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# Research on the Structural Changes of Cast Iron by Contact Melting with Various Oxides\*

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## Synopsis

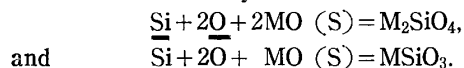
This investigation has been made to confirm how the structure of cast irons is influenced by oxides which constitute refractory and slag. Synthetic Fe-C and Fe-C-Si cast irons have been melted in contact with the various oxides under oxidizing atmosphere, argon and carbon monoxide at 1 atm. pressure at 1,300 and 1,350°C.

The experimental results and the considerations are as follows :

(1) In the case of the oxidizing atmosphere, the structure of synthetic Fe-C-Si cast irons becomes eutectic graphite or white cast iron structure. The structural changes are strongly controlled by the oxidation of the oxidizing atmosphere.

(2) In the cases of argon and carbon monoxide, the original flake graphite structure becomes fine in the order SiO<sub>2</sub>, MgO, BaO or CaO. In the case of Al<sub>2</sub>O<sub>3</sub>, the original structure is retained, and in the cases of BaO and CaO, the structure is most fine. The original sulphur content of the cast irons is also reduced in the similar order.

(3) In the case of argon atmosphere, it may be deduced from the thermodynamic consideration that the Fe-C-Si alloys are deoxidized in the following processes.



(4) In the case of CO atmosphere, it may be considered that the structural changes between flake graphite and fine eutectic graphite structure of Fe-C and Fe-C-Si alloys are due to the changes of sulphur contents of the alloys. In the case of argon atmosphere, it may be considered that the structural changes of Fe-C-Si alloys are due to the deoxidation and desulphurization of the alloys.

## I. Introduction

Molten steel and cast iron always contact during refining with oxides which constitute refractories and slag. Few studies have been made on the effect of oxides on the structure of cast iron. For the purpose of confirming the effect of oxide, cast iron was contact-melted with various oxides in the actual oxidizing atmosphere, pure argon and carbon monoxide atmospheres. Studies were made of the structural changes of cast iron and the changes in chemical compositions accompanying them.

## II. Experimental procedure

The experiments were carried out by the following three method :

- (1) Contact-melting in oxidizing atmosphere,
- (2) Contact-melting in argon or carbon monoxide atmosphere,

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(3) Sulphur addition.

Chemical compositions of cast irons used are shown in Table 1. All specimens were the synthetic cast irons except D-1 and C-54-C.

Experiment (1) is first described. The melting furnace used was a silicon carbide furnace. Three kinds of atmosphere were used, air, weak oxidizing atmosphere prepared by covering a graphite block on the crucible and argon gas flow. In the case of covering a graphite block on the crucible, the atmosphere is composed of a mixture of CO, CO<sub>2</sub>, N<sub>2</sub> and O<sub>2</sub> so that it can be considered as an oxidizing atmosphere weaker than air. The atmosphere of argon flow can also be regarded as a weak

Table 1. Chemical composition of cast irons.

Mark	C	Si	Mn	P	S
A-1	4.04	3.07	0.028	0.005	0.025
A-3	3.88	3.18	0.008	0.004	0.045
A-5	3.91	3.06	0.005	0.006	0.027
B-1	3.24	2.86	0.022	0.0038	0.019
B-2	3.69	2.91	nil	0.004	0.025
B-3	3.34	1.66	trace	0.007	0.018
C-4	3.94	0.074	trace	0.002	0.026
Mo3Y	4.79	—	—	—	—
D-1	3.65	1.98	0.25	0.246	0.0098
C-54-C	3.13	1.65	0.44	0.130	0.020

oxidizing atmosphere, since the furnace tube is porous and air in the tube is not removed before passing argon, and therefore air is mixed. Cast iron covered by oxides which had been in various conditions shown in Tables 2 and 3, was put in a crucible, heated up to and kept at 1,300°C or 1,350°C for 30 minutes to 2 hours,

Table 2. Relation between experimental condition in contact-melting with oxides under oxidizing atmosphere and structure.

Synthetic cast iron		Oxide		c.i.(g): oxide(g)	Melting		Treated time(hr)			Atmosphere
Mark	Form	kind	Preservative condition		Temp. (°C)	State of oxide	0.5	1.0	2.0	
B-1	Block	—	—	—	1350	—	II	III	V	W.O.A.
B-1	Block	CaO	in d.	10 : 5	1350	Solid	II ~ III	III	V	W.O.A.
B-1	Block	CaO	in d. after heating at 800°C.	10 : 5	1350	Solid	IV	—	—	Air
B-1	Block	CaO	in atm.	10 : 5	1350	Solid	V	—	—	Air
B-2	Block	CaO	in atm. for long period	10 : 5	1300	Solid	III	—	—	Argon flow
B-2	Block	CaO	in d. after heating at 1200°C	10 : 2	1300	Solid	III	—	—	Argon flow
B-2	Block	Ca(OH) <sub>2</sub>	in atm.	10 : 2	1300	Solid	V + III	—	—	Argon flow
D-1	Lathe chip	MgO	in d. after heating at 1400°C	20 : 3	1350	Solid	II	—	—	W.O.A.
B-3	Block	MgO	in atm.	10 : 2	1300	Solid	III	—	—	Argon flow
B-1	Block	SiO <sub>2</sub>	in atm.	10 : 2	1350	Solid	—	II	—	W.O.A.
D-1	Lathe chip	SiO <sub>2</sub>	in d. after heating at 1400°C.	10 : 2	1350	Solid	II	—	—	W.O.A.
B-1	Block	Al <sub>2</sub> O <sub>3</sub>	in atm.	10 : 5	1350	Solid	—	III	—	W.O.A.
B-1	Block	Dolomite	in atm.	10 : 5	1350	Solid	—	III	—	W.O.A.
B-1	Block	T.B.S.	in atm.	10 : 5	1350	Liquid	I	II	—	Air

