Equilibrium of Carbon and Oxygen in Molten Iron Saturated with Carbon*

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It has been known experimentally that oxygen contents in cast iron products often show remarkably scattering values even in a same kind of products, the unexpectedly high or low values of which are hardly comparable with those evaluated from previous works on the equilibrium between carbon and oxygen in carbon-saturated molten iron. This can be attributed to the difficulty in determining the oxygen content in cast iron owing to the presence of graphite. In order to examine the equilibrium of carbon and oxygen in carbon-saturated molten iron, experiments were carried out in the graphite crucible under CO atmosphere by means of a sampling method established by the present authors: The method consisted of sucking white iron samples from the melt by a thin silica tube and immersion into mercury. Analysis of oxygen was carried out by measuring the electric conductivity in argon-carrier fusion which has the accuracy of less than ± 2 p.p.m. within the range of less than the 10 p.p.m. oxygen content.

The results obtained are as follows:

- (1) The solubility of carbon in molten iron will be expressed by

$$\text{C}\% = 1.33 + 2.59 \times 10^{-3} \times t^{\circ}\text{C}.$$

- (2) Relations between carbon and oxygen in carbon-saturated molten iron will be

$$\log K_s (= P_{\text{CO}}/\text{O}) = 613/T + 2.775,$$

$$\log K_4 (= P_{\text{CO}_2}/P_{\text{CO}} \times \text{O}) = 9,018/T - 6.045,$$

$$\log K_7 (= P_{\text{CO}}/\text{C}\% \times \text{O}\%) = 1.239/T + 1.711.$$

- (3) The activity coefficient of carbon and oxygen in carbon-saturated molten iron will be

$$\log f_c = -847/T + 2.055 - \log \{1.33 + 2.59 \times 10^{-3} (T - 273)\},$$

$$\log f_o = 300/T - 1.283.$$

- (4) The oxygen content of carbon-saturated molten iron is extremely low. Consequently, the equilibrium product (C).(O) does not show a large value, and the activity coefficient of oxygen obtained is not an extremely small value.

- (5) To determine the exact oxygen content in carbon-saturated molten iron it is essential to prevent graphite from precipitation in samples as much as possible. Furthermore it is necessary to establish an analytical method which is possible to determine an extremely low oxygen content up to the level of 0.0001%.

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I. Introduction

There have been many investigations⁽¹⁾⁻⁽⁵⁾ that oxygen in cast iron gives an important influence on properties of irons. Many unknown problems, however, still remain with respect to the quantitative influence of oxygen on their properties. The experiments at our plant have revealed that of oxygen contents in cast iron products often show remarkably scattering values even in a same or similar kind of products and the values are unexpectedly high or low as compared with those evaluated from previous

works on the equilibrium between carbon and oxygen in molten iron saturated with carbon. A major cause of it is the difficulty of precisely analyzing the oxygen content in cast iron, but it seems necessary to re-examine the conventional equilibrium values between carbon and oxygen in carbon-saturated molten iron.

Therefore, investigations were first made on the sampling and preparation methods to precisely determine oxygen contents in molten iron, by establishing an appropriate method, and the equilibrium between carbon and oxygen in carbon-saturated molten iron was examined.

II. Experimental Procedure

1. Analytical method and its accuracy

Analysis of oxygen were carried out by measuring the electric conductivity in an argon-carrier fusion. In order to determine the analytical accuracy of this method, comparison was made with the vacuum-fusion micro-orsat method and the vacuum fusion-measuring pressure method, and the reproducibility of the present method was examined, using the standard

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Table 1 Analytical conditions

Method	Preparation temp. (°C)	Preparation temp. (hr) time	Analysis temp. (°C)	Extraction time of gas (min)	Sample wt. (g)
Vacuum fusion (micro-orsat)	2000~2100	2.5~3.0	1850~1900	15~20	5~10
Inert-gas fusion (measuring electric conductivity)	2200~2250	0.5~1.0	1850~1900	2.5~5	1~2
Vacuum fusion (measuring pressure)	2100~2200	2.0~2.5	1850~1900	3~5	0.5~1

Table 2a Oxygen analysis by vacuum fusion and inert-gas fusion (standard sample B)

Method	Oxygen content, (ppm)	Mean value (ppm)	Standard deviation
Vacuum fusion (micro-orsat)	35, 35, 36, 37, 37, 37, 38, 39, 39, 39, 41, 41, 42, 42, 43, 43, 44, 44, 45, 46, 47, 48, 49, 49,	41.5 $n = 24$	4.3
Inert gas fusion (measuring electric conductivity)	38, 39, 40, 41, 41, 42, 43, 43, 43, 45, 46, 46, 46, 47, 48, 48, 48, 48, 49, 49, 49, 50, 51, 51, 51,	45.4 $n = 25$	3.9
Vacuum fusion (measuring pressure)	40, 41, 41, 42, 43, 43, 43, 43, 43, 44, 44, 44, 45, 47, 48, 48, 49, 49, 50, 50, 50, 51, 51, 51,	45.8 $n = 24$	4.0

n ; numbers of sample
oxygen contents are tabulated from the side of lower values

Table 2b Reproducibility of inert-gas fusion.

