftarrow 10^{\circ}\text{C}$ per min. $\rightarrow 730^{\circ}\text{C}$ or 740°C (kept) \leftarrow furnace cooling \rightarrow room temperature.

The heat treatment was always carried out in an air-tight dilatometer the same as in the previous experiment, and it was recorded in every case by a recording pyrometer. Although keeping such high temperatures constant for a long time was thought to be very difficult, a constancy of temperature with a maximum variation of 2°C at the annealing temperature for the graphitization in the first stage, and 1°C at the annealing temperature for the graphitization in the second stage, could be obtained throughout the experiments, by the regulation of the temperature with special care. The reading of the scale was taken every 10°C or 20°C during heating and cooling, and every 10 minutes during the time in which the temperature was kept constant.

B. Influence of quenching temperature.

Specimens of two different composition were used in this experiment. The analyses are given below :

Table VI.

Specimen No.	Composition (%)					
	C	Si	Mn	P	S	Cu
P	2.80	1.21	0.28	0.193	0.072	0.17
Q	2.38	1.24	0.30	0.102	0.053	0.24

Specimen No. *P* was quenched in water at 24°C , and Specimen

No. Q in rape-seed oil at 12°C , from various temperatures as summarised in Table VII, and the water-quenched specimens were annealed in two steps at 920°C and 740°C , and the oil-quenched specimens only at 925°C . The heating and cooling curves are shown in Fig. 5, in which the abscissa represents the temperature and the ordinate the scale reading

Fig. 5-a.

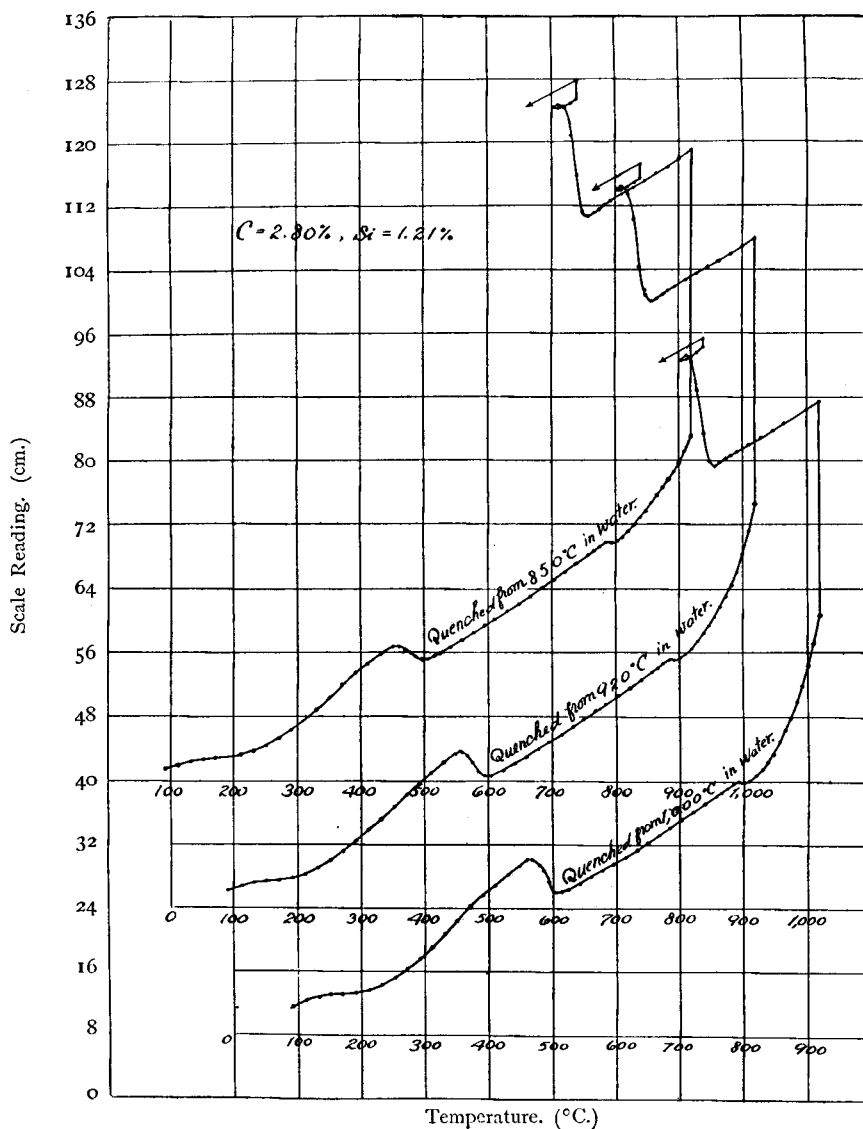
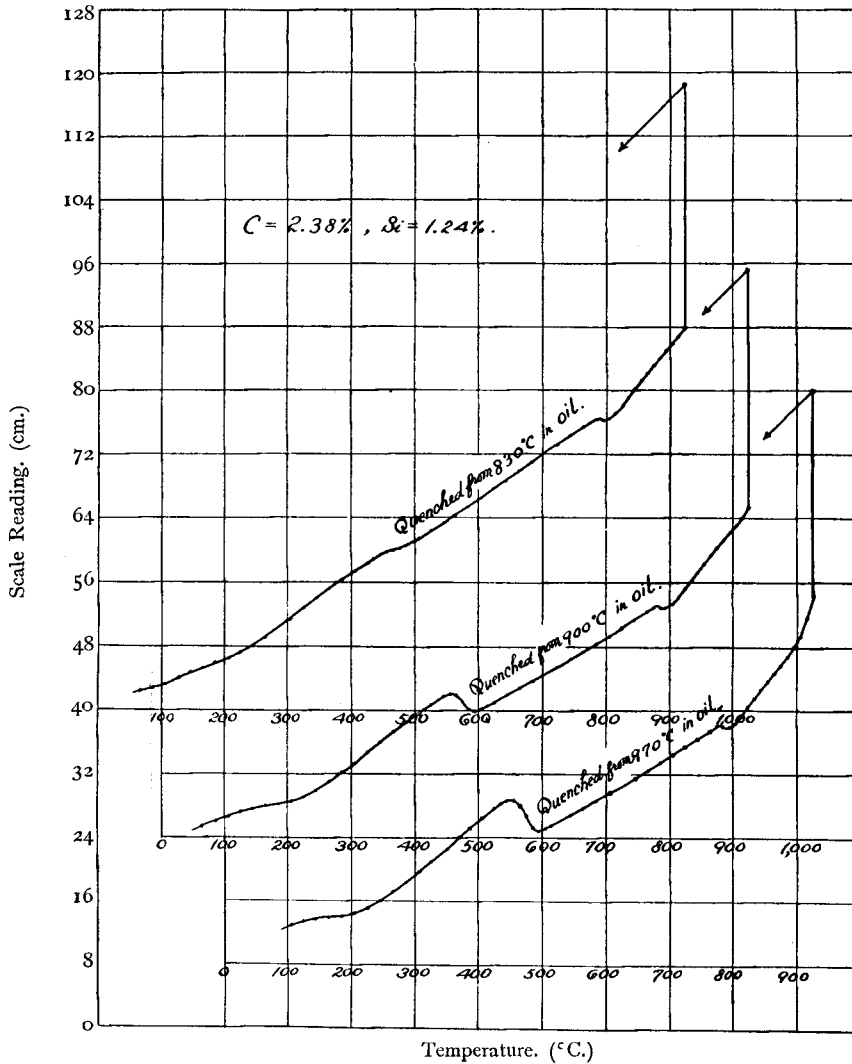


Fig. 5-b.



corresponding to the dilation of the specimen. The scale of temperature in the figure is slipped every 100° C in order to avoid overlapping of the curves.

From these curves, the fact is known that all the water-quenched specimens and the oil-quenched specimens from 970° C, had grown owing to their partial graphitization before they were raised to the annealing temperature for the graphitization in the first stage. The oil-quenched

specimens from 900° C and 830° C had begun to graphitize after they were raised to the temperature above cited.

Fig. 6-a.

Water-quenched specimens.

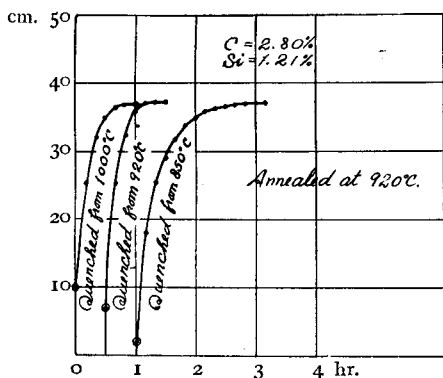


Fig. 6-b.

Oil-quenched specimens.

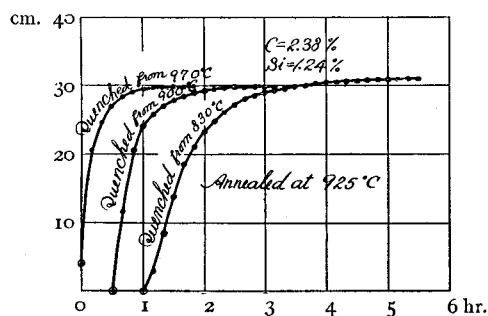
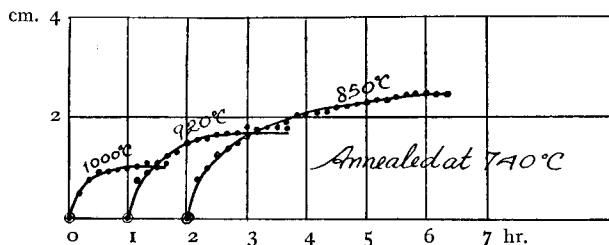


Fig. 7.

Water-quenched specimens.



The dilation of the specimens during the time in which the annealing temperatures for the graphitization in the first and the second stages were kept constant is shown in these curves as straight lines perpendicular to the abscissa at these temperatures.

Figs. 6 and 7 show respectively the progress of graphitization at the annealing temperatures for the graphitization in the first and the second stages; and Fig. 6-a relates to the water-quenched specimens and Fig. 6-b to the oil-quenched specimens. In these figures, the abscissa represents the time in hours during which the specimens were kept at the temperatures above-mentioned and the ordinate the dilation on the scale in centimeter

which is proportional to the amount of cementite graphitized. The dilation due to the partial graphitization which had occurred before the specimens were raised to the annealing temperature for the graphitization in the first stage is shown as the dilation at the start of the annealing on the curves corresponding to these specimens in Fig. 6.

The time required to complete the graphitization in the first and the second stages which should be determined on Figs. 6 and 7, as well as other data in this experiment are summarised in Table VII.

Table VII.

Specimen No.	Quenching temperature. (°C.)	Time required to complete the graphitization.		Remarks.
		In the first stage. (hrs.—mins.)	In the second stage. (hrs.—mins.)	
P. a. 1	850	1 50	4 0	Always quenched in water at 24°C.
„ 2	920	0 50	1 30	
„ 3	1,000	0 50	1 0	
Q. 1	830	4 0		Always quenched in rape-seed oil at 13°C.
„ 2	900	2 0		
„ 3	970	1 30		

The results evidently show that, in both the cases, the higher the quenching temperature of white cast iron, the easier proceeds its graphitization in the first stage. The time required to complete the graphitization in the second stage of white cast iron is also liable to be shorter.

C. Influence of quenching medium.

Four iron rods of Specimen No. *P* (in Table VI) were always quenched from 850° C respectively in the four kinds of quenching medium as given in Table VIII, in which they were cooled at different cooling rates. The quenched specimens were then annealed in two steps, at 920° C, and at 740° C. The graphitization-time curves are shown in Figs. 8 and 9.

Table VIII.

Specimen No.	Quenching medium.	Temperature of quenching medium. (°C.)	Time required to complete the graphitization.		Remarks.
			In the first stage. (hrs. - mins.)	In the second stage. (hrs.-mins.)	
P. b. 1	Salt water.	-10	1 30	3 0	Always quenched from 850°C.
" 2	Water.	25	1 40	3 30	
" 3	Water.	80	2 30	2 30	
" 4	Rape-seed oil.	28	6 0	9 0	

Fig. 8.

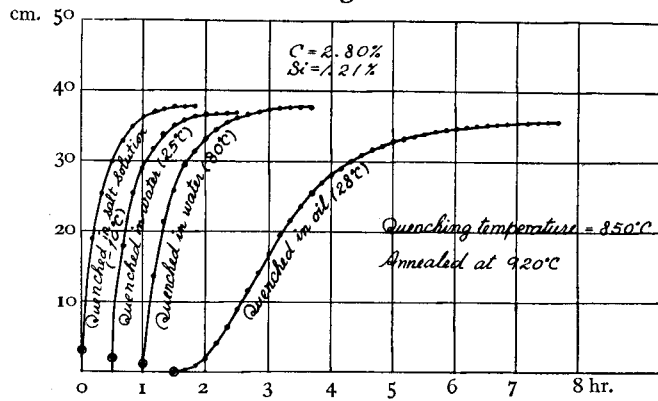
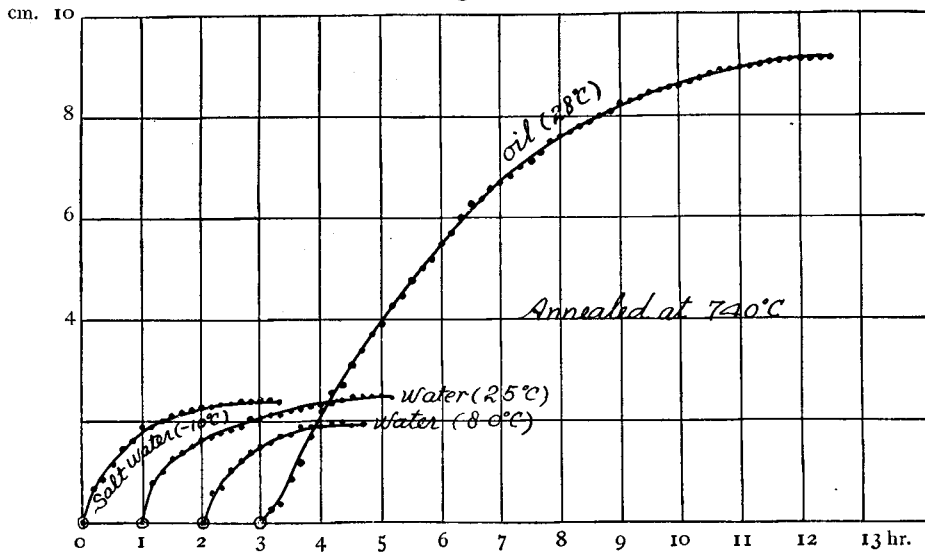


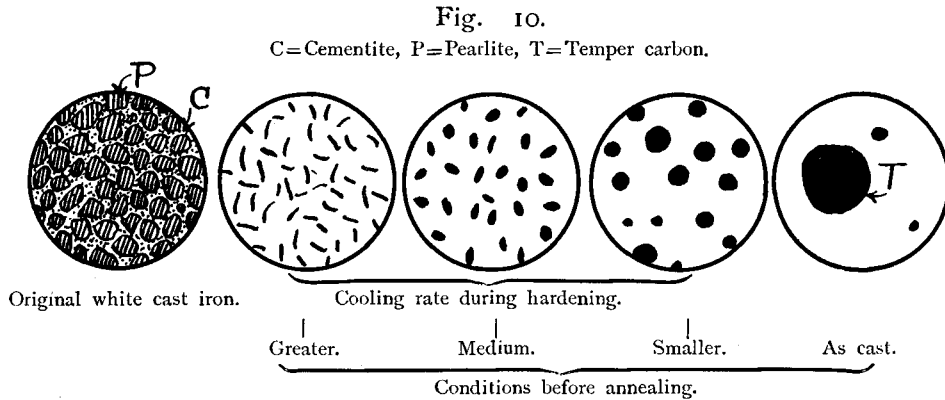
Fig. 9.



The former relates to the graphitization in the first stage and the latter to that in the second stage. The time required to complete the graphitization as well as other data are summarised in Table VIII.

From these results, the general tendency can be ascertained that the greater the cooling rate of white cast iron during quenching, the easier proceeds its graphitization in the first stage and the shorter the time required to complete the graphitization in the second stage.