Note T.B.S. is CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> (47 : 42 : 11) which was melted before use.

I : Flake graphite structure II : Rose graphite structure III : Eutectic graphite structure V : white cast iron structure d. : desiccator atm. : atmosphere W.O.A. : Weak oxidizing atmosphere c.i. : cast iron

and then cooled at the rate of 400°C per minute at the vicinity of its freezing point. For comparison with these results cast iron alone was melted in a weak oxidizing atmosphere. Temperature was measured by a Pt-Pt·Rh thermocouple. In the case of the weak oxidizing atmosphere, alumina crucibles which were bonded with clay were used, and commercial magnesia silicate crucibles were used in the case of argon atmosphere.

Table 3. Relation between experimental condition in contact-melting with slags contained iron oxide and structure.

Mark of cast iron	Oxide		Cast iron (g) : Oxide (g)	Melting		Treating time (hr)		Atmosphere
	Kind	Composi- tion		Temp°C	State of oxide	0.5	1.0	
B-1	Hematite	100%	10 : 5	1350	Liquid	—	V	Air
B-1	Hematite -T.B.S.	1 : 1	10 : 5	1350	Liquid	—	Steely Structure	Air
B-1	Hematite -T.B.S.	1 : 4	10 : 5	1350	Liquid	—	V	Air
B-1	Hematite -T.B.S.	1 : 6	10 : 5	1350	Liquid	—	III	Air
A-3	Fe <sub>2</sub> O <sub>3</sub> -SiO <sub>2</sub>	1 : 1	50 : 10	1400	Liquid	III	—	Air
A-3	Fe <sub>2</sub> O <sub>3</sub> -SiO <sub>2</sub>	2 : 1	50 : 10	1400	Liquid	V	—	Air
A-1	FeO-SiO <sub>2</sub>	1 : 1	5 : 1	1350	Liquid	—	Steely Structure	Argon
A-1	FeO-SiO <sub>2</sub>	2 : 1	5 : 1	1350	Liquid	Steely Structure	—	Argon

Note FeO was prepared by the heat decomposition of ferrous oxalate. T.B.S. is the same as one of the table 2.

Melting under argon gas was made in molybdenum furnace evacuated before heating.  
Fe<sub>2</sub>O<sub>3</sub> : Ferric oxide for reagent III and V are the same as those in table 2.

Table 4. Comparison of the structure of cast irons obtained by melting those only with that of the cast irons contact-melted with SiO<sub>2</sub>.

Cast iron		Oxide		Cast iron (g) : Oxide	Melting		Treating time		Note
Mayk	Grainsize (mesh)	Kind	Grain size (mesh)		Temp.°C	State of oxide	10min.	20min.	
B-3	17~19	SiO <sub>2</sub>	100	5 : 0.75	1300	Solid	I ~ II		(1)
B-3	17~19	—	—	5 : 0	1300	—	I ~ II		(1)
B-3	30~60	SiO <sub>2</sub>	100	5 : 0.75	1300	Solid	I ~ II		(1)
B-3	30~60	—	—	5 : 0	1300	—	I ~ II		(1)
C-54-C	17~19	SiO <sub>2</sub>	100	5 : 0.75	1300	Solid	I ~ II		(2)
C-54-C	17~19	—	—	5 : 0	1300	—	III		(2)
C-54-C	17~19	SiO <sub>2</sub>	100	5 : 0.5	1300	Solid		I ~ II	(2)
C-54-C	17~19	—	—	5 : 0	1300	—		I ~ II	(1)
B-3	30~60	SiO <sub>2</sub> qa	100	5 : 0.5	1300	Solid	I ~ II		(1)
B-3	30~60	—	—	5 : 0	1300	—	I ~ II		(1)

Note SiO<sub>2</sub> : Anhydrous acid for reagent

SiO<sub>2</sub>aq : Silicic acid (Water 12.2%) I, II and III are the same as those in the table 2.

(1) : Argon was filled into furnace at room temp. after evacuation.

(2) : Argon was filled into furnace during heating after evacuation.