Standard sample	Oxygen content (ppm)	Mean value (ppm)	Standard deviation
C $n = 24$	8, 8, 8, 9, 9, 9, 9, 9, 9, 10, 10, 11, 11, 11, 12, 12, 12, 12, 12, 13, 13, 13, 13, 14,	10.7	1.9
D $n = 24$	4, 4, 4, 4, 4, 5, 5, 5, 5, 5, 5, 5, 5, 6, 6, 6, 7, 7, 7, 7, 8, 8, 8, 8,	.8	1.5

samples with varying oxygen contents.

The analytical conditions and results of each method are shown in Table 1 and Tables 2a and 2b, respectively.

From the tables it can be said the results by measuring the electric conductivity in the argon carrier fusion almost coincided with those of the other method, and the reproducibility was also confirmed to be highly reliable.

However, to improve the accuracy in this experiment the weight of samples for analysis is determined to be more than 5 gm. In this case, the accuracy became higher almost two times that of the conventional weight; the accuracy was less than ± 2 p.p.m. (reliability; 95%) within the range of less than the 10 p.p.m. oxygen content.

2. Analysis of carbon

Carbon contents in the samples weighing 0.2 to 0.3 gm. were determined by the combustion-coulometric method. The analytical accuracy was $\pm 0.07\%$ within the range of carbon contents in this experiment.

3. Sampling and preparation methods for oxygen analysis in molten iron saturated with carbon

Sampling methods from carbon-saturated molten iron in this experiment can be conventionally divided into two; one is to cut off samples for analysis from iron solidified quickly in the crucible and the other is to suck up and quench molten iron by using a thin tube.

(1) The method to rapidly solidify molten iron in the crucible

This method was investigated by blowing argon gas against molten iron in the reaction tube (hereafter called A-apparatus) used for the experiment of equilibrium shown in Fig. 5 and by using another apparatus (B-apparatus) shown in Fig. 1 in order to make blowing stronger.

Experiment No. 1 Experiment No. 2

A) Apparatus: A B

B) Crucible: graphite crucible (15 mm in i.d., 60 mm in height, 5 mm in thickness)

Fig. 1 Apparatus for a quick solidifying test with Ar jet

	Experiment No. 1	Experiment No. 2
C) Material:	electrolytic iron saturated with carbon	
D) Weight:	50 gm.	
E) Atmosphere	CO	air
F) Temperature	1350°C	held for 15 minutes
G) Cooling (Experiment No. 1)	Blow argon gas (20°C) against the surface of molten iron at the rate of 3000 cc/min immediately after putting off the power source of the	

high frequency induction furnace.
(Experiment No. 2)

Blow argon gas (20°C) against molten iron at the rate of 10,000 cc/min immediately after putting off the power source of the high frequency induction furnace.

After complete solidification the ingot was cut vertically at the center to investigate its structure, and specimens were cut off from each part of the section to analyze the oxygen content. Fig. 2 shows the macro-structures and the distribution of sampling spots for oxygen analysis in the section, and Photos. 1 and 2 also shows the micro-structures and oxygen contents, respectively.

From these results, it is known that the white iron sample can hardly be obtained by quenching in the melting crucible and even a higher degree of quenching as in experiment No. 2 gives rise to white and mottle portions. Since there is a great difference in the oxygen content by the portions, it is difficult to decide which portion shows a reliable oxygen content in the melt. Accordingly, it is questionable to prepare a sample for oxygen analysis by quenching molten iron in the crucible.

Fig. 2 Location of samples for oxygen analysis and macrostructure of the longitudinal section.

Photo. 1 Structures and oxygen contents in the sample.
(Experiment No. 1) ($\times 100$)

Photo. 2 Structures and oxygen contents in the sample.
(Experiment No. 2) ($\times 100$)

(2) The method to solidify quickly by means of suction of molten iron with a thin tube*

Various investigations were made on the sampling method to suck and quench molten iron by using thin tubes. That is to say, comparison was made on the methods to use the thin tubes with several different inside diameters, vacuum sampling tubes and copper pipes, and the result shows that the most reproducible values are obtained by the method of sucking molten iron by a 3 mm I.D. silica tube and quenching in mercury. Fig. 3 shows the result of analysis.