It is interesting to find the fact that the size and form of the temper carbon produced greatly depend on the cooling rate during the quenching of the white cast iron; the temper carbon in the iron which was severely quenched before annealing is flaky and fine, but, as the cooling rate during the quenching of white cast iron is small, the temper carbon produced gradually becomes nodular and large as shown in Photos Nos. 6, 7 and 8. Fig. 10 represents the ideal case of the above phenomena.



D. Influence of repeated quenchings.

A specimen belonging to Specimen No. *P* and another kind of white cast iron, the analysis of which is shown in Table IX, were adopted in this experiment. Specimen No. *P* was quenched from 850° C in water at 24° C and Specimen No. *R* in rape-seed oil at 14° C from 900° C repeatedly predetermined times as given in Table X. The water-quenched specimen was then annealed at 920° C and the oil-quenched one at 925° C. Fig. 11 shows the graphitization-time curves of the water-quenched specimens,

and Fig. 12 that of the oil-quenched specimens. The time required to complete the graphitization in the first stage as well as other data are summarised in Table X.

Table IX.

Specimen No.	Composition (%).					
	C	Si	Mn	P	S	Cu
R	2.49	1.07	0.32	0.121	0.051	0.23

Table X.

Specimen No.	Number of times of quenching.	Time required to complete the graphitization in the first stage. (hrs.—mins.)	Remarks.
P. c. 1	1	1 40	Always quenched in water at 24°C from 850°C.
„ 2	2	1 0	
„ 3	3	0 50	
R. 1	1	4 0	Always quenched in rape-seed oil at 14°C from 900°C.
„ 2	2	2 30	
„ 3	3	2 0	

Fig. 11.

Water-quenched specimens.

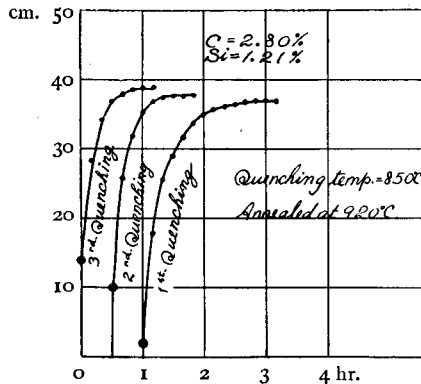
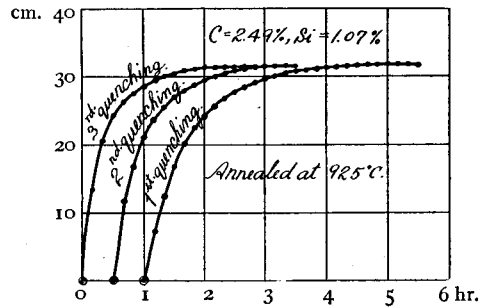


Fig. 12.

Oil-quenched specimens.



From the results obtained here, it was found that as the quenchings of white cast iron were repeated, its stability become smaller. But there is probably a limit to this influence.

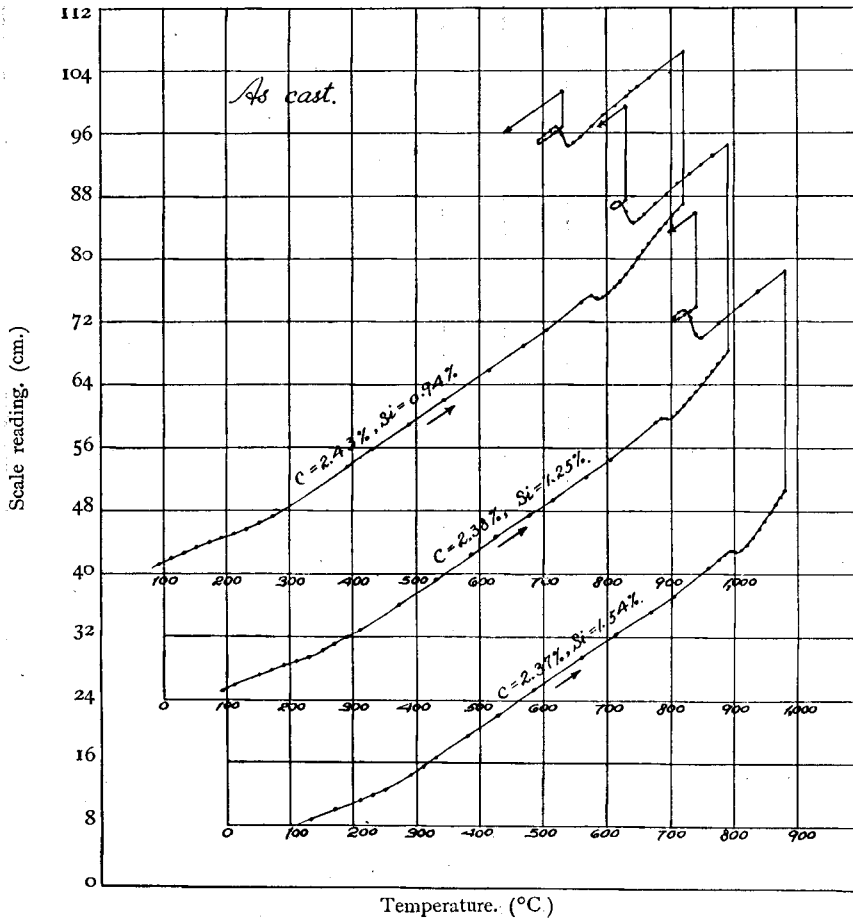
§IV. RELATION BETWEEN THE STABILITY OF QUENCHED WHITE CAST IRON AND ITS CARBON AND SILICON CONTENT.

A. Method of experiment.

The method of this experiment is just the same as in the previous experiment.

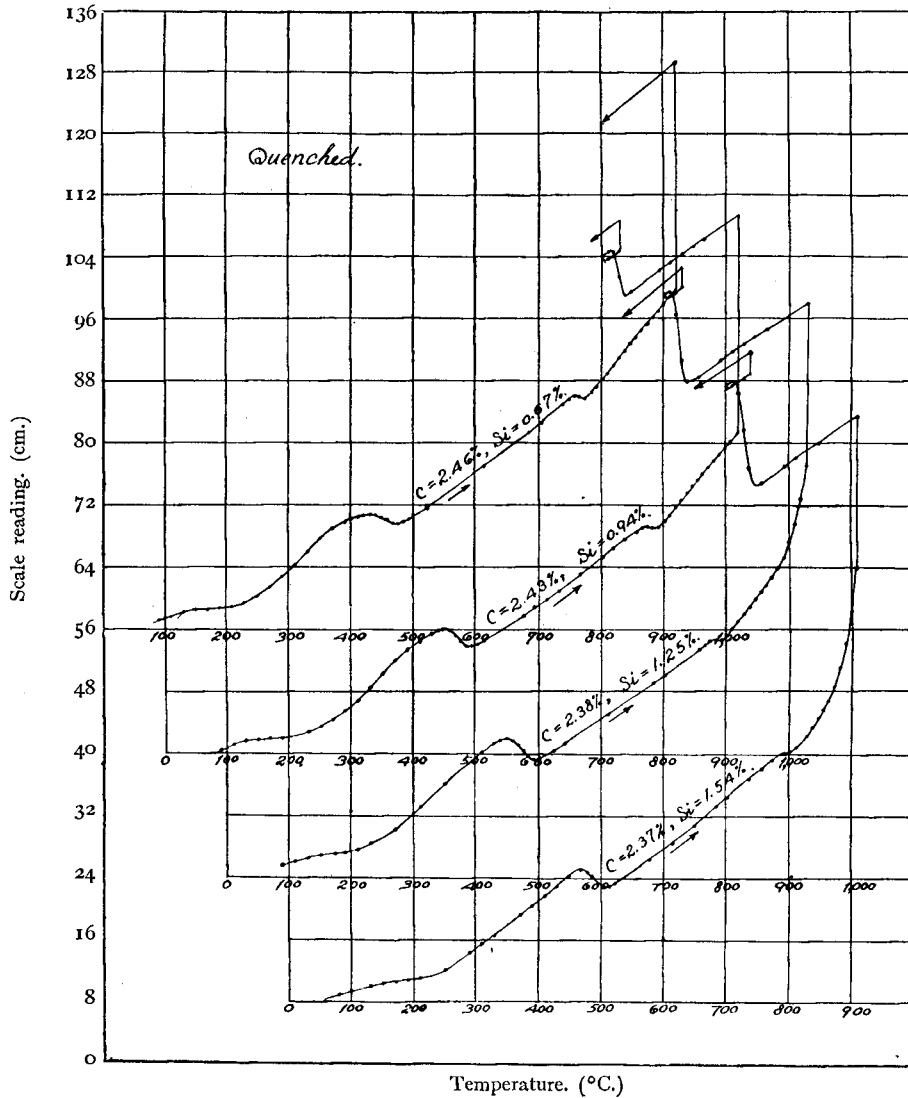
Recently Dr. Kikuta⁽¹⁾ measured the time required to complete the graphitization in the first stage of white cast irons containing different

Fig. 13.



(1) Loc. cit.

Fig. 14.

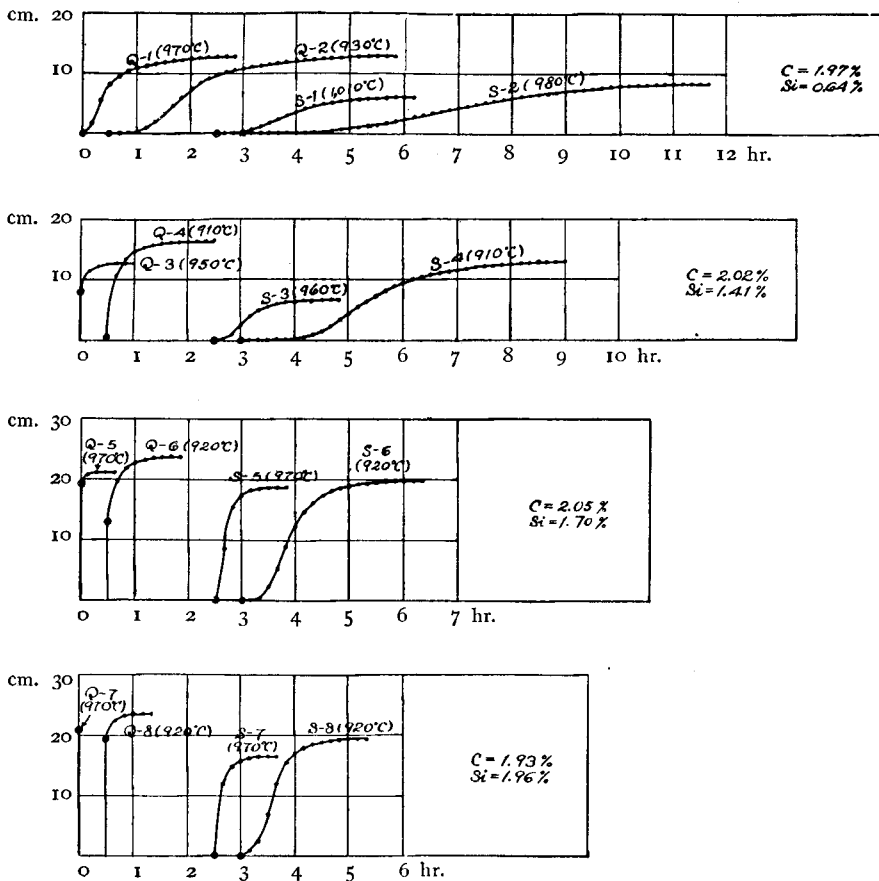


amounts of carbon and silicon, keeping their temperature constant at a predetermined temperature—925° C. The object of the present experiment is to determine what influence the quenching of white cast iron has on its graphitization. As, for this purpose, it is necessary to get exact knowledge as to the stability of white cast iron in its cast state, the present writers were compelled to repeat Dr. Kikuta's experiment. In the present

experiment, however, pieces of white cast iron in its cast state were kept to be annealed at various temperatures above the A_1 point, and the relation among the carbon and silicon contents of the irons, the annealing temperature and the time required to complete the graphitization were experimentally confirmed. The same relations as above were also found in the quenched white cast iron for comparison.

The time required to complete the graphitization in the second stage was measured only on the cast irons which were recognized as necessary for the application to practice.

Fig. 15-a.



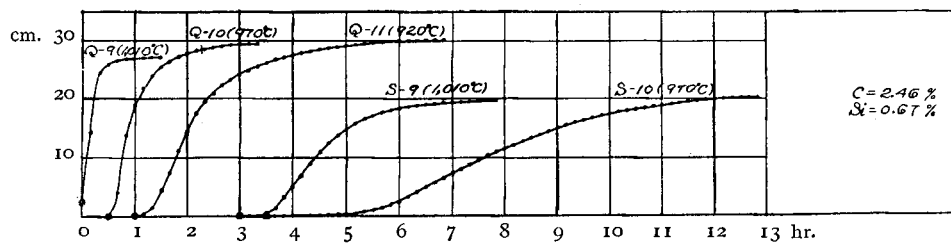
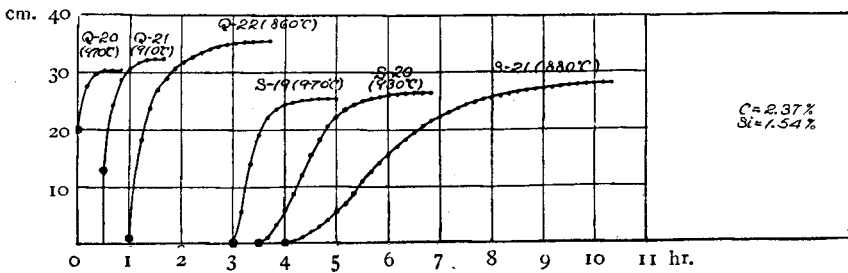
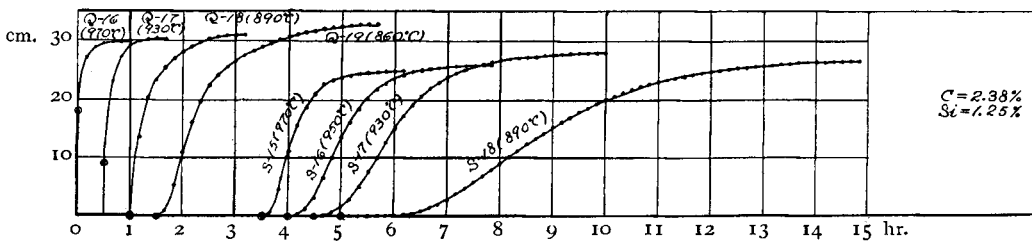
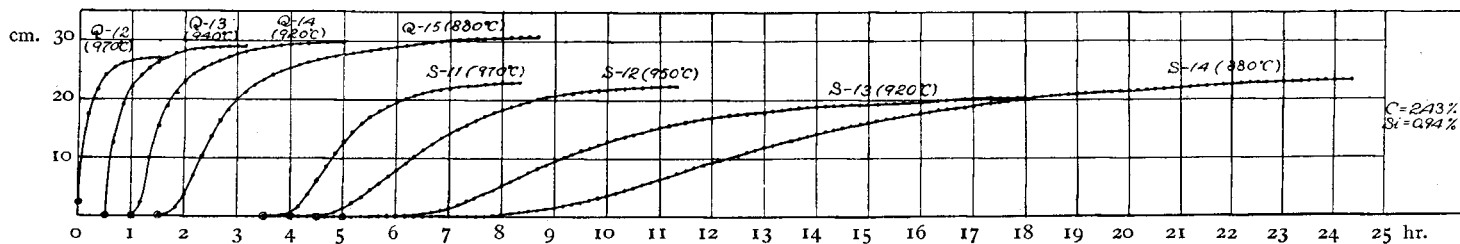


Fig. 15-b.