In experiment (2) a molybdenum furnace was used. The experiments except those given in Table 4 are first described. 5 to 20 gr of synthetic cast iron was covered with various oxides powder and placed in the furnace, and heated after slowly evacuating the furnace by a mechanical vacuum pump. Argon or CO gas was introduced until latm. pressure when it was heated up to between 600°C and 700°C, and kept at  $1,350^{\circ}\text{C} \pm 15^{\circ}\text{C}$  for 30 minutes at 1 atm pressure. Commercial pure argon was used and CO gas was prepared from concentrated sulphuric acid and formic acid. The crucibles used were commercial alumina and graphite crucibles, and the latter was made of a graphite rod containing less than 0.1 per cent of ash. Temperature was measured by an optical pyrometer through a sight glass attached to a glass cap of the molybdenum furnace. In the case of graphite crucible, its temperature was measured directly, but in the case of alumina crucible, temperature of the adjacent graphite block was measured. The cooling velocity by means of cooling in the furnace was 50 to 60°C per minute at the vicinity of the freezing point.

The molybdenum furnace used was that in which a furnace tube was wound with molybdenum wire and set in a silica tube and the whole furnace was made gas tight by glass caps connected to the silica tube by rubbing against it. This furnace could be used for vacuum melting or non-oxidizing atmosphere melting at optional temperature up to 1,400°C. Two specimens could be melted simultaneously under the same condition. In the experiment shown in Table 4., granulated cast iron alone and that in mixture with  $\text{SiO}_2$  powder were heated in argon 1 atm at 1,300°C for 10 or 20 minutes in the furnace after evacuating. Temperature was measured by a Pt-Pt-Rh thermocouple in the case of synthetic B-3 cast iron, but in the case of C-54-C specimen, temperature of the adjacent graphite block to the crucible was measured by the pyrometer. The crucible used was commercial magnesia silicate crucible which was treated at melting temperature of cast iron in vacuo before the use.

Experiment (3) is next described. 50 gr each of Fe-C-Si (B-2) and Fe-C (C-4) synthetic cast iron was melted at 1,350°C for 30 minutes or 1 hour in a graphite crucible in molybdenum furnace in vacuo. For the purpose of adding 0.01 to 0.23 per cent sulfur to these alloys, after crushing these alloys, about 10 gr each of the alloys was mixed with Fe-C-Si-S (1.15%) and Fe-C-S (1.12%) alloys and melted in an alumina crucible at 1,350°C for 15 minutes in argon atmosphere. Fe-C-S alloys used were prepared by adding sulfur in the form of commercial first grade ferrous sulfide to Fe-C-Si (B-2) and Fe-C (C-4) synthetic cast irons in argon atmosphere which had been melted in a graphite crucible in vacuo. The Fe-C-Si (A-3) synthetic iron was melted in an alumina crucible in vacuo and added sulfur in the form of commercial sulfide in argon atmosphere. The microscopic examination of structure was made on the longitudinal section across the center of specimens in the experiments (1), (2) and (3).

### III. Experimental results and discussion

The relationship between the structure changes by oxide-contact-melting in oxidizing atmosphere and experimental conditions are shown in Tables 2 and 3. The structure changes shown in Table 2 correspond to the structure changes<sup>(1) (2)</sup> in oxidizing cast iron which have been studied by one of the authors, that is, the structure changes from (I) flake graphite to (II) rose graphite structure-(III) eutectic graphite structure-(IV) inverse chilled structure-(V) white cast iron structure depending upon the progress of oxidation. As shown in Table 2, the structure changes are similar to those of cast iron melted alone except in CaO containing water, and it is impossible to point out any significant difference caused by various oxides. Therefore in the structure changes, the effect of atmosphere was considered to be more dominant than the effect of each oxide. In CaO containing water, oxidation progressed further than in dried one, and its structure showed white cast iron structure, as shown in the 4th and 7th lines in Table 2. The difference between these structures can be considered as the effect of water contained in CaO. On treatment with CaO which was exposed in air for a long time, the structure did not change to white cast iron structure so that this phenomenon may be considered to be the elimination of water content by changing CaO into CaCO<sub>3</sub>. In the case of treatment by T.B.S., flake graphite structure was observed even after 30 minutes, as shown in the last line in Table 2. It is considered that the rate of oxidation might have been retarded, since T.B.S. was liquid. Table 3 shows the cases treated by slags containing iron oxide, and with the increase in the

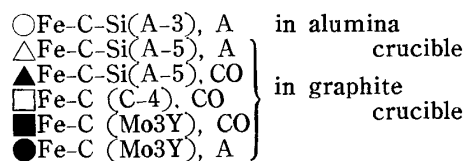
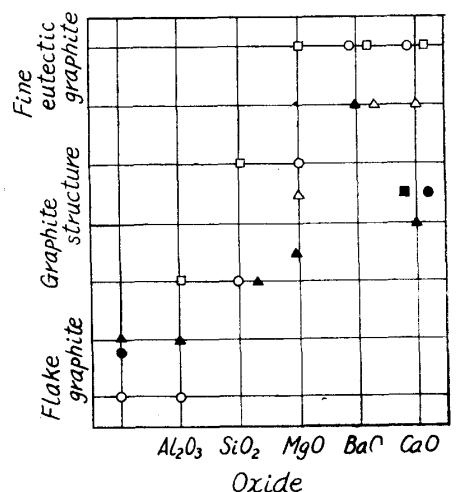