(3) Preparation of the samples for oxygen analysis

Cutting off specimens sucked from molten iron, grinding and washing were carefully carried out on the basis of a method developed by the authors, and the time from sampling to analysis was shortened as much as possible.

4. Experimental procedure of equilibrium between carbon and oxygen

(1) Crucibles and samples

The crucibles used for the equilibrium experiment are pure graphite ones 27 mm in i.d., 50 mm in depth and 5 mm in thickness, being used for the vacuum fusion method. They were blank heated at 1500°C under 10^{-2} mmHg before use. Materials used for the experiment were 120 gm. of electrolytic iron melted in the graphite crucible by the high frequency induction furnace and cast into a 26 mm i.d. metal mould, to which 50 gm. of electrolytic iron was added

Fig. 3 Distribution of oxygen contents in samples. Samples were sucked from carbon-saturated iron with the 3 mm silica-tube. Atmosphere, CO gas; Temperature, 1200°C

to obtain a higher oxygen content in the iron melt during the early stage of holding.

Chemical compositions of mother materials cast into the metal mould are shown below:

C	Si	Mn	P	S
4.5%	tr.	tr.	tr.	tr.

When electrolytic iron is not added to the samples, it is necessary to reduce the carbon content and kish graphite as much as possible. Otherwise, the experimental performance will become difficult due to the coverage of kish graphite on the surface of the iron melt.

* Refer a detailed report in "IMONO" published by the Japan Foundry Association. Vol. 38, p. 78.

Fig. 4 Schematic diagram of the apparatus.

(2) Experimental apparatus

Fig. 4 shows a diagram of the experimental apparatus.

(3) Experimental furnace (the reaction tube)

Fig. 5 shows a schematic diagram of the experimental furnace. CO gas is deduced into the silica tube 65 mm in i.d. at the height of 35 mm above the surface of the melt. There are two holes 8 mm in diameter in the cap of the reaction tube to insert thermo-couples and sampling tubes.

Fig. 5 Reaction chamber.

The graphite crucible for melting was set up in the alumina crucible for shielding, and the gap of the two crucibles was filled with graphite powder dried fully. Silica sand was laid at the bottom of the reaction tube to fix the crucibles.

(4) Carbon monoxide gas producer

CO gas was produced by a reduction method in which pure CO_2 gas (99.6%) was made contact with graphite rods at a high temperature. As the graphite rods, poles of high purity for spectroanalysis were used after blankheating for one hour at 1300°C

under a vacuum of 10^{-2} mmHg to remove moisture. In order to prevent the oxidation of graphite and to remove gases absorbed in graphite solids, argon gas was carried until the temperature of the reduction furnace rose to 1200°C .

(5) Purification apparatus

CO gas produced in the reduction furnace was purified by soda lime, concentrated potassium hydroxide solution, alkalipyrogallol, concentrated sulfuric acid, and phosphorous pentoxide as shown in Fig. 4.

(6) Temperature measurement

The optical pyrometer or Pt-PtRh thermocouples was used to measure the temperature of the iron melt.

The readings of the optical pyrometer were calibrated with those of the thermocouple under an experimental condition, and the difference between them was found to be within $\pm 5^\circ\text{C}$. However, as the measurement of temperature by the optical pyrometer was likely to be disturbed by the presence of kish graphite at a higher temperature, the temperature of the iron melt was controlled by the optical pyrometer and confirmed by the Pt-PtRh thermocouple after sampling. The Pt-PtRh thermocouple was corrected by measuring melting points of electrolytic iron or nickel under argon atmosphere after it had been melted in the magnesia crucible by the high frequency induction furnace under hydrogen atmosphere.

(7) Experimental procedure

The atmosphere inside the reaction tube was replaced by a carrier of CO gas for 40 minutes after the sample had been charged in the fully dried crucible in the reaction tube. The gas exhausted from the reaction tube during this replacement was more than 99% CO without CO_2 . The replacement seemed to further proceed because it took 25 minutes to completely melt the sample in the CO carrier at a high frequency. The sampling was carried out by the method of suction using 3 mm. i.d. silica tubes shown in Fig. 6 after molten iron had reached the equilibrium stage at given temperatures. The inside of silica tubes had been replaced by argon before sampl-

Fig. 6 Sampling tube (Silica tube).

ing, and consequently the samples were prevented from being exposed to the oxidation atmosphere.