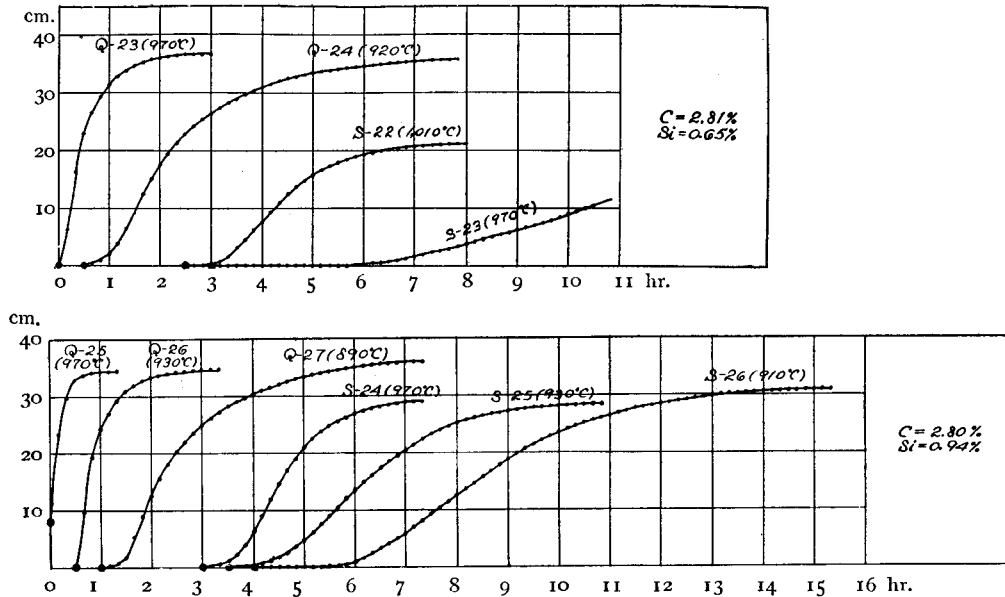
B. On white cast iron quenched in water.

Specimens:— The analysis of the specimens used in this experiment is given in Table XI in which the specimens are separated in five groups, *L-a* to *L-e*, according to the carbon content. As required, the specimens were quenched always in water at 24° C from 850° C.

Dilatometer experiment:— Figs. 13 and 14 show respectively the typical cooling curves of the specimens in their cast and quenched states before annealing, the other curves of the same kind being omitted here.

The progress of graphitization in the first stage at various temperatures is shown in Fig. 15 in which the curves marked with an *S* relates to the specimens in the cast state and those marked with a *Q* to the quenched specimens. The graphitization-time curves in the second stage are shown in Fig. 16, the letters marked on the curves having the same meaning as above. In these curves, No. *S'-21'*, for example, represents the graphitization curve in the second stage of the specimen, the graphitization in the first stage of which was completed as the curve No. *S-21* in Fig. 15-b.

Fig. 15-c.



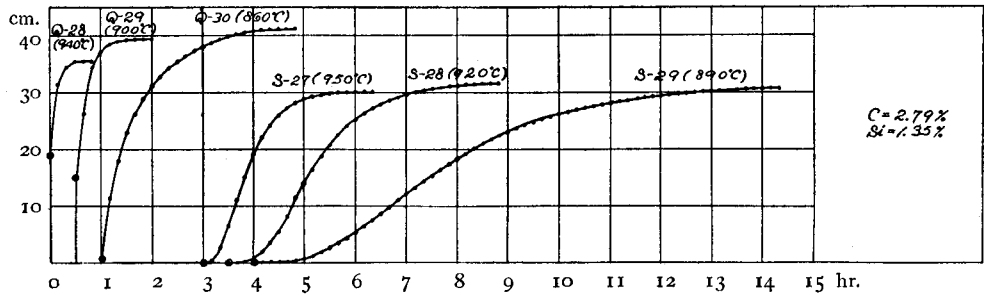


Fig. 15-d.

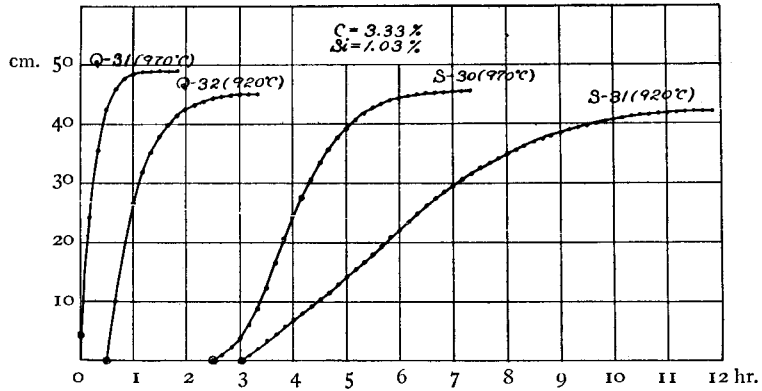


Fig. 15-e.

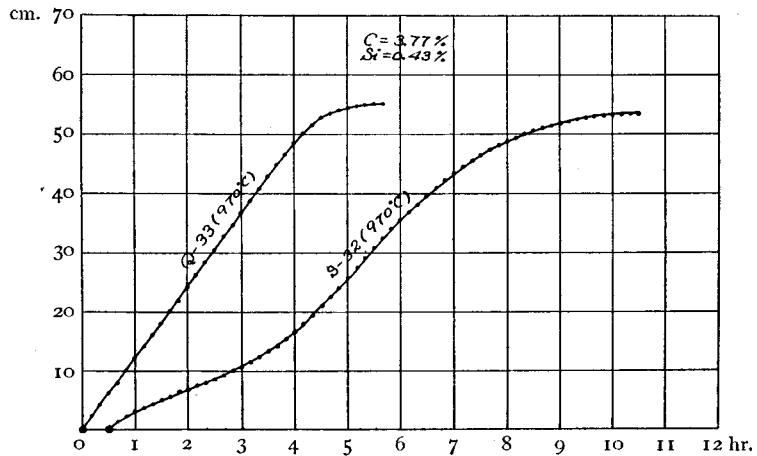


Fig. 16-a.

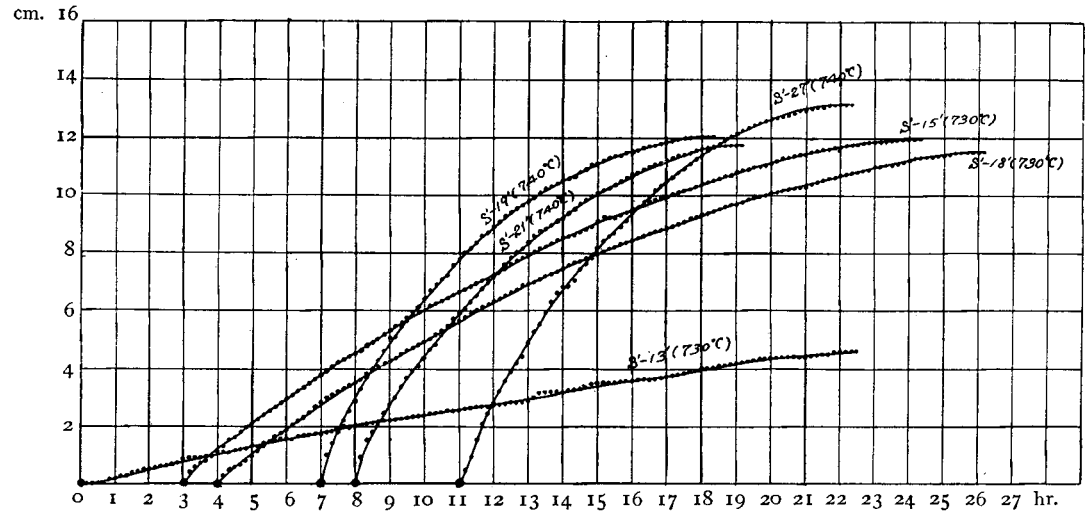


Fig. 16-b.

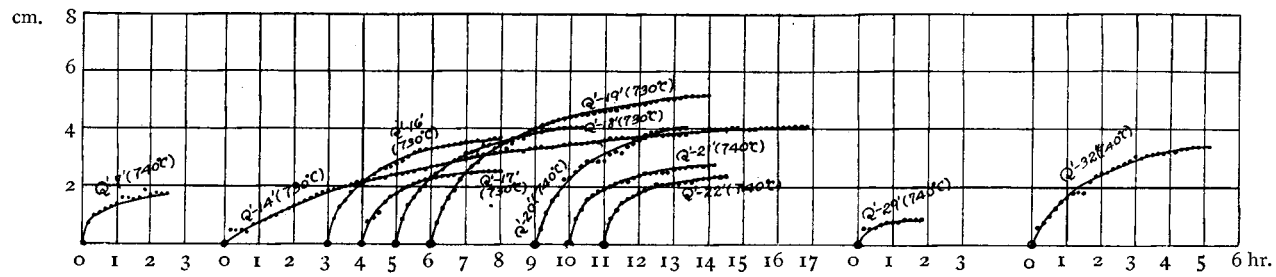


Table XI.

Specimen No.		Composition (%).						Condition of specimen before annealing.	Heat treatment No.	Graphitization curve No.	Annealing temperature.		Time required to complete the graphitization.		
		C	Si	Mn	P	S	Cu				In the first stage.(°C.)	In the second stage.(°C.)	In the first stage.(hrs.-mins.)	In the second stage.(hrs.-mins.)	
L-a	1	1.97	0.64	0.35	0.088	0.051	0.21	As cast	1 2	S-1 S-2	1,010 980		3 20 8 20		
								Quenched	3 4	Q-1 Q-2	970 930		2 30 5 0		
	2	2.02	1.41	0.39	0.123	0.059	0.17	As cast	5 6	S-3 S-4	960 910		2 0 5 30		
								Quenched	7 8	Q-3 Q-4	950 910		0 40 1 50		
	3	2.05	1.70	0.35	0.102	0.051	0.22	As cast	9 10	S-5 S-6	970 920		1 0 3 0		
								Quenched	11 12	Q-5 Q-6	970 920		0 10 1 0		
	4	1.93	1.96	0.30	0.101	0.052	0.22	As cast	13 14	S-7 S-8	970 920		0 50 2 0		
								Quenched	15 16	Q-7 & Q'-7' Q-8	970 920	740	0 0 0 30	2 30	
	L-b	1	2.46	0.67	0.32	0.099	0.057	0.23	As cast	17 18	S-9 S-10	1,010 970		4 30 9 0	
									Quenched	19 20 21	Q-9 Q-10 Q-11	1,010 970 920		1 20 2 30 5 30	
		2	2.43	0.94	0.34	0.102	0.057	0.23	As cast	22 23 24 25	S-11 S-12 S-13 & S'-13' S-14	970 950 920 880	730	5 0 7 0 13 0 40(*) 0	23+X
									Quenched	26 27 28 29	Q-12 Q-13 Q-14 & Q'-14' Q-15	970 940 920 880	730	1 20 2 30 3 30 7 0	20+X
3		2.38	1.25	0.37	0.095	0.058	0.23	As cast	30 31 32 33	S-15 & S'-15' S-16 S-17 S-18 & S'-18'	970 950 930 890	730	2 10 3 20 5 0 9 30	21 0 22 0	

L-c	4	2.37	1.54	0.37	0.102	0.057	0.23	Quenched	34	Q-16 & Q'-16'	970	730	0 40	5 0
									35	Q-17 & Q'-17'	930	730	1 0	4 0
									36	Q-18 & Q'-18'	890	730	2 0	5 30
									37	Q-19 & Q'-19'	860	730	4 0	8 0
								As cast	38	S-19 & S'-19'	970	740	1 30	11 30
									39	S-20	930		3 0	
	1	2.81	0.65	0.24	0.102	0.060	0.24	Quenched	41	Q-20 & Q'-20'	970	740	0 30	4 0
									42	Q-21 & Q'-21'	910	740	1 10	3 30
									43	Q-22 & Q'-22'	860	740	2 30	3 0
								As cast	44	S-22	1,010		5 10	
									45	S-23	970		8+λ	
								Quenched	46	Q-23	970		2 30	
2	2.80	0.94	0.21	0.109	0.058	0.23	Quenched	47	Q-24	920		7 0		
							As cast	48	S-24	970		4 0		
								49	S-25	930		7 0		
								50	S-26	910		11 0		
							Quenched	51	Q-25	970		1 0		
								52	Q-26	930		2 30		
3	2.79	1.35	0.28	0.179	0.072	0.11	As cast	53	Q-27	890		6 0		
								54	S-27 & S'-27'	950	740	3 0	11 0	
								55	S-28	920		5 0		
								56	S-29	890		10 0		
							Quenched	57	Q-28	940		0 30		
								58	Q-29 & Q'-29'	900	740	1 20	1 30	
L-d	1	3.33	1.03	0.15	0.088	0.049	0.18	As cast	59	Q-30	860		3 30	
									60	S-30	970		4 30	
									61	S-31	920		9 0	
								Quenched	62	Q-31	970		1 30	
									63	Q-32 & Q'-32'	920	740	2 30	5 0
								As cast	64	S-32	970		10 0	
L-e(*)	1	3.77	0.43	0.05	0.010	0.016	0.06	Quenched	65	Q-33	970		5 30	

(*) Estimated from the graphitization curve and the structure of the annealed iron.

(*) A trace of mottling was found on the fracture.

Examining these curves carefully, we can recognize several phenomena which will be discussed in sequence below :

(1) The larger the amount of carbon in the specimens, the higher the graphitization curve in the first stage. It is, of course, due to the fact that the larger the amount of carbon in the specimens, the greater the amount of free cementite taking part in the graphitization in the first stage.

(2) For the specimens containing the same amount of carbon, the larger the amount of silicon, the higher the graphitization curve in the first stage. It is also evident from the study of the equilibrium diagram⁽¹⁾ of iron, carbon and silicon, that this phenomenon is due to the fact that the higher the silicon content of cast iron having the same amount of carbon, the larger the amount of free cementite.

(3) In general, the graphitization curve in the first stage of a specimen in the quenched state is far higher than that of the specimen of the same kind but in the cast state ; on the other hand, the graphitization curve in the second stage of the former is far lower than that of the latter. This is an important phenomenon both theoretically and practically, because it means that the amount of free cementite graphitised in the two stages depends on the state of the white cast iron before annealing ; the amount of free cementite graphitised during the theoretical time just required to complete the graphitization in the first stage is greater in the case of the annealing of white cast iron in the quenched state than in the case of the annealing of an iron of the same kind but in its cast state, and, on the contrary, the amount of cementite to be graphitized in the second stage in the former is smaller than that in the latter. This phenomenon will be further touched upon from the standpoint of microscopic study.

(4) The graphitization in the first stage is generally completed in white cast irons in the quenched state in much shorter time than in irons of the same kind but in the cast state. This fact will be discussed below more concretely.

(1) Honda and Murakami : J. I. & S. Inst., No. 1 (1923) p. 545.

Fig. 17-b.

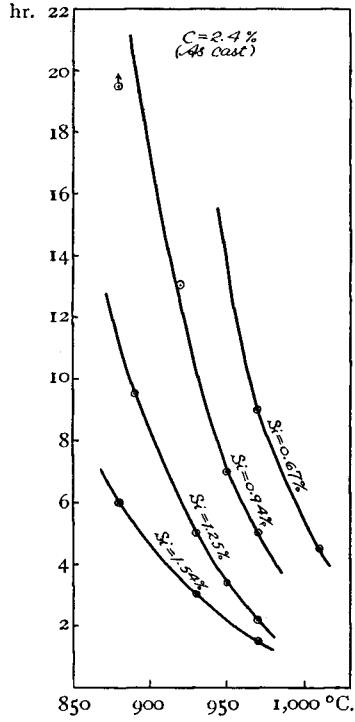


Fig. 17-a.

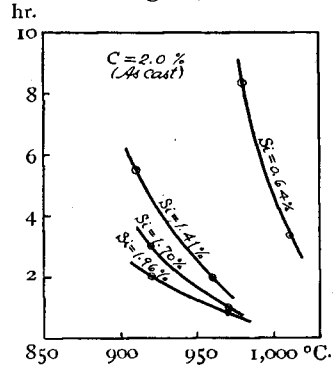


Fig. 17-c.