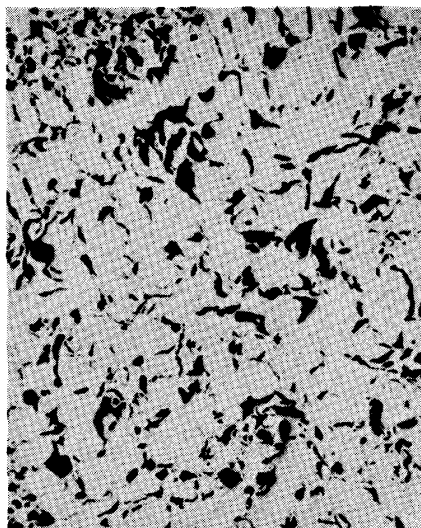
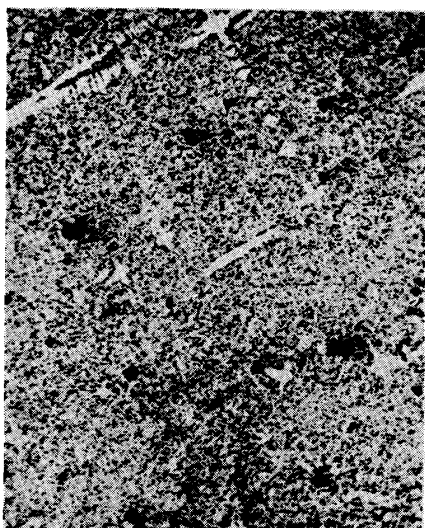
Fig. 1. Relation between oxides and graphite structure.

concentration of iron oxides the oxidation of cast iron progressed markedly and the structure changed to white cast iron structure or steely structure, regardless of atmosphere, oxidizing or non-oxidizing.

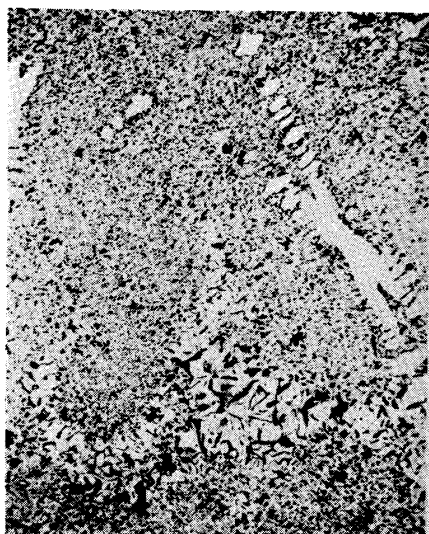
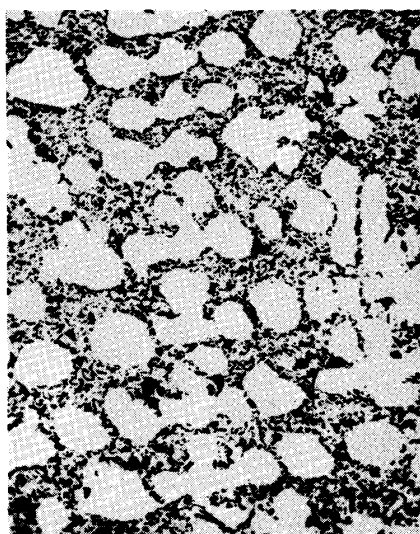
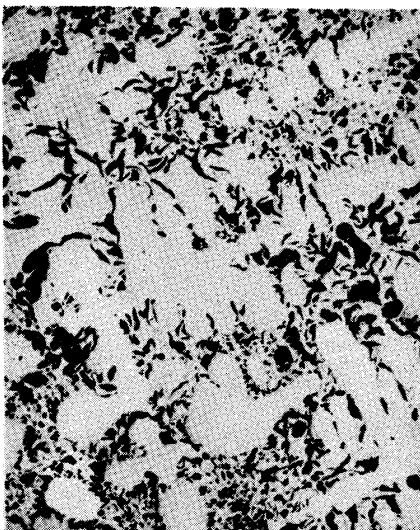
The relationship between the structure and the kind of oxides treated in carbon monoxide atmosphere is shown in Fig. 1. When the alumina was used, the structure was similar to the original flake graphite structure, but showed a tendency to decrease the amount of graphite flake and became finer eutectic graphite structure in the order SiO<sub>2</sub>, MgO, BaO and CaO in both Fe-C-Si and Fe-C alloys. In contact-melting with BaO and CaO in argon atmosphere, the structure almost changed to fine eutectic graphite structure and both showed similar structures. Photos. 1 and 2 show the photo-

(1) M. Homma, Y. Hashimoto, M. Fuse and K. Iwase, J. Japan Inst. Metals, 16 (1952), 260

(2) M. Homma and Y. Hashimoto, J. Japan Inst. Metals, 16 (1952), 486.