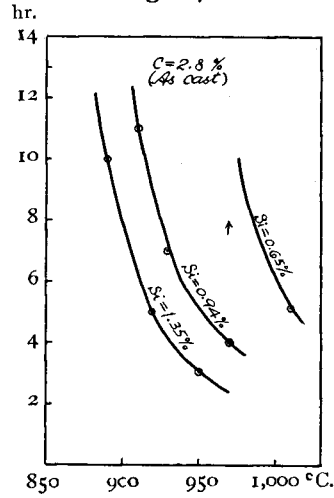


Fig 18-a.

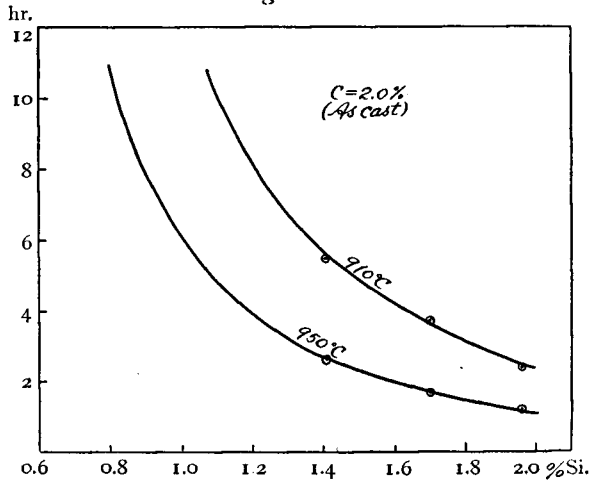


Fig. 17-d.

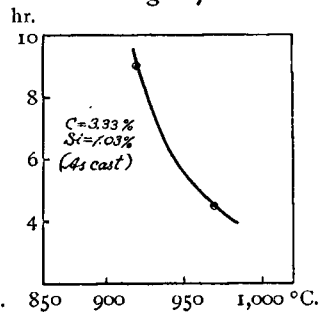


Fig. 18-b.

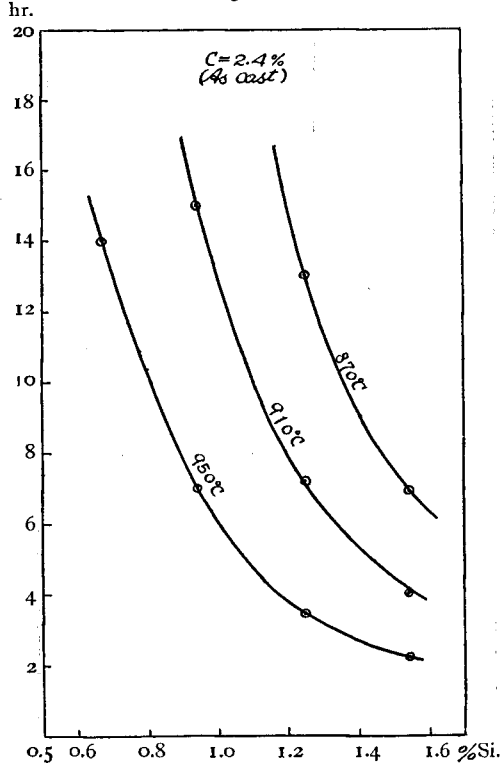


Fig. 18-c.

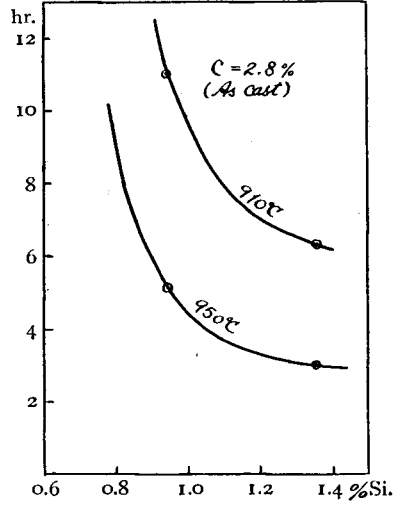


Fig. 19-a.

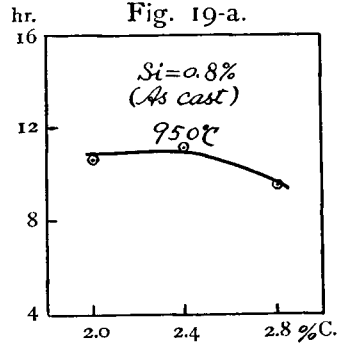


Fig. 19-b.

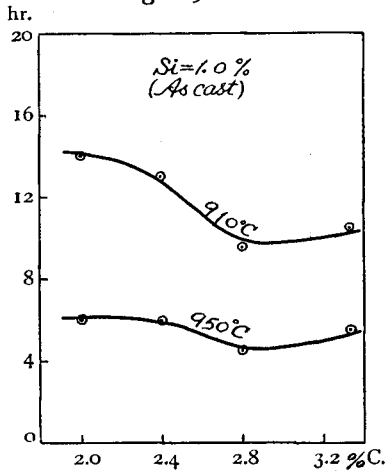


Fig. 19-c.

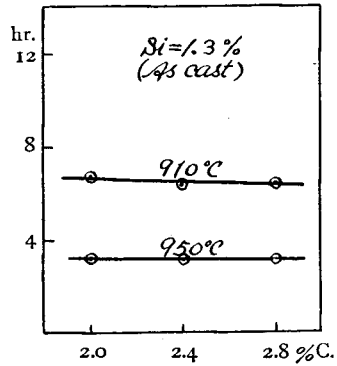


Fig. 20-a.

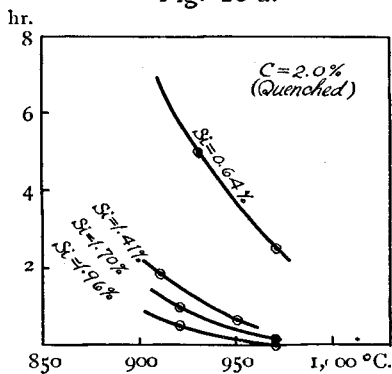


Fig. 20-b.

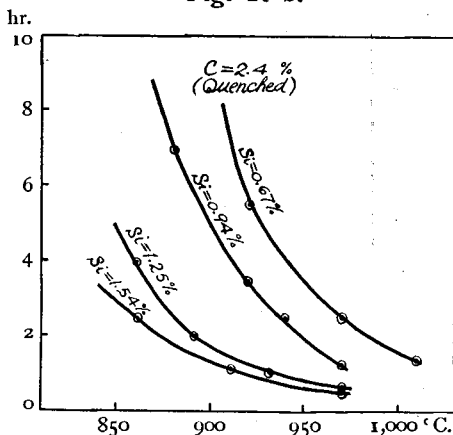


Fig. 20-c.

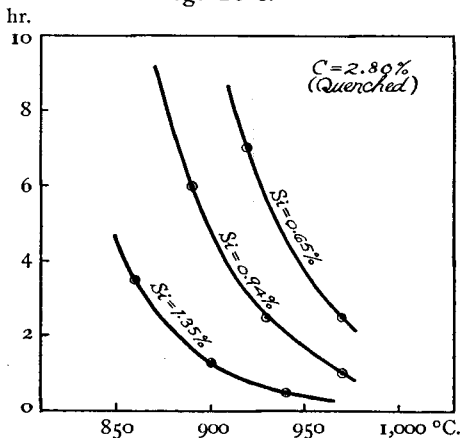


Fig. 20-d.

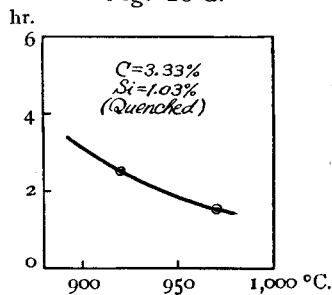


Fig. 21-a.

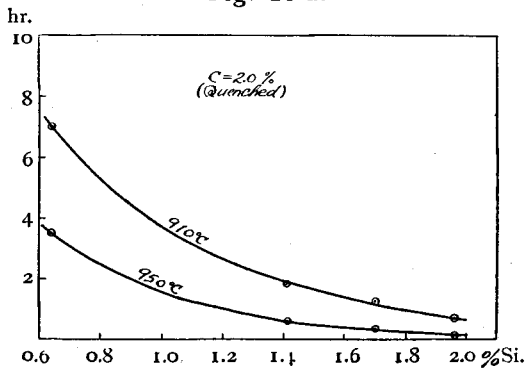
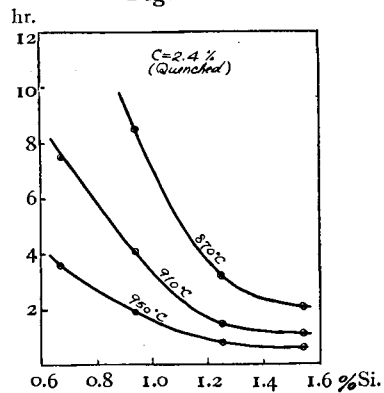
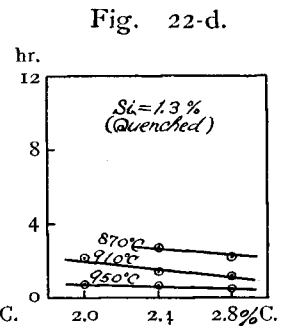
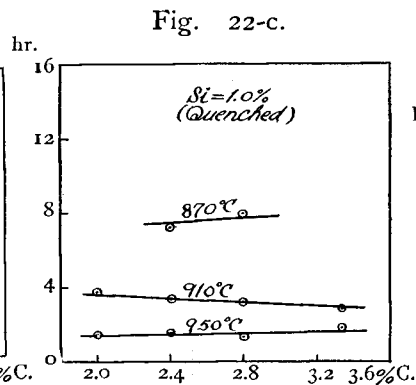
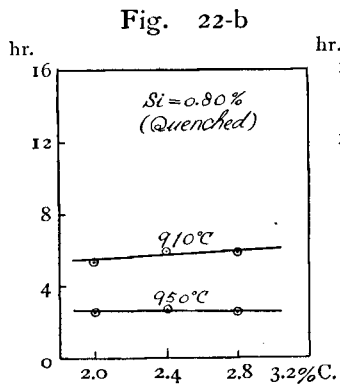
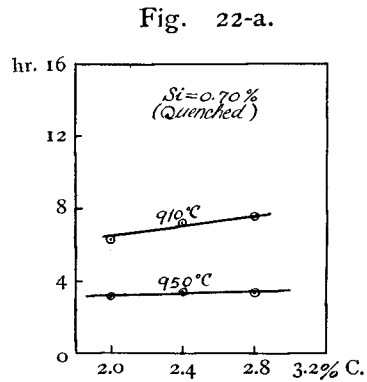
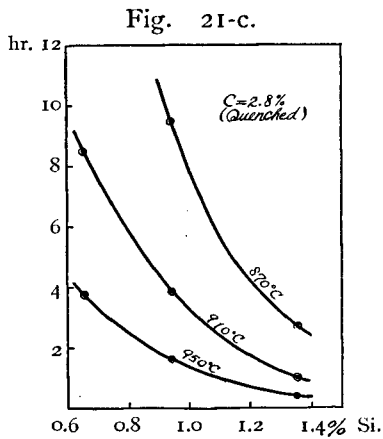


Fig. 21-b.





From the graphitization curves, the time required to complete the graphitization in the first and in the second stages is determined as summarised in Table XI, in which other experimental data also are given. Thus, the curves showing the relation between the time required to complete the graphitization in the first stage and the annealing time are shown in Figs. 17 and 20. Fig. 17 relates to the specimens in the cast state and Fig. 20 to the specimens in the quenched state. From these curves, the relation between the annealing time and the silicon content and that between the annealing time and the carbon content are obtained in turn as shown in Figs. 18, 19, 21 and 22. Among these figures, Figs. 18 and 21 show the former relation and Figs. 19 and 22 the latter; and Figs. 18 and 19 relate to the specimens in the cast state and Figs. 21 and 22 to

those in the quenched state. From these curves the following facts are found, irrespective of the state of the specimens before annealing :

(i) For a given iron, the graphitization in the first stage is completed in a much shorter time at the higher temperatures than at the lower temperatures.

(ii) For a given iron, silicon materially reduces the time for the completion of the graphitization in the first stage.

(iii) For a given iron in the cast state, the influence of carbon on the graphitization in the first stage is not great, although a slight fluctuation is noticeable on the specimens having 1.0 per cent of silicon. The influence of carbon on the graphitization in the first stage of the specimens in the quenched state is almost invariable no matter what the silicon content may be.

Table XII.

Composition of Specimen (%)		Time required to complete the graphitization in the first stage.				Time required to complete the graphitization in the second stage.		Ratio of annealing time required to complete the graphitization. (A/B.)		
		Annealing temperature.				As cast.	Quenched.	In the first stage.		In the second stage.
		95° C.		910° C.				Annealing temperature.		
C	Si	As cast (A). (hrs. — mins.)	Quenched (B). (hrs. — mins.)	As cast (A). (hrs. — mins.)	Quenched (B). (hrs. — mins.)	(hrs. — mins.)	(hrs. — mins.)	95° C.	910° C.	
2.00	0.70		3 0		6 20					
	0.80	10 40	2 30		5 20			4.3		
	1.00	6 0	1 30	14 0	3 50			4.0	3.7	
	1.30	3 10	0 40	6 40	2 10			4.8	3.1	
2.40	0.70	13 0	3 20		7 10	(Si=0.9%) 50* 0	25* 0	3.9		(Si=0.9%) 2
	0.80	11 0	2 40		6 0	(Si=1.25%) 20 0	5 0	4.1		(Si=1.25%) 4.4
	1.00	6 0	1 30	13 0	3 30			4.0	3.5	
	1.30	3 10	0 40	6 20	1 30	(Si=1.54%) 11 0	3 0	4.8	4.2	(Si=1.54%) 3.7
2.80	0.70		3 20		7 30					
	0.80	9 0	2 30		5 50			3.6		
	1.00	4 30	1 20	9 30	3 10	(Si=1.35%) 11 0	1 0	3.4	3.0	(Si=1.35%) 11
	1.30	3 10	0 30	6 20	1 10			6.3	5.4	
3.33	1.03	5 30	1 50	10 30	2 50			3.3	3.7	
3.77	0.43	10 0 (970° C.)	5 30 (970° C.)					1.8 970° C.		

* Estimated.

The fact that when white cast iron is hardened in water it changes to a very unstable state, is clearly recognized by comparing the time required to complete the graphitization in the first stage on the specimens of the different states kept at 950° C and 910° C as given in Table XII.

That is, in short, the time required to complete the graphitization in the first stage of the specimens in the quenched state is sufficient with a time $\frac{1}{3.5}$ to $\frac{1}{4}$ times of the theoretical annealing time of specimens in the cast state.

The explanation of this phenomenon will be given in the following paragraph.

(5) The graphitization in the second stage is completed in a much shorter time in the specimens in the quenched state than in those of the same kind but in the cast state. The time required to complete the graphitization in the second stage is summarized in Table XI and the exact comparison about the above point is given in Table XII on some specimens. As may be seen from Table XI, silicon and especially carbon have a strong effect on the time required to complete the graphitization in the second stage of the specimens both in the cast and in the quenched state. It is an attractive fact that especially carbon has also a remarkable effect on the ratio of the annealing time for complete graphitization in the second stage (A/B in Table XII); that is, it is only 3.7 on the iron containing 1.54 per cent of silicon and 2.4 per cent of carbon but 11 on the iron containing 1.35 per cent of silicon and 2.8 per cent of carbon.

Microscopic study :— The typical structure of the specimens in the cast state used in the present experiment is shown in Photo. No. 5. Photos. Nos. 9 to 28 show the typical structures of the annealed specimens. A great difference is observed in the structure of the annealed specimens according to the state of the irons before annealing :

(1) The temper carbon produced in the specimens in the quenched state before annealing is far finer than that produced in those in the cast state before annealing. The former took a somewhat flaky form when it

was quickly produced in the irons containing a higher content of silicon and carbon.

(2) In general, the ratio of the amount of pearlite (P) to that of ferrite (F) in the matrix of the annealed specimens P/F is larger in the irons in the cast state before annealing than in those of the same kind but in the quenched state before annealing. For example, the analysis of the annealed specimens of the same kind but in a different state which were subjected to Heat treatment, Nos. 56 and 59, (in Table XI) is given below :

Table XIII.

Specimen No.	Condition of the specimen before annealing.	Heat treatment No.	Analysis (%)		
			Total C.	Graphite C.	Combined C.
L-c	As cast	56	2.74	2.23	0.51
L-c	Quenched	59	2.76	2.70	0.06

In other words, during the time just required to complete the graphitization in the first stage, free cementite is graphitized in the specimens in the quenched state in a far greater amount than in those of the same kind but in the cast state ; as a consequence, the pearlite cementite to be decomposed in the following stage remains in the former in a far smaller amount than in the latter. These relations well coincide with the result of the dilatometer experiments mentioned before. The second relation is a cause of the phenomenon that the graphitization in the second stage is completed in the specimens in the quenched state in a much shorter time than in those of the same kind but in the cast state. That is, the second relation is no more than a result of the first phenomenon.

The ratio P/F depends, of course, on the silicon and carbon contents in white cast iron of two different kinds ; for a given iron, the greater the amount of the silicon or the carbon content, the smaller the ratio. But the rate of decrease of the ratio depending on the silicon or the carbon content is not the same in the two different kinds of iron. Therefore the

ratio of the annealing time for complete graphitization in the second stage (A/B in Table XII) depends on the silicon, especially on the carbon content of the iron as estimated from the results in Table XII.

Dr. Kikuta⁽¹⁾ explained the strong effect of the carbon content on the time required to complete the graphitization in the second stage by the accelerating action of the grains of temper carbon, the number of which is increased with an increase of the carbon content, assuming that the graphitization of pearlite cementite begins from the boundary of temper carbon. But the present writers consider the amount of eutectoid as the principal cause of the effect in question as above-mentioned.

C. On white cast iron quenched in rape-seed oil.

Specimens:— In the present experiment, the specimens were used whose compositions are usually adopted in the practice of black heart malleable casting industry. The analyses are given in Table XIV.

Table XIV.

Specimen No.	Composition (%)						Heat treatment No.	Graphitization curve No.	Annealing temperature (°C.)	Time required to complete the graphitization in the first stage. (hrs.—mins.)	
	C	Si	Mn	P	S	Cu					
K-a	1	2.34	0.97	0.41	0.170	0.059	0.11	66	q-1	965	2 0
								67	q-2	925	4 0
								68	q-3	885	7 30
K-a	2	2.36	1.30	0.30	0.170	0.070	0.10	69	q-4	965	0 40
								70	q-5	925	1 30
								71	q-6	885	3 0
K-b	1	2.82	0.99	0.36	0.183	0.072	0.11	72	q-7	965	1 30
								73	q-8	925	3 30
								74	q-9	885	7 0
K-b	2	2.78	1.31	0.33	0.204	0.072	0.09	75	q-10	965	0 40
								76	q-11	905	2 10

(1) Loc. Cit.

Taking the results described in the section *C* of paragraph III into consideration, the present writers quenched all the specimens from 900° C in rape-seed oil at 14° C.

Dilatometer experiment :— In this experiment, only the time required to complete the graphitization in the first stage was measured, and the time required to complete the graphitization in the second stage was estimated from the micro-structure of the annealed specimens. The graphitization-time curves are shown in Fig. 23. The time required to complete the graphitization in the first stage as well as other experimental data are summarised in Table XIV. The relation between the time in question and the annealing temperatures is shown in Fig. 24, in which the same relations on the specimens quenched in water from 850° C and on those in the cast state are also shown. Data concerning these irons are deduced from the results of previous experiments. After these results, the graphitization in the first stage is completed in the irons quenched in rape-seed oil before annealing in a somewhat longer time than in those quenched in water before annealing but in a much shorter time than in those in the cast state.

Fig. 23-a.

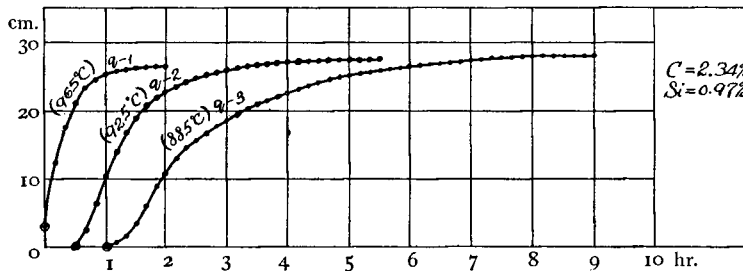


Fig. 23-b.

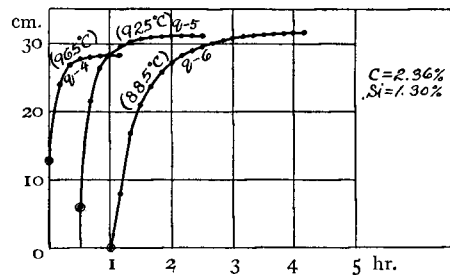


Fig. 23-c.

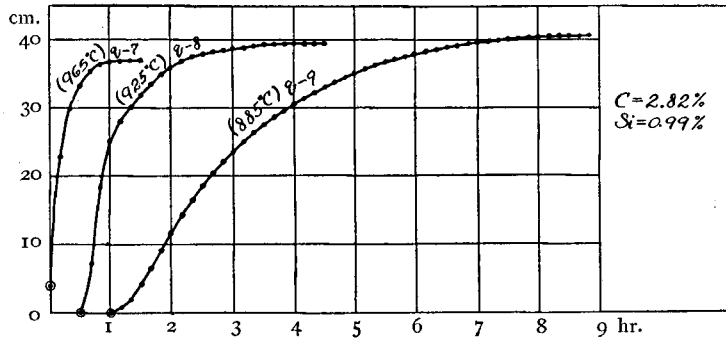


Fig. 23-d.

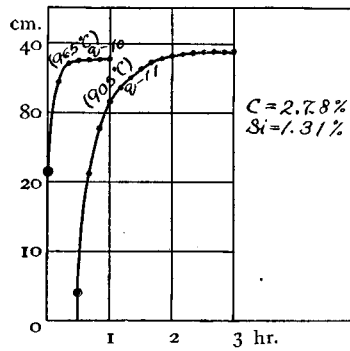


Fig. 24-a.

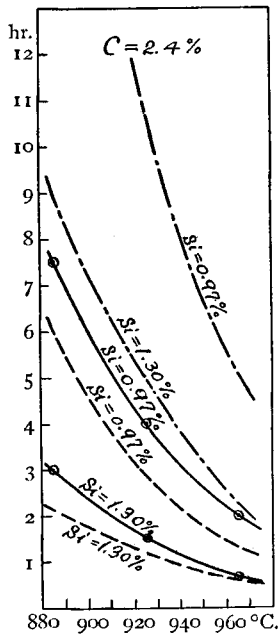
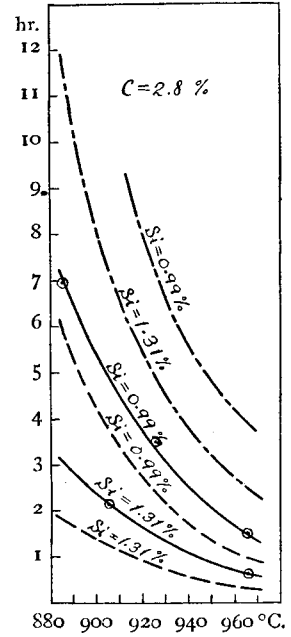


Fig. 24-b.

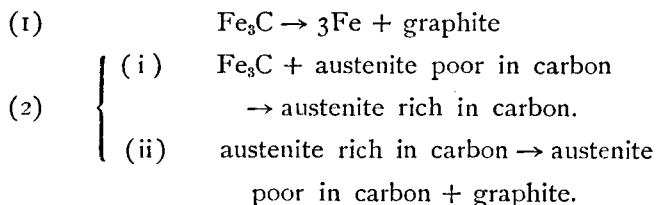


Microscopic study:— The typical structures of the annealed specimens are shown in Photos. Nos. 29 to 32. Discussions are omitted, because here we found phenomena almost similar to those found in the structure of the annealed irons quenched in water before annealing.

§ V. THEORETICAL CONSIDERATION OF THE NEW PHENOMENON.

The focus of this subject is to clear up why free cementite in white cast iron becomes very unstable when the iron is quenched.

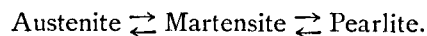
In a former paper,⁽¹⁾ one of the present writers considered that the following two changes proceed simultaneously during the graphitization in white cast iron:



He then proposed 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 present phenomenon can be easily explained by this consideration.

It is a well known fact that when a carbon steel in the normal state is cooled from a temperature above its A_1 point, its dilation changes with the temperature, as shown in Fig. 25, according to the cooling rate.

According to Prof. Honda's⁽²⁾ theory of quenching, the A_1 transformation in carbon steel consists of the following stepped changes:



As the specific volumes of these structures satisfy the relations

$$V_{\text{aust.}} < V_{\text{mart.}} > V_{\text{pearl.}}$$

(1) Loc. Cit.

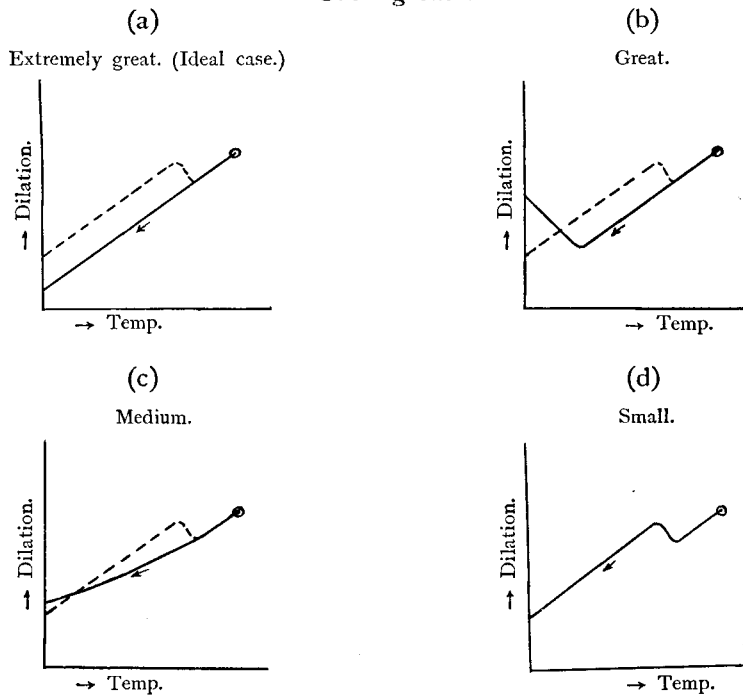
(2) Sci. Rep. Tohoku Imp. Univ., vol. 8 (1919), p. 181.

and

$$v_{\text{aust.}} < v_{\text{pearl.}},$$

when the cooling rate of a carbon steel is great, only martensitization proceeds at a lower temperature and thus produces martensite which is all retained at room temperature resulting in the greatest expansion of the iron. When the cooling velocity is not so great, pearlitization takes place, following martensitization, and the degree of expansion of the iron depends on the amount of martensite retained at room temperature, that is, on the cooling rate.

Fig. 25.
Cooling rate.



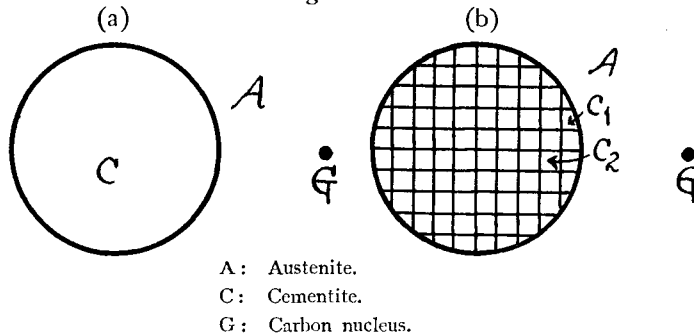
Continuous line: Dilation curve in question.

Dotted line: Dilation curve of a steel slowly cooled.

The above phenomenon must also occur during the quenching of white cast iron which consists of austenite and cementite. Accordingly, it is a natural thing that free cementite, a very brittle compound, which

intimately mixes with austenite, is finely crushed when the abnormal volume increase due to martensitization takes place during quenching. Such cracks could be observed under the microscope to a certain degree.

Fig. 26.



Now, assume Fig. 26-a to be a figure showing the structure at the annealing temperature in the first stage of a white cast iron in its cast state, and Fig. 26-b the structure at the same temperature of an iron of the same kind but in the quenched state. A massive cementite observed in Fig. 26-a must be crushed into a great number of cementite-fragments in Fig. 26-b. As seen from Fig. 26, all free cementites in white cast iron in the cast state before annealing are enveloped by austenite. Hence, they can be easily absorbed by austenite as required. On the contrary, all the fragmental free cementites in white cast iron in the quenched state before annealing have much free surface. The graphitization of the latter must mean the decomposition of the cementite itself. Therefore, in the case, when in white cast iron in its cast state, temper carbon is produced under the mechanism of precipitation graphitization, decomposition graphitization may proceed predominantly if the iron is annealed after quenching. Moreover, as cementites having free surface graphitize more easily than those surrounded by austenite, and also the unit of cementite in quenched white cast iron is far finer than that in the iron in its cast state, the graphitization of the former begins at a lower temperature and is completed in a much shorter time than the latter.

This consideration is supported without exception by the experimental facts so far obtained, further description of which is omitted here.

§ VI. SUMMARY.

The results so far obtained may be summarised as follows :

(1) The present writers found a new phenomenon, viz., that when white cast iron is hardened it becomes very unstable.

(2) The quenching temperature of white cast iron has a relation to its stability, i. e., when the temperature in question is raised graphitization is facilitated.

(3) It was found that there is an intimate relation between the cooling rate of white cast iron during quenching and its stability, i. e., as the cooling rate is higher, the iron becomes more unstable.

(4) When white cast iron is quenched repeatedly, it becomes more unstable.

(5) The relations of the annealing temperature, the silicon and carbon contents and the time required to complete the graphitization in the first and in the second stages were experimentally determined on white cast irons in the cast state, and in water- or rape-seed oil-quenched state before annealing.

(6) The graphitization in the first and in the second stages is completed in white cast irons in the quenched state in a much shorter time than in those of the same kind but in the cast state.

(7) As the cooling rate of white cast iron during quenching increases, the size of the temper carbon produced becomes smaller and its nodular form gradually changes into flaky.

(8) From the dilatometer experiments and from microscopic study, it was confirmed that during just the time required to complete the graphitization in the first stage, free cementite was graphitized in white cast irons in the quenched state in a much larger amount than in irons of the same kind but in the cast state.

(9) It was also found that during the time required to complete the graphitization in the second stage, pearlite cementite was graphitized in white cast irons in the quenched state in a much smaller amount than in irons of the same kind but in the cast state.

(10) The present phenomenon was theoretically discussed on the base of the results so far obtained.

Free cementite in white case iron must be finely crushed during quenching on account of a great abnormal expansion of the structure mixing with cementite which is due to the martensitization of austenite. These cementite-fragments have much free surface and are liable to be decomposed to iron and graphite. Owing to these conditions, free cementite in white cast irons in the quenched state begins to graphitize at a lower temperature and to be graphitized in a much shorter time than that in irons of the same kind but in the cast state. Moreover, decomposition graphitization proceeds predominantly in the former while in the latter precipitation graphitization. As a consequence, the phenomenon as described in (8) and (9) makes its appearance.

(11) The fact that the time required to complete the graphitization in the second stage is much shortened by quenching white cast irons before annealing is due to the phenomenon described in (9).

PART II.

PRACTICAL APPLICATION OF THE NEW PHENOMENON.

§I. SOME EXPERIMENTS ON THE DIFFUSION OF TEMPER CARBON IN γ -IRON.

A. Method of experiment.

The method of this experiment was the same as that in the previous part.

B. Experiment.

In order to find the effect of the excessive continuation of annealing at the annealing temperature in the first stage on the time required to complete the graphitization in the second stage, four pieces of Specimen No. L. c. 3 (in Table XI) were quenched in water at 23° C from 850° C. They were heated to a predetermined temperature, 900° C, at which various durations of excessive time had elapsed after the completion of the graphi-

tization in the first stage, and then they were cooled to 700°C and again heated to 740°C at which the time required to complete the graphitization in the second stage was measured. The duration of the excessive times which had elapsed at the higher annealing temperature was respectively 0 hr., 1 hr., 3.5 hrs. and 6 hrs.