Photo. 1.  $\times 67$  A-3Photo. 2.  $\times 67$  B-3Photo. 3.  $\times 67$  A-3—CaOPhoto. 4.  $\times 67$  B-3—CaO

micrographs of synthetic cast iron specimens A-3 and B-3 melted at 1,350°C for 1 hour in almina crucible in argon atmosphere without oxide cover. In A-3, a small amount of fine graphite was present at the bottom of longitudinal section of the specimen. Photos. 3 to 8 show the photomicrographs of synthetic cast iron specimens A-3 and B-3 which were contact-melted with CaO, MgO and SiO<sub>2</sub> at 1,350°C for 1 hour in argon atmosphere. The photographs of A-3 show a part of fine graphite structure, and the whole structure of longitudinal section of the specimens was not fine, flake graphite being present in the upper part of the specimens. In the specimen treated with SiO<sub>2</sub>, considerable amount of graphite flake was present in the upper part of the specimen. On the contrary, in the specimen B-3, the structure in the whole part of the longitudinal section was similar to Photos. 4, 6 and 8. It was found from these photographs that the structures became finer in order of SiO<sub>2</sub>, MgO and CaO. In Al<sub>2</sub>O<sub>3</sub>, the structure was similar to the original one, and in BaO, the structure was similar to that of CaO, and so photographs are

Photo. 5.  $\times 67$  A-3—MgOPhoto 6.  $\times 67$  B-3—MgOPhoto. 7.  $\times 67$  A-3—SiO<sub>2</sub>Photo. 8.  $\times 67$  B-3—SiO<sub>2</sub>

not given.

As mentioned above, in both CO and argon atmospheres, the original graphite structure became finer in the order of SiO<sub>2</sub>, MgO, BaO or CaO. But in contact-melting with CaO and MgO of the same Fe-C-Si alloy (A-5) in both CO and argon atmospheres, the degree of refinement of graphite in CO atmosphere was smaller than that in argon atmosphere, as shown in Fig. 1. The desulfurization by the oxides of CaO, BaO, MgO, and SiO<sub>2</sub> may be considered to be one of the causes for the refinement of graphite in contact-melting, as will be mentioned later. The difference of graphite-refinement by contact-melting in argon and CO atmosphere can be considered to clarify that the deoxidation is also the cause of graphite refinement.

By vacuum melting the graphite structure continues to be finer even after the limit of desulfurization, which is considered to be due to the progress of deoxidation<sup>(3)</sup>. This will be discussed in the next paper.

(3) M. Homma and R. Ohno, Read at the 52nd Meeting of Japan Assoc. of Casting.



Kayama et al. investigated SiO<sub>2</sub> cast iron contact-melting<sup>(4) (5)</sup>. Cast iron specimens were machined to shavings to facilitate easy contact with SiO<sub>2</sub>. They were mixed with excess anhydrous silicic acid powder and the mixture was transferred to an alumina Tammann tube and melted in a Tammann furnace in argon flow. From the result obtained it is concluded that SiO<sub>2</sub> interrupted graphitization of cast iron, showing an oxidizing reaction. On the other hand, the oxidizing reaction of SiO<sub>2</sub> itself was not observed by the authors, as shown in Table 4. The mixture of granular cast iron and SiO<sub>2</sub> powder was treated at 1,300°C in argon atmosphere after evacuating air completely from the mixture before melting. As shown in Table 2, although block or powdered cast iron was treated with SiO<sub>2</sub> powder in weak oxidizing atmosphere no tendency of oxidation of SiO<sub>2</sub> itself except the effect of atmosphere was observed.

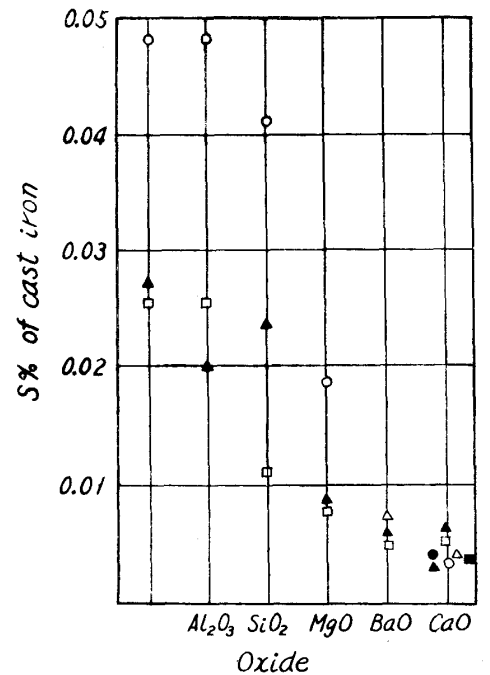
In Fig. 2 are shown the analytical values of sulfur in the alloys after various oxides contact-melting. The specimens for sulfur analysis are the same as those used in the investigation of structure shown in Fig. 1, so that the signs used in Fig. 2 the correspond to those in Fig. 1. As seen in Fig. 2, the sulfur concentration in Al<sub>2</sub>O<sub>3</sub> after treatment remained unchanged except A-5 which was treated in CO atmosphere. In other cases, the sulfur concentration was decreased in the order SiO<sub>2</sub>, MgO and BaO or CaO. By comparing Fig. 1 with Fig. 2, it was found that the graphite structure became finer with decrease in sulfur concentration.