Fig. 27-a.

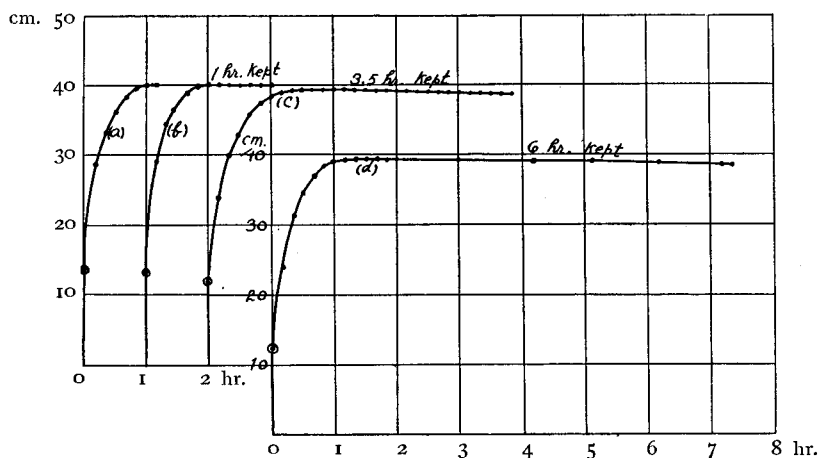
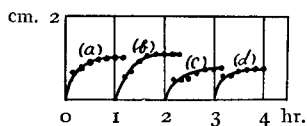


Fig. 27-b.



The results of this experiment are shown in Fig. 27. Referring to the graphitization curves of the same specimen but in its cast state (Graphitization curve No. S-27 and S'-27' in Figs. 15-c and 16-a), it is

expected that the diffusion of temper carbon thus produced in γ -iron is probably very difficult even at such high temperature and, therefore, excessive continuation of annealing at the annealing temperature in the first stage has almost no effect upon the time required to complete the graphitization in the second stage.

The completely graphitised specimen in the above experiment was heated again to 900°C at which temperature it was kept for 5 hrs. and then cooled to 700°C , and heated again to 740°C , at which the time required to complete the graphitization in the second stage was measured. The results are shown in Figs. 28 (curve a), 29 (curve a), and 30, the

first of which shows the dilation-temperature curve during heating and cooling, the second the dilation-time curve during the time 900° C was maintained and the last the graphitization curve of the second stage.

Fig. 28.

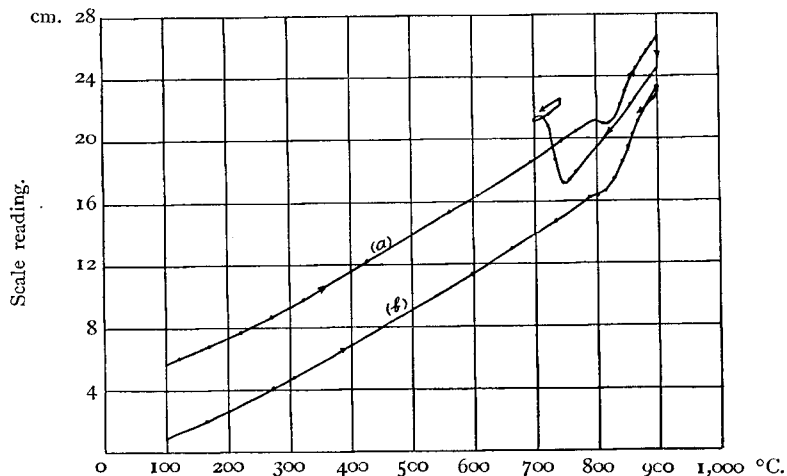


Fig. 29.

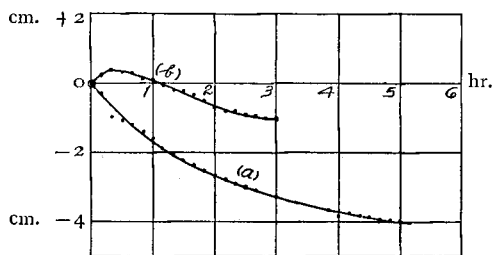
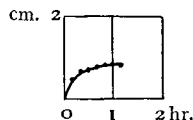


Fig. 30.



Comparing Figs. 27 and 30, the present writers emphasize the above mentioned presumption, and also estimate that the temper carbon produced by the graphitization in the second stage can be easily absorbed by the γ -iron. The diffusion of the temper carbon of this kind in γ -iron will probably relate to the abnormal expansion of the specimen at the temperature just above the A_{c1} point as shown in Fig. 28. But it is interesting phenomenon that the specimen gradually contracts during the maintenance of the high temperature of 900° C., as shown in Fig. 29. Another example of this phenomenon is shown in Figs. 28 (curve b) and 29 (curve b).

These are the results of the re-annealing of the completely graphitized Specimen No. P. b. 3 which was subjected to the experiments described in Section C, Paragraph III, Part I. In this case, however, the specimen first somewhat expands and then gradually contracts as time elapses. This expansion will probably be due to the continuation of the diffusion of temper carbon produced by the graphitization of the pearlite cementite in γ -iron, as the amount of temper carbon of this kind is comparatively great as shown in Fig. 9.

§ II. QUENCHING EXPERIMENTS ON SOME KINDS OF WHITE CAST IRON CASTINGS.

It is a well known fact that cracks are often produced during quenching of high carbon steel in water or oil. This tendency will probably be more increased as the carbon content of the iron increases. This is, naturally, a great barrier to the application of the present phenomenon to practice.

The object of this experiment is to confirm by what method of quenching some kinds of white cast iron castings can be safely quenched.

A. Sample.

Five kinds of white cast iron castings as summarised in Table XV were adopted for this experiment. They were supplied by some company producing black heart malleable castings in our country. The forms of these castings are shown in Photo. No. 33.

Table XV.

Sample No.	Kind of Sample.	Approximate composition (%).		Surface condition.
		C	Si	
A—I	Photo. No. 33-A.	2.87	1.06	Cleaned. With sand and oxide crust.
A—II	Ditto.	Ditto.	Ditto.	
B	Photo. No. 33-B.	2.85	1.13	Cleaned.
C	Photo. No. 33-C.	2.74	1.03	Ditto.
D	Photo. No. 33-D.	Ditto.	Ditto.	Ditto.

B. Method of experiment.

The sample was heated on a roasting dish in a Hoskin's electric muffle furnace having an inner capacity of 19 cm. x 13 cm. x 35 cm. The hot junction of a thermocouple was placed just above the sample. When the sample was required to be quenched, it was taken out of the furnace and thrown into a quenching bath as quick as possible. After the temperature of the quenched sample became equal to that of the quenching bath, the sample was taken out of the bath and the quenching liquid adhering to the sample was wiped off with a cloth, taking care of the cleaned surface if the quenching liquid oozed out of it. If it did, it was considered to be due to concealed cracks. As quenching media, water and rape-seed oil were adopted.

C. Results.

First, the sample was quenched in water and rape-seed oil respectively, after it was heated at various heating rates. The results are summarised in Table XVI.

It is confirmed by these results that,

(1) The quenching crack is more liable to be produced in white cast iron castings with cleaned surface than in those with uncleaned surface. This is due to the fact that the surface condition of the castings have a relation to the cooling rate during quenching.

Fig. 31.

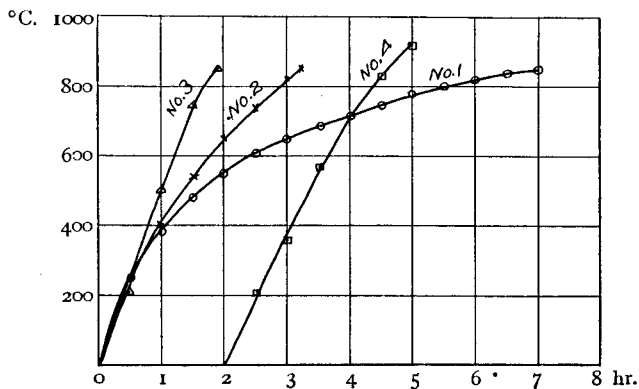


Table XVI.

Experiment No.	Sample No.	Method of heat treatment.	Quenching medium.	Number of Sample.	
				No crack produced.	Crack produced.
1	A-II D	Heated at the rate shown in Curve No. 1 in Fig. 31 and quenched as soon as their temperature was raised to 850°C.	Water (25°C) Ditto.	3 1	
2	A-II	Heated at the rate shown in Curve No. 2 in Fig. 31 and quenched as soon as their temperature was raised to 850°C.	Water (25°C)	4	
3	A-II	Heated at the rate shown in Curve No. 3 in Fig. 31 and quenched as soon as their temperature was raised to 850°C.	Water (25°C)	4	
4	A-II	Heated at the rate shown in Curve No. 4 in Fig. 31 and quenched as soon as their temperature was raised to 920°C.	Water (25°C)	4	
5	A-II D	Taken into the furnace which was previously heated to 850°C and quenched after they were kept at the same temperature for 10 minutes.	Water (25°C) Ditto.	4 1	
6	A-II C D	Taken into the furnace which was previously heated to 920°C and quenched after they were kept at the same temperature for 10 minutes.	Water (25°C) Ditto. Ditto.	6 6 3	4
7	A-I	Quenched as soon as their temperature was raised to 850°C. The heating rate was not recorded, but it is certain that their heating curve lies between Curves No. 1 and No. 2 in Fig. 31.	Rape-seed oil (24°C)	6	
8	A-I	Treated by the same method as in Experiment No. 1.	Water (25°C)		5
9	A-I	Treated by the same method as in Experiment No. 1.	Water (80°C)		5
10	A-I	Treated by the same method as in Experiment No. 6.	Rape-seed oil (24°C)	4	

(2) Occurrence of quenching crack partly depends on the heating rate of the castings before quenching. As the castings are heated at a greater rate, the tendency of cracking is more increased. It is probably due to the lack of uniformity of temperature at various parts of the castings which may take place when they are quickly heated.

(3) White cast iron castings of simple form can be safely quenched even in water if the heating rate before quenching be carefully regulated.

(4) Even white cast iron castings of somewhat complicated form can be safely quenched in oil, though they are heated before quenching at a very quick rate.

Hereupon, the present writers quenched the castings in water over which rape-seed oil of various thicknesses was floated in order to find a safer and cheaper quenching medium. For this purpose, three cans having an inner volume of 23 cm. x 23 cm. x 35 cm. were filled up with water up to the height of 27 cm. from the bottom over which rape-seed oil of various thicknesses was floated. The temperature of the quenching bath was always 11° C for each quenching. The results of this experiment are summarised in Table XVII.

Table XVII.

Experiment No.	Sample No.	Thickness of oil layer. (cm.)	Method of heat treatment.	Numbers of Sample.	
				No crack produced.	Crack produced.
11	A-I B	1	Always taken into the furnace which was previously heated to 900°C and quenched after they were kept at the same temperature for 10 minutes.		3 3
12	A-I B	3		2	1 3
13	A-I B	5		0 0	

These results evidently show that even white cast iron castings with cleaned surface of somewhat complicated form can be safely quenched in such a kind of quenching bath. The thickness of oil layer necessary for the safe quenching, of course, has to be determined from various directions; form, size, etc. of the castings.

§ III. TENSILE STRENGTH AND ELONGATION OF THE BLACK HEART MALLEABLE CASTINGS MANUFACTURED BY THE APPLICATION OF THE NEW PHENOMENON.

From the previous experiments, we knew the safe methods of quenching of some kinds of white cast iron castings. The object of the present experiment was to find some important mechanical properties of black heart malleable casting prepared by annealing white cast iron previously quenched by these safe methods for a shorter time

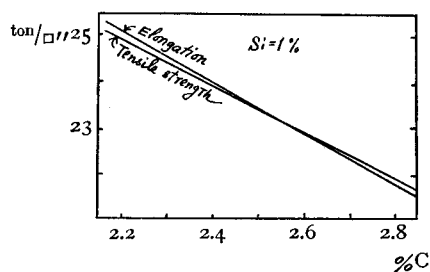
The important mechanical properties of black heart malleable casting are, of course, tensile strength and elongation. The present writers summarise these two properties specified in various directions in the following table to which the results of the present experiment are to be referred.

Table XVIII.

	Specification for.		
	Tensile strength. kg./□m.m.	ton/□in.	Elongation. (%)
American Society for Testing Materials (1922). ⁽¹⁾	35.1	22.3	10
British Engineering Standards Association. ⁽²⁾	31.5	20.0	7.5
Department of Railways in Japan. ⁽³⁾	28.0	17.8	5

For the same purpose, Fig. 32 is reproduced here from Dr. Kikuta's paper⁽⁴⁾, which shows the relation between tensile strength or elongation of the test bars having about 1 per cent silicon and various carbon contents. These data were obtained in daily practice in his factory. The dimensions and the method of casting

Fig. 32.



- (1) H. A. Schwartz: American Malleable Cast Iron. p. 276.
- (2) Foundry Trade Journal; vol. 34, (1926), p. 462.
- (3) Catalogue of the Tobata Foundry Co.
- (4) "Kinzo no Kenkyu"; vol. 3, (1926), p. 215.

of these test bars were just the same as those of the test bars used in the present experiment.

As to the content of other impurities, they are approximately similar.

A. Test Bar.

Test bars used in this experiment have been supplied by a foundry company who cast them from the molten bath prepared for the casting of some white cast iron castings to make malleable castings. Their dimensions and analyses are given in Fig. 33 and Table XIX respectively.

Fig. 33.

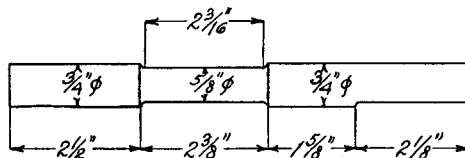


Table XIX.

Test bar No.	Composition (%)					
	C	Si	Mn	P	S	Cu
S	2.86	1.02	0.28	0.136	0.046	0.11
T	2.47	1.09	0.34	0.207	0.060	0.11
U	2.75	1.12	0.28	0.173	0.053	0.12

B. Method of experiment.

(a) Method of quenching.

Method of quenching in water:— Referring to the results of the experiment described in Paragraph II in this part, Test bar No. S was heated in the muffle furnace, which was used in the quenching experiment of white cast iron castings up to 850°C at the heating rate shown in Heating curve No. 2 in Fig. 31 and after being kept at that temperature for 5 mins. it was quenched in water at 22°C .

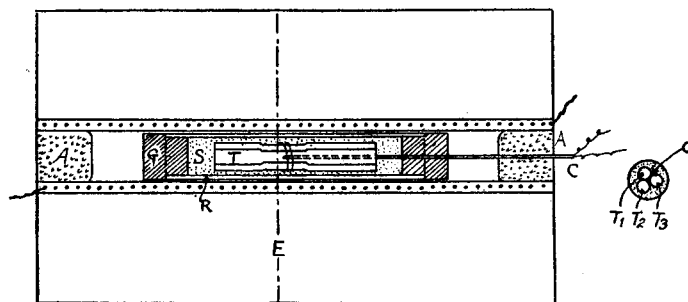
Method of quenching in oil:— Referring to the results of the experiment described in Paragraph II in this part, Test bar No. *T* and two test bars belonging to No. *U* were taken into the muffle furnace which was previously heated to 900° C and after being kept at that temperature for 10 mins. they were quenched in rape-seed oil at 13° C.

Method of quenching in water covered with a rape-seed oil layer of 5 cm. thickness:— Test bar No. *U* was used in this quenching. The method was just the same as above described.

(b) Method of annealing.

Two or three test bars parallel bound were put in the middle of a cast iron cylinder 5.3 cm. in inner diameter, both ends of which were closed with graphite stoppers or graphite crucibles filled with charcoal pieces. The inner space of the cylinder holding the test bars was packed with silica sand or remained as it was. In order to heat the test bars, a large electric tube furnace was employed in which the iron cylinder holding the test bars was laid as shown in Fig. 34.

Fig. 34.

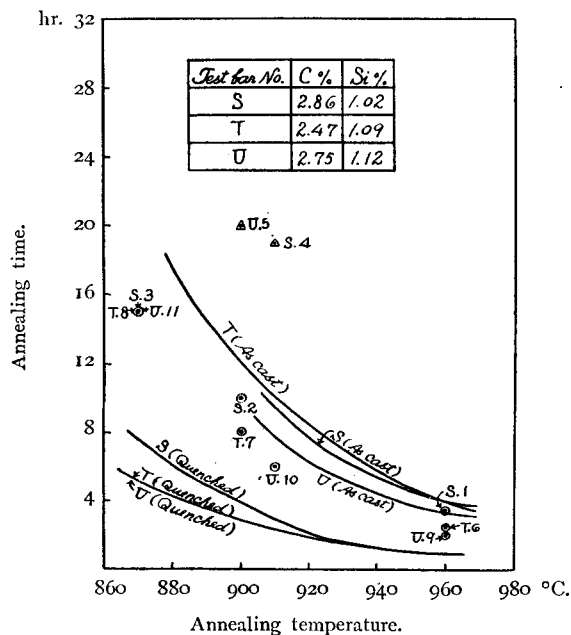


- A: Asbestos stopper.
- C: Thermocouple.
- E: Electric furnace.
- G: Graphite stopper.
- R: Cast iron pipe.
- S: Sand.
- T: Test bars.

The temperature of the test bars was measured with a thermocouple, the hot junction of which was set in a middle space among them.

Fig. 35 shows the relation between the annealing temperature and the time required to complete the graphitization in the first stage of white cast irons both in the cast and in the water-quenched state, the compositions of which are approximately similar to those of the test bars used in this experiment. It is deduced from Figs. 18 and 21. In the present experiment, as the annealing time about two times of that shown in Fig. 35 was adopted, taking the cooling rate of the test bars during quenching into consideration. Its actual position in Fig. 35 is represented by the mark \odot . The figures attached to the mark represent the number of the experiment. As the annealing temperature in the second stage, 740° C or 750° C was adopted at which the quenched test bars were kept for 6.5 to 11 hrs.

Fig. 35.



The heating and cooling rate of the test bars were almost the same in all heats. Only one example will be shown in the following :

Experiment No. 2.

Room temp. ← 7 hrs. → 900° C ← (10 hrs. kept) → 900° C ← 3 hrs. →
700° C ← 30 mins. → 740° C ← (7.5 hrs. kept) → 740° C ← 3 hrs. → 450 C.

C. Results.

(a) Results of the experiment on the test bars which were quenched in water.

The results in question as well as the experimental data are summarised in Table XX. In these experiments, No. 4 was carried out for the complete annealing of the test bars in the cast state. In Experiment No. 1, one test bar in the cast state was annealed a shorter time with the quenched bars. These results evidently show that the tensile strength of the annealed test bars which were quenched before annealing is far greater than that of the bars of another kind, but as to elongation, the former is

Table XX.

Experiment No.	Test bar No.	Condition of test bar before annealing.	Method of heat treatment.				Mechanical property.			State of fracture.	
			Annealing temperature.		Annealing time.		Tensile strength in		Elongation (5 cm.) in %.		
			In the first stage. (°C.)	In the second stage. (°C.)	In the first stage. (hrs.—mins.)	In the second stage. (hrs.—mins.)	kg./□ m m.	ton/□ in.			
1	S	Quenched.	960	740	3 30	6 30	33.9	21.5	5.8	Black. Ditto. White.	
		Ditto. As cast.					38.7	24.6			3.3
2	S	Quenched.	900	740	10 0	7 30	35.3	22.4	5.7	Black. Ditto. Ditto.	
		Ditto. Ditto.					34.2	21.7			>5
3	S	Quenched.	870	740	15 0	6 30	40.8	25.9	5.8	Black. Ditto. Ditto.	
		Ditto. Ditto.					36.4	23.1			5.2
4	S	As cast.	910	740	19 0	11 0	32.6	20.7	7.5	Black. Ditto. Ditto.	
		Ditto.					32.1	20.4			7.5
		Quenched.					36.1	22.9			5.7

* Ruptured at the outside of the gauge length.

inferior to the latter. The fracture of the annealed test bars was black (Photo. No. 34-B) except one annealed in Experiment No. 1 which was white as shown in Photo. No. 34-A, on account of the presence of a large amount of free cementite remaining undecomposed as shown in Photo. No. 35. The micro-structure of other test bars indicated that the annealing was sufficient. But in the structure of the annealed bars which were quenched before annealing, a great number of small and flaky temper carbons were found (Photo. No. 36). In the structure of the annealed bars of another kind, on the contrary, a small number of large and nodular temper carbons were found (Photo. No. 37).

(b) Results of the experiment on the test bars which were quenched in rape-seed oil.

The results as well as the experimental data are summarised in Table XXI.

Table XXI.

Experiment No.	Test bar No.	Condition of test bar before annealing.	Method of heat treatment.				Mechanical property.			State of fracture.		
			Annealing temperature.		Annealing time.		Tensile strength in		Elongation (5 cm.) in %.			
			In the first stage. (°C.)	In the second stage. (°C.)	In the first stage. (hrs.—mins.)	In the second stage. (hrs.—mins.)	kg./□ m.m.	ton/□ in.				
5	U	As cast.	900	750	20	0	11	0	34.7	22.0	10.0	Black. Ditto. Ditto. Ditto.
		Ditto.							35.1	22.3	10.0	
		Quenched.							34.8	22.1	9.7	
		Ditto.							35.9	22.8	8.5	
6	T	Quenched.	960	750	2	30	10	0	42.0	26.7	10.6	Black. Ditto.
		Ditto.							42.7	27.1	10.8	
7	T	Quenched.	900	750	8	0	10	0	41.3	26.2	12.5	Black. Ditto.
		Ditto.							40.8	25.9	14.0	
8	T	Quenched.	870	750	15	0	10	0	42.0	26.7	12.3	Black. Ditto.
		Ditto.							42.4	26.9	12.9	

Experiment No. 5 was carried out for the complete annealing of the test bars in the cast state. Comparing these results with those obtained in practice (refer to Fig. 32), we can recognize that the tensile strength of the annealed test bars which were quenched before annealing is greater than that of the bars of another kind annealed in practice and the elongation of both kinds of irons is almost equal. The micro-structure of the annealed bars revealed no trace of free cementite and eutectoid cementite remaining undecomposed. The temper carbon produced in the annealed bars which were quenched before annealing is nodular in form and it is far smaller in size and is far greater in number than that produced in the bars of another kind as shown in Photos, Nos. 38 and 39.

- (c) Results of the experiment on the test bars which were quenched in water covered with a rape-seed oil layer 5 cm. thick.

The results as well as the experimental data are summarised in Table XXII. In this experiment, a test bar in the cast state was treated with the quenched bars at each experiment.

Table XXII.

Experiment No.	Test bar No.	Condition of test bar before annealing.	Method of heat treatment.				Mechanical property.			State of fracture.		
			Annealing temperature.		Annealing time.		Tensile strength in		Elongation (5 cm.) in %.			
			In the first stage. (°C.)	In the second stage. (°C.)	In the first stage. (hrs.—mins.)	In the second stage. (hrs.—mins.)						
			kg/□ m.m.	ton/□ in.								
9	U	As cast.	960	750	2	0	9	0	37.0	23.5	4.5	White. Black. Ditto.
		Quenched.							37.5	23.8	11.0	
		Ditto.							36.4	23.1	8.1	
10	U	As cast.	910	750	6	0	10	0	40.0	25.4	4.5	White. Black. Ditto.
		Quenched.							36.9	23.4	9.7	
		Ditto.							36.5	23.2	10.0	
11	U	As cast.	870	750	15	0	10	0	39.4	25.0	3.9	White. Black. Ditto.
		Quenched.							39.4	25.0	11.6	
		Ditto.							36.4	23.1	8.3	

These results also show that there exists almost the same relation as above. The fact that the annealed test bars which were in the cast state before annealing are strong but brittle is due to the shortness of the annealing time as may be seen from their fractures (Photo. No. 40) and structure (Photo. No. 41). The temper carbon produced in the annealed test bars which were quenched before annealing is fine and nodular as shown in Photo. No. 42. But it is still finer than that produced in those which were quenched in rape-seed oil only before annealing.

Summarising all the above results, the following conclusions are obtained :

(1) The black heart malleable castings prepared by annealing white cast iron after quenching are stronger but somewhat less malleable than those prepared by annealing white cast iron of the same kind but in the cast state.

(2) The difference in the mechanical properties of the black heart malleable castings prepared by these different kinds of processes is probably due to the remarkable difference of structure as before mentioned.

(3) By utilizing the new phenomenon we can prepare the black heart malleable castings having superior quality in far shorter time than that required in the present practice.

§ IV. CHARACTERISTICS OF THE NEW METHOD OF MANUFACTURING BLACK HEART MALLEABLE CASTINGS.

The chief merits to be obtained by applying the present new phenomenon to practice are enumerated from the economical point of view as follows :

(1) The annealing time required to complete the graphitization of free cementite and eutectoid cementite is greatly reduced. Accordingly, the fuel cost required for annealing is greatly saved.

(2) On account of the fact that one heat cycle can be greatly shortened, the productive capacity of a factory is greatly increased resulting in the reduction of the cost of production.

(3) Quenched white cast iron can be annealed at lower temperatures than that adopted in the present practice in the same annealing time. The low temperature annealing has the following merits :

- (i) Fuel is saved.
- (ii) The life of the annealing pot is prolonged.
- (iii) The damage to the annealing furnace, etc , is reduced.

§ V. SUMMARY.

The results so far obtained may be summarised as follows :

(1) It was found that the excessive continuation of the annealing of white cast iron, which was quenched before annealing, at the annealing temperature in the first stage has almost no effect upon the time required to complete the graphitization in the second stage. It is probably due to the fact that the temper carbon produced in the first stage of graphitization hardly diffuses in γ -iron.

(2) Some kinds of white cast iron castings were quenched in three kinds of quenching media, i. e., water, rape-seed oil and water covered with a rape-seed oil layer, and the safe quenching method was experimentally found in each case.

White cast iron castings of a simple form can be safely quenched in water if they are slowly heated before quenching. They are also safely quenched in rape-seed oil or water covered with a rape-seed oil layer even if they are quickly heated before quenching.

(3) The test bars which were quenched by the safe method previously found were annealed in a far shorter time than that adopted in the present practice and then their tensile strength and elongation were compared with those of the test bars annealed in practical operation. The tensile strength of the former is greater than that of the latter but the elongation of the former is liable to be somewhat inferior to that of the latter.

(4) From the economical standpoint, the merits of the new process of manufacturing black heart malleable castings were enumerated.

(5) From all the results of the present investigation, the fact was confirmed that the new process can be applied to practice with a moderate economical profit.

Acknowledgment.

In conclusion, the present writers wish to express their sincere thanks to Mr. T. Murayama, the managing director of the Kizugawa Factory of the Tobata Foundry Co., and to Dr. T. Kikuta, the engineer of the Tobata Foundry Co., for their kindness in supplying some materials used in the present investigations, and also to Mr. G. Koda for his zealous assistance throughout the present work.

Illustrations.

All specimens for microscopic study were etched with dilute nitric acid.

Photo. No. 1	Specimen No. A. a. 1	Annealed as the curve shown in Fig. 2.
" 2	" " 4	" " "
" 3	" " 5	" " "
" 4	" " 8	" " "
" 5	" L. b. 2	as cast.
" 6	" P. b. 1	Annealed as the curves shown in Figs. 8 and 9.
" 7	" " 3	" " "
" 8	" " 4	" " "
" 9	" L. a. 1	Annealed as the curve in Fig. 15-a, S-1.
" 10	" " "	" " Q-1.
" 11	" L. a. 3	" " S-6.
" 12	" " "	" " Q-6.
" 13	" L. b. 1	" " Fig. 15-b, S-9.
" 14	" " "	" " Q-11.
" 15	" L. b. 2	" " S-14.
" 16	" " "	" Figs. 15-b and 16-b, Q-14 and Q'-14.'
" 17	" " "	" Figs. 15-b and 16-a, S-13 and S'-13.'
" 18	" " "	" Fig. 15-b, Q-15.
" 19	" L. b. 3	" Figs. 15-b and 16-a, S-18 and S'-18.'
" 20	" " "	" Figs. 15-b and 16-b, Q-18 and Q'-18.'
" 21	" L. c. 1	" " Fig. 15-c, S-22.
" 22	" " "	" " Q-24.
" 23	" L. c. 2	" " S-24.
" 24	" " "	" " Q-25.
" 25	" L. c. 3	" " S-28.
" 26	" " "	" " Q-28.
" 27	" L. d. 1	" " Fig. 15-d, S-31.
" 28	" " "	" " Q-32.
" 29	" K. a. 1	" " Fig. 23-a, q-2.
" 30	" " 2	" " Fig. 23-b, q-5.
" 31	" K. b. 1	" " Fig. 23-c, q-8.
" 32	" " 2	" " Fig. 23-d, q-11.
" 33	" " "	White cast iron castings.
" 34-A	" " "	Fracture of the as cast test bar annealed in Exp. No. 1.
" 34-B	" " "	" quenched " " "
" 35	" " "	Micro-structure of the as cast test bar annealed in Exp. No. 1.
" 36	" " "	" quenched " " "
" 37	" " "	" as cast " " No. 4.
" 38	" " "	" as cast " " No. 5.
" 39	" " "	" quenched " " "
" 40-A	" " "	Fracture of the as cast test bar annealed in Exp. No. 9.
" 40-B ₁	" " "	" quenched " " "
" 40-B ₂	" " "	" " " " "
" 41	" " "	Micro-structure of the as cast test bar annealed in Exp. No. 9.
" 42	" " "	" quenched " " "

Pl. I.

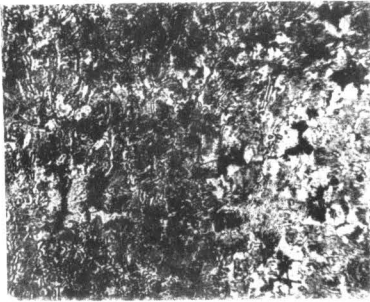


Photo. No. 1.
× 100
C=2.14%, Si=1.42%.

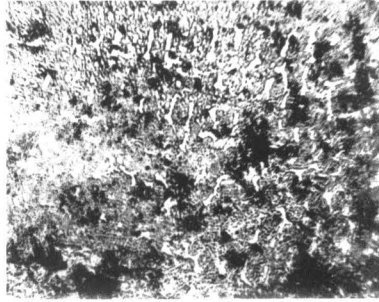


Photo. No. 2.
× 100
C=2.14%, Si=1.42%.

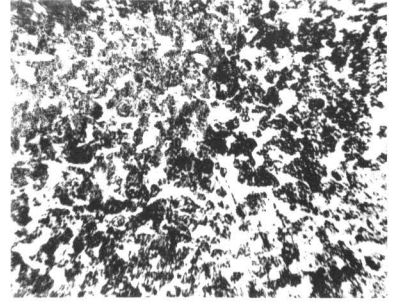


Photo. No. 3.
× 100
C=2.14%, Si=1.42%.

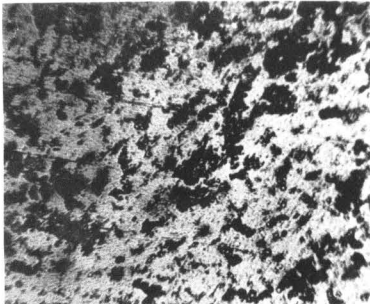


Photo. No. 4.
× 100
C=2.14%, Si=1.42%.

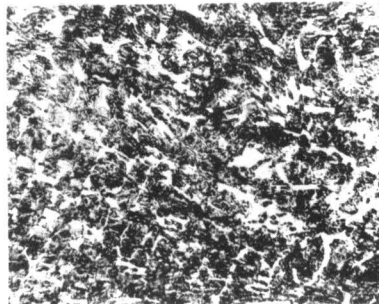


Photo. No. 5.
× 100
C=2.42%, Si=0.94%.