The degree of limit of desulfurization by oxides can be estimated from  $\Delta F^\circ$ , standard free energy change in a reaction



i.e. 
$$\log [S\%] = \log \frac{P_{CO}}{a_C \cdot f_S} + \frac{\Delta F^\circ}{2,303 RT} \dots \dots \dots (2)$$

where MO and MS in equation (1) mean the oxide and sulfide respectively, and [S%] in equation (2) means the sulfur concentration in metal in equilibrium. If  $P_{CO}$ ,  $f_S$ ,  $a_C$  in equation (2) are constant, [S%] at the equilibrium condition can be determined by  $\Delta F^\circ$ . From the values of  $\Delta F^\circ$ , the order of oxide which lowers the limit of desulfurization can be arranged as follows: CaO < BaO < MgO < Al<sub>2</sub>O<sub>3</sub> or SiO<sub>2</sub>.



○ Fe-C-Si (A-3), A in alumina crucible  
 △ Fe-C-Si (A-5), A  
 ▲ Fe-C-Si (A-5), CO  
 □ Fe-C-Si (C-4), CO } in graphite crucible  
 ■ Fe-C (Mo3Y), CO  
 ● Fe-C (Mo3Y), A

Fig. 2. Relation between oxides and S% in cast irons.

(4) N. Kayama and T. Ishino, Imono, 26 (1954), 520.

(5) N. Kayama and K. Saito, Imono, 27 (1955), 593.

In  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$ , the desulfurization is impossible from the values of  $\Delta F^\circ$ . However, the desulfurization was actually observed in  $\text{SiO}_2$  as shown in Fig. 2. Marincek<sup>(6)</sup> explained that (since the sublimation point of silicon sulfide is low.) the desulfurization by  $\text{SiO}_2$  would occur according to the following reaction :



Fig. 3 shows the results of the graphite structure changes by changing sulfur concentration itself. On melting Fe-C alloy (C-4), Fe-C-Si alloy (B-2) in a graphite crucible in vacuo, desulfurization occurred and the sulfur concentration was decreased to 0.01 per cent and 0.005 per cent respectively; the structures became finer; and about one third of longitudinal section area of the specimens showed fine eutectic graphite structure. With increasing sulfur concentration in these specimens in argon atmosphere, fine eutectic graphite decreased and flake graphite increased.

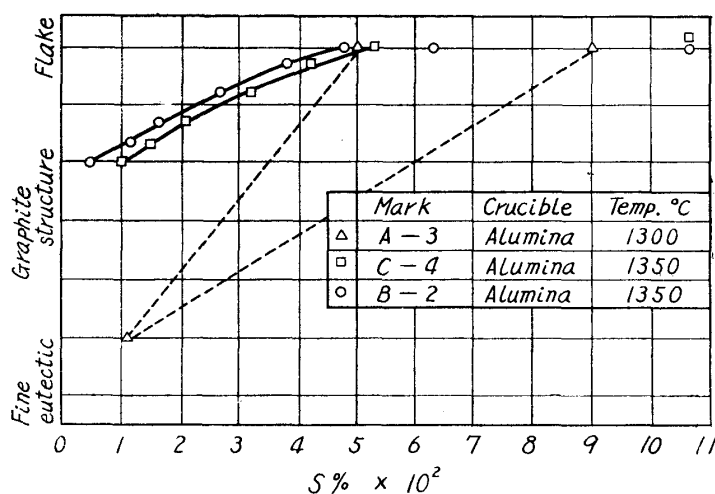


Fig. 3. Relation between S concentration and graphite structure.

As shown in Fig. 3, when sulfur concentration became 0.04 to 0.05 per cent, almost structure changed into flake graphite structure in both Fe-C and Fe-C-Si alloys. On melting in vacuum Fe-C-Si alloy (A-3) with flake graphite structure in the alumina crucible, almost structure changed into fine eutectic graphite structure. This structure changed inversely into flake graphite structure by the addition of sulfur. From these experiments, it can be seen that the structure change between flake graphite structure and fine eutectic graphite structure depends upon a little change in sulfur concentration.

The similar effect of sulfur was recognized by Boyles<sup>(7)</sup>, La Planche<sup>(8)</sup>, and S. Garber<sup>(9)</sup> in the experiments in which sulfur was added to hypo-eutectic Fe-C-Si alloy in nitrogen atmosphere. In the investigation on Fe-C alloy and Fe-C-Si alloy the similar effect was also observed by Williams<sup>(10)</sup>. In recent experiments with

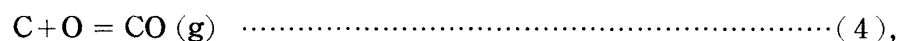
- (6) B. Marincek, Rev. Mét., 53 (1956), 1.  
 (7) A. Boyles, Trans. AIME, 125 (1937), 141.  
 (8) H. Laplanche, Fonderie 32 (1948), 1253.  
 (9) S. Garber, J. Iron Steel Inst., 181 (1955), 291.  
 (10) W. J. Williams, J. Iron Steel Inst., 164 (1950), 407.

Fe-C-Si alloy by, S. Garber<sup>(9)</sup> supercooled graphite disappeared with the addition of 0.026 per cent S and changed completely into flake graphite. As Boyles<sup>(7)</sup> stated sulfur concentration required for changing into 100 per cent flake graphite will be lower with decreasing saturation degree of carbon  $S_c$ .

Therefore it is certain that the graphite-refinement by oxide-contact melting depends upon desulfurization. But according to the experiment<sup>(3)</sup> in vacuum melting mentioned above, it is unthinkable that the structure change is controlled by desulfurization alone; it might be due to deoxidation as will be mentioned in the next section.

The amount of flake graphite treated in CO atmosphere was always larger than that treated in argon atmosphere, although sulfur concentration was the same in contact-melting in both CO and argon atmosphere as mentioned above. This fact shows that the graphite-refinement of structure does not depend upon desulfurization alone. When Fe-C-Si alloy was contact-melted with CaO, MgO or BaO in argon atmosphere, it may be deduced that oxygen concentration becomes smaller than that produced by contact-melting in CO atmosphere.

Independently of the oxide contact-melting, Fe-C-Si alloys containing 3.06 per cent and 4.16 per cent Si were melted in vacuo in a graphite crucible at 1340°C for 1 hour and melted continuously in 1 atm CO atmosphere for 1 hour, the flake graphite increased<sup>(3)</sup> certainly compared with that melted in vacuo at 1,530°C for 1 hour. The concentration of oxygen in the alloys prepared by vacuum melting and under 1 atm CO may be considered thermodynamically to be as follows: there is an equilibrium relationship<sup>(5)</sup> between dissolved in Fe-C-Si alloy  $\underline{O}$  and CO gas in reaction (4)



i.e. 
$$K = \frac{P_{\text{CO}}}{a_c \cdot a_o} \left( = \frac{P_{\text{CO}}}{f_c[\text{C}\%] f_o[\text{O}\%]} \right) \dots\dots\dots(5)$$

where  $K$  is an equilibrium constant. If temperature is constant,  $K$  is constant.

When a graphite crucible is used, the activity of carbon  $a_c$  is constant, and the activity coefficient of oxygen  $f_o$  is constant, if the alloy of the same composition is considered. Therefore the equation (5) can be simplified as follows:

$$K' = \frac{P_{\text{CO}}}{[\text{O}\%]} \left( [\text{O}\%] = \frac{P_{\text{CO}}}{K'} \right) \dots\dots\dots(6)$$

If  $P_{\text{CO}}$  approximately equals to total pressure in the vacuum and CO atmosphere melting,  $[\text{O}\%]$  in the alloys melted in vacuum and CO atmosphere can be expressed by  $[\text{O}\%]$  which are obtained from the equation (6) when  $P_{\text{CO}}=10^{-4}$  atm (vacuum pressure) and  $P_{\text{CO}}=1$  atm respectively. Therefore, it is seen that the oxygen concentration in the alloy is higher in specimens melted in CO atmosphere than that melted in vacuum. The increase of amount of graphite flake of Fe-C-Si alloy containing Si 3 per cent and 4 per cent in the case of melting in CO atmosphere relates to the increase of oxygen concentration in the alloy.

Therefore, the difference in the degree of graphite-refinement between argon

atmosphere and CO atmosphere contact-melting can be considered to have relation with the difference in oxygen concentration in cast iron. Therefore, it is supposed that the graphite-refinement progressed markedly in argon atmosphere

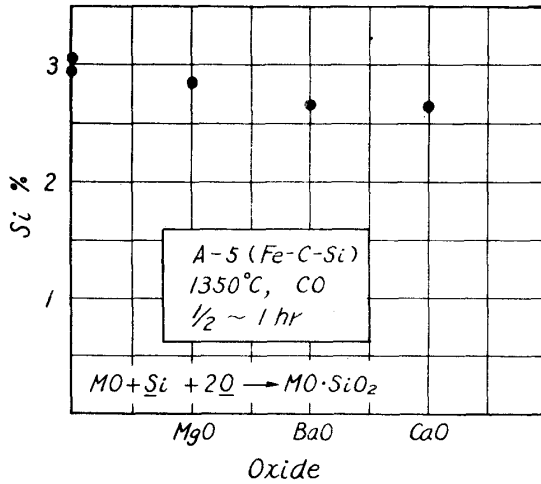


Fig. 4 Si concentrations in an Fe-C-Si alloy contact-melted with various oxides in CO atmosphere.