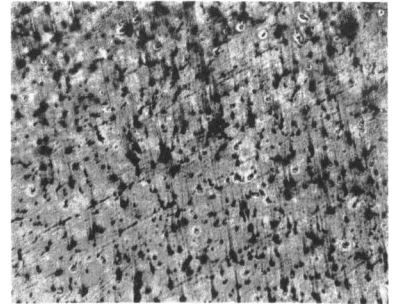


Photo. No. 6.
× 100
C=2.80%, Si=1.21%.

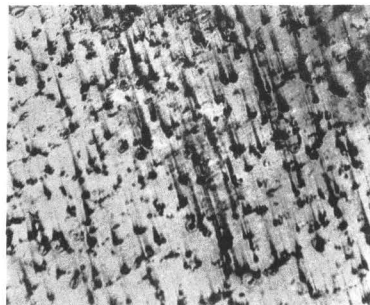


Photo. No. 7.
× 100
C=2.80%, Si=1.21%.



Photo. No. 8.
× 100
C=2.80%, Si=1.21%.

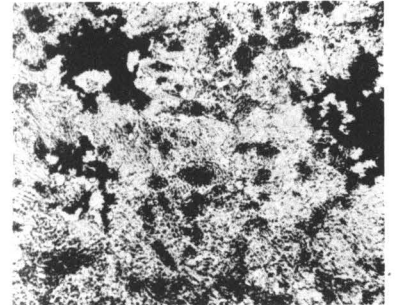


Photo. No. 9.
× 100
C=1.97%, Si=0.64%.

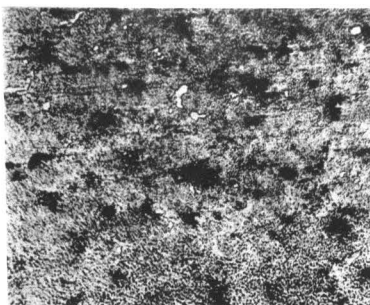


Photo. No. 10.
× 100
C=1.97%, Si=0.64%.

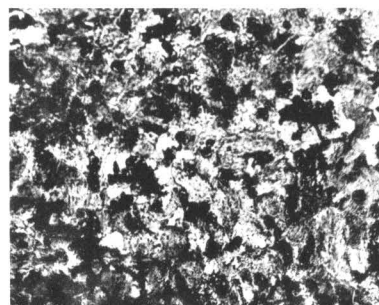


Photo. No. 11.
× 100
C=2.05%, Si=1.70%.

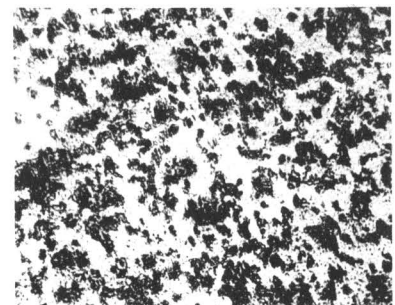


Photo. No. 12.
× 100
C=2.05%, Si=1.70%.

Pl. II.

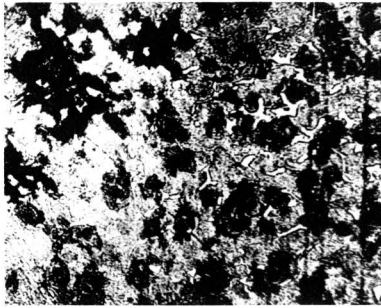


Photo. No. 13.
× 100
C=2.46%, Si=0.67%.

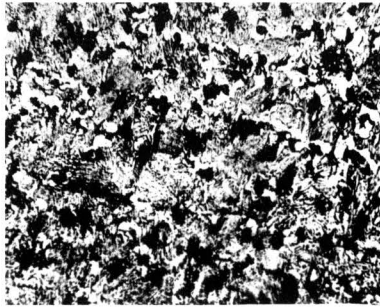


Photo. No. 14.
× 100
C=2.46%, Si=0.67%.

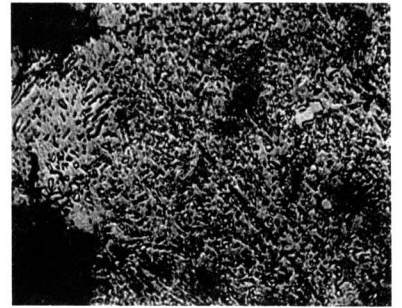


Photo. No. 15.
× 100
C=2.43%, Si=0.94%.

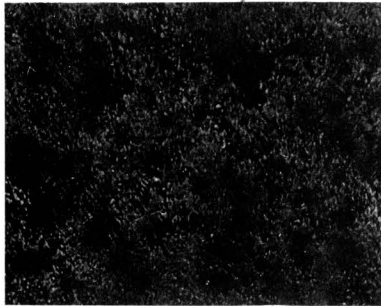


Photo. No. 16.
× 100
C=2.43%, Si=0.94%.

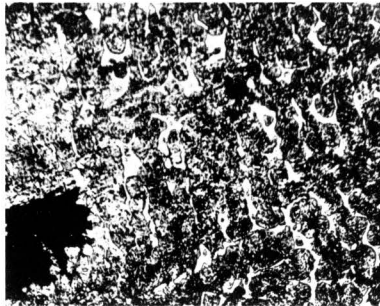


Photo. No. 17.
× 100
C=2.43%, Si=0.94%.

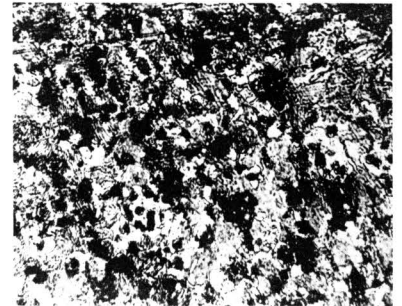


Photo. No. 18.
× 100
C=2.43%, Si=0.94%.

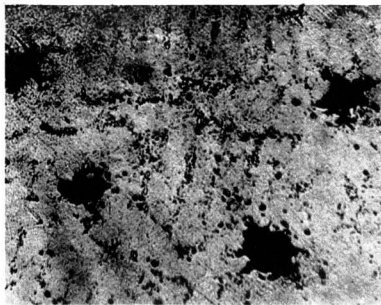


Photo. No. 19.
× 100
C=2.38%, Si=1.25%.

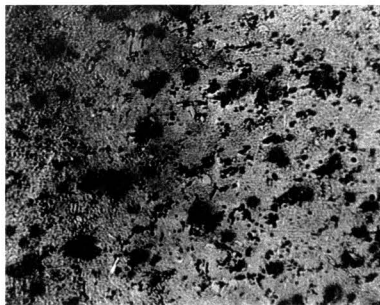


Photo. No. 20.
× 100
C=2.38%, Si=1.25%.

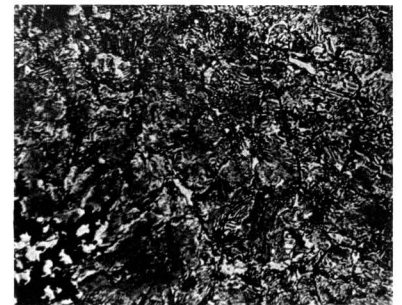


Photo. No. 21.
× 100
C=2.81%, Si=0.65%.

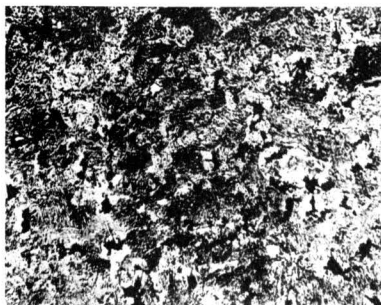


Photo. No. 22.
× 100
C=2.81%, Si=0.65%.

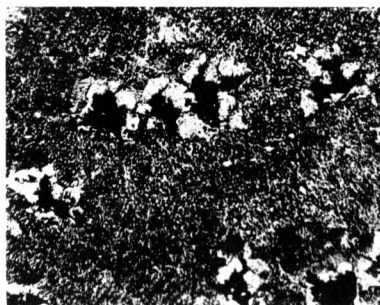


Photo. No. 23.
× 100
C=2.80%, Si=0.94%.

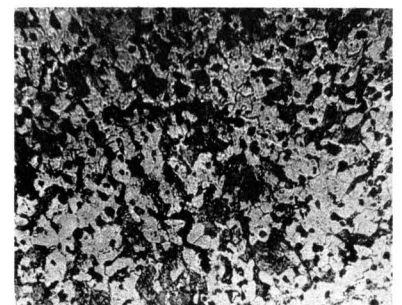


Photo. No. 24.
× 100
C=2.80%, Si=0.94%.

Pl. III.



Photo. No. 25.
× 100
C=2.79%, Si=1.35%.

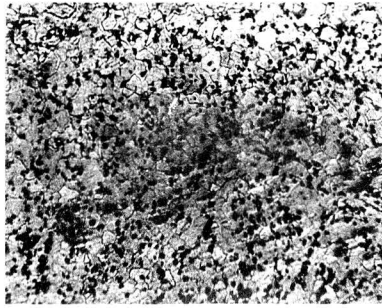


Photo. No. 26.
× 100
C=2.79%, Si=1.35%.

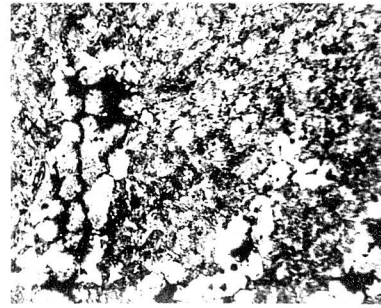


Photo. No. 27.
× 100
C=3.33%, Si=1.03%.

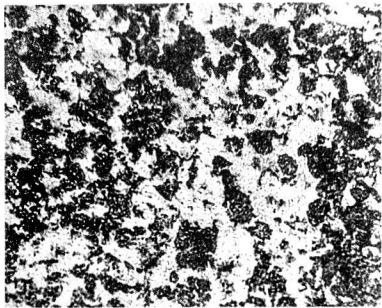


Photo. No. 28.
× 100
C=3.33%, Si=1.03%.

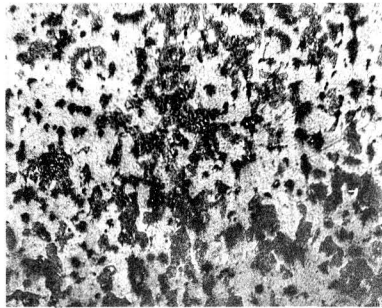


Photo. No. 29.
× 100
C=2.34%, Si=0.97%.

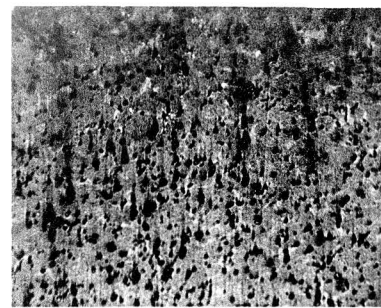


Photo. No. 30.
× 100
C=2.36%, Si=1.30%.

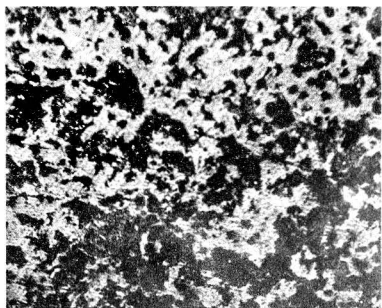


Photo. No. 31.
× 100
C=2.82%, Si=0.99%.

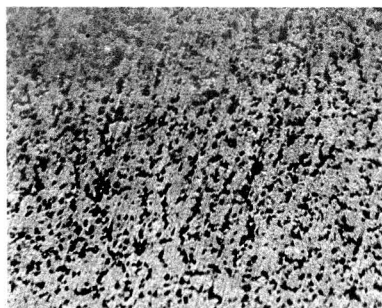
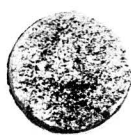
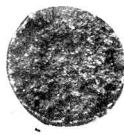


Photo. No. 32.
× 100
C=2.78%, Si=1.31%.



A

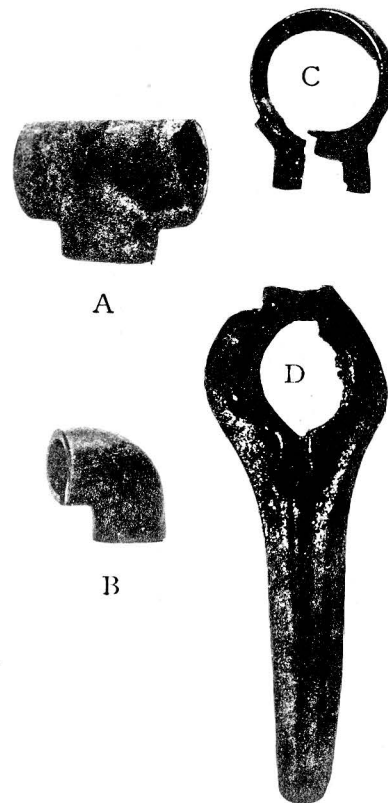


B

Photo. No. 34.
× 1
C=2.86%, Si=1.02%.



Photo. No. 35.
× 100
C=2.86%, Si=1.02%.



A

B

C

D

Photo. No. 33.
× 1/3

Pl. IV.

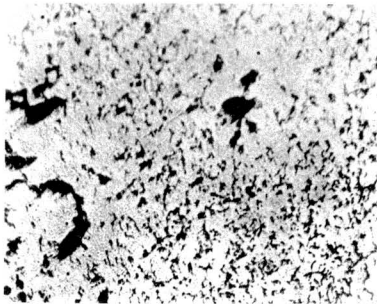


Photo. No. 36.
× 100
C=2.86%, Si=1.02%.

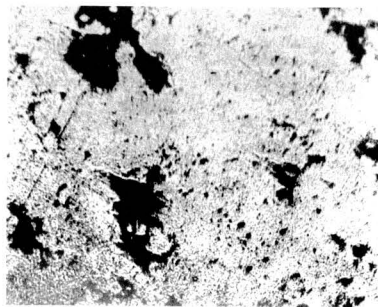


Photo. No. 37.
× 100
C=2.86%, Si=1.02%.

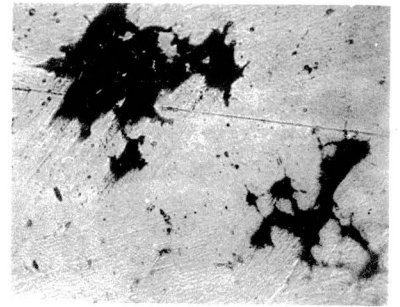


Photo. No. 38.
× 100
C=2.75%, Si=1.12%.

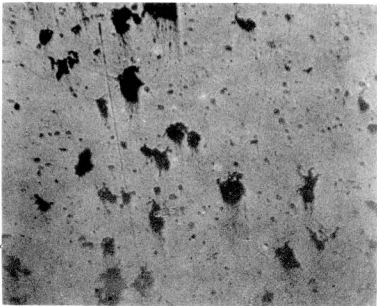


Photo. No. 39.
× 100
C=2.75%, Si=1.12%.

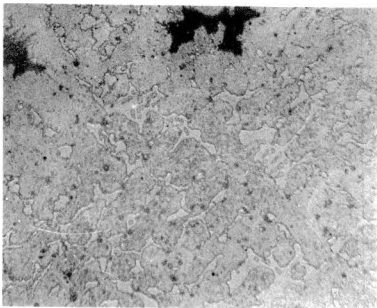


Photo. No. 41.
× 100
C=2.75%, Si=1.12%.

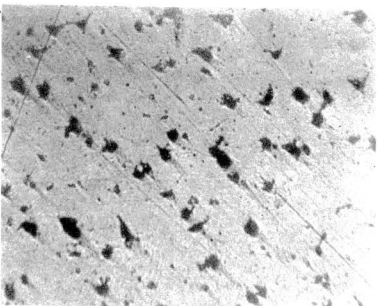
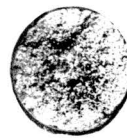


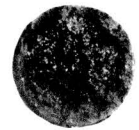
Photo. No. 42.
× 100
C=2.75%, Si=1.12%.



A



B₁



B₂

Photo. No. 40.
× 1
C=2.75%, Si=1.12%.