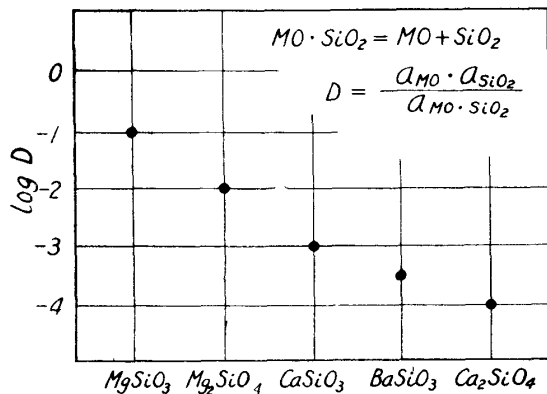
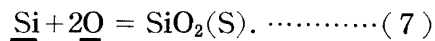


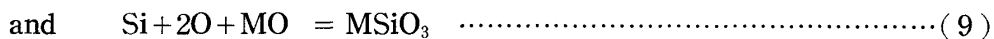
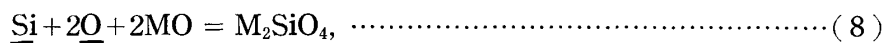
Fig. 5. Dissociation constants of various silicates at 1350°C.

melting because of lower oxygen concentration by deoxidation, compared with that melted in CO atmosphere. As to the deoxidation process by oxides in contact-melting in argon atmosphere, the processes of equation (8) and (9) can be considered from the following experimental results and consideration.

In contact-melting of Fe-C-Si alloy (A-5) with CaO, BaO and MgO at 1,350°C, the Si concentration decreased compared with that before treatment, as shown in Fig. 4. The dissociation constants of silicates of Ca, Ba and Mg at 1,350°C are shown in Fig. 5 on the basis of Richardson's paper<sup>(11)</sup>. For a standard state of activity, pure substances are selected. On the other hand, from the authors' experiment, the following equilibrium is considered to be established between Si 4 per cent and 5 per cent in the case of carbon-saturated Fe-C-Si alloy at the vicinity of 1,350°C, in 1 atm CO, i.e.



That is to say, the activity of SiO<sub>2</sub> is equal to pure SiO<sub>2</sub>(S). Therefore, the activity of SiO<sub>2</sub> of carbon-saturated Fe-C-Si alloy containing 3 per cent Si at 1,350°C in 1 atm CO is considered to be about unity. On the other hand, if the activities of oxide and silicate are assumed to be unity, it may be considered from the dissociation constant D of silicate in Fig. 5 that a<sub>SiO<sub>2</sub></sub> in the case of contact-melting with oxide at 1,350°C becomes equal to D and considerably smaller value than unity. Therefore, the decrease of Si content on contact-melting with oxide in CO atmosphere mentioned above is considered to depend upon the following reaction processes:



where M<sub>2</sub>SiO<sub>4</sub> and MSiO<sub>3</sub> are silicates. In the case of contact-melting with oxide in

(11) F.D. Richardson et al., J. Iron Steel Inst, 166(1950), 213.

argon atmosphere, the deoxidation was carried out on the processes of (8) and (9) and silicates may be produced at interface between metal and oxide.

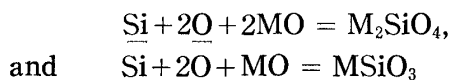
### Summary

(1) In contact-melting of Fe-C-Si synthetic cast iron with various oxides under oxidizing atmosphere, the graphite structure became finer and further changed into white cast iron structure. The structure changes are considered to be brought about not by oxides themselves, but by the oxidation by the atmosphere. In the case of CaO containing water, oxidation was observed.

(2) In contact-melting of Fe-C-Si synthetic cast irons with various oxides in argon and CO atmospheres, the original flake structure became finer and the sulfur concentration in cast irons decreased in order of  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ , MgO and BaO or CaO. In the case of  $\text{Al}_2\text{O}_3$ , both the structure and sulfur content are similar to those of original cast irons. In both BaO and CaO, the structures are finest and the sulfur content is minimum. In contact-melting of Fe-C-Si alloy (A-5) with CaO and MgO in argon and CO atmospheres, the graphite-refinement in argon atmosphere progressed more than that in CO atmosphere.

(3) By adding sulfur to Fe-C and Fe-C-Si alloys in argon atmosphere which were melted in graphite crucible at  $1,350^\circ\text{C}$  in vacuo, fine eutectic graphite vanished at 0.04 to 0.05 per cent S. Structures almost changed to flake graphite structure. In melting of Fe-C-Si alloys (3.06 per cent and 4.16 per cent) which were melted in a graphite crucible in vacuo, at  $1,350^\circ\text{C}$  for 1 hour in 1 atm CO, the amount of graphite flake increased.

(4) When Fe-C-Si alloy (A-5) was contact-melted with CaO, MgO and BaO in CO atmosphere, the concentration of Si decreased. This is considered to be due to the following reaction processes from the dissociation constants of silicates and the authors' experiment:



(5) The graphite-refinement in the case of contact-melting of Fe-C, Fe-C-Si alloys with oxides in CO atmosphere is due to the desulfurization of alloys. On the other hand, in the case of contact-melting of Fe-C-Si alloy in argon atmosphere, the structure change is considered due to both deoxidation and desulfurization.