The samples sucked to be 140 to 160 mm in length were quenched by immersing in a mercury bath after sampling. The experimental temperatures were fixed at 1223, 1325, 1423, and 1520°C, and if the atmosphere in contact with the molten samples in the reaction tube at those high temperature reaches the Boudouard equilibrium, a very small amount of CO_2 will be present.

The present analytical method is unable to determine the amount of CO_2 . In fact, the presence of CO_2 was not confirmed even by the determination of gas in the molten samples. Thus, the atmosphere was considered to have a composition of the Boudouard equilibrium, judging from the fact that the velocity of reactions was extremely rapid, and the rate of the CO carrier was selected at 1200 cc/min. The flow of CO gas was determined in consideration of the temperature drop on the surface of molten iron and conditions for the measurement of temperature by the optical pyrometer. It may be apprehended that the air will be mixed when

Fig. 7 Sample for oxygen and carbon analyses.

the cap on the hole was removed for sampling but it was not problematical because the pressure inside the reaction tube was 8 mm Hg higher than that of the atmosphere and the operation was carried out in a short period of time. The analytical samples were prepared from the sucked specimens shown in Fig. 7

III. Experimental Results

1. The time to reach the equilibrium

The time to reach the equilibrium depends on the carbon or oxygen content in molten iron, heating conditions after melting, and holding temperature. Compositions of the molten samples were almost constant and the holding time at given temperatures after melting was fixed at 10 minutes in this experiment. The time from the equilibrium state at given temperatures to sampling was determined as follows. As the molten samples prepared by adding 50 gm. of electrolytic iron the 0.065% oxygen content to about 120 gm. of iron with the 4.5% carbon content, the equilibrium state was always attained from the side of a higher oxygen content and from the side of a lower carbon content. In the preliminary experiment to determine the holding time by sampling, 20 gm. of Fe_2O_3 powder was added to the molten iron in order to lower the carbon content and to increase the oxygen content after holding at given temperature. The molten iron was in advance melted with 120 gm. of iron with the 4.0% carbon content and 50 gm. of electrolytic iron to prolong the time to reach the equilibrium. The sampling was carried out after the addition of Fe_2O_3 under the above condition, and the time to reach the equilibria carbon and oxygen was determined, respectively.

The results are shown in Fig. 8.

As shown in Fig. 8, the periods of time to reach the

Fig. 8 Variations in carbon and oxygen contents after Fe_2O_3 addition.

equilibria of carbon and oxygen are almost constant, that is 25 minutes at 1186 °C, about 10 minutes at 1370°C, less than 10 minutes at 1435°C and 7 minutes at 1520°C.

From these results, the holding time in the equilibrium experiment was determined as follows:
Experimental temperature (°C) 1223 1325 1423 1520
Holding time (minutes) 30 20 15 15

2. Results and discussion

Equilibrium experiment for 10 heats were carried out at 1223, 1325, 1423 and 1520°C by the method described already. The results are shown in Tables 3, 4, 5, and 6, where $\log K_3$ and $\log K_4$ will be described later.

Table 3 Experimental results at 1223°C

Heat No	C %	Q% $\times 10^4$	$\log K_3$	$\log K_4$
E-23	4.53	8	3.0969	2.4408
E-25	4.50	6	3.2218	2.5686
E-26	4.48	5	3.3010	2.6498
E-27	4.48	7	3.1549	2.5036
E-28	4.52	7	3.1549	2.4998
E-89	4.49	6	3.2218	2.5696
E-96	4.48	7	3.2549	2.5036
E-97	4.48	6	3.2218	2.5706
E-106	4.46	8	3.0969	2.4476
E-107	4.54	6	3.2218	2.5648

Table 4 Experimental results at 1325°C

Heat No	C %	Q% $\times 10^4$	$\log K_3$	$\log K_4$
E-17	4.81	6	3.2218	2.5397
E-29	4.74	5	3.3010	2.6253
E-108	4.79	5	3.3010	2.6234
E-109	4.71	7	3.1549	2.4819
E-113	4.72	7	3.1549	2.5171
E-119	4.74	9	3.0458	2.3700
E-125	4.78	7	3.1549	2.4755
E-126	4.71	8	3.0969	2.4239
E-142	4.79	7	3.1549	2.4746
E-143	4.76	6	3.2218	2.5442

Table 5 Experimental results at 1425°C

Heat No	C %	Q% $\times 10^4$	$\log K_3$	$\log K_4$
E-7	5.02	9	3.0458	2.3451
E-15	5.04	7	3.1549	2.4525
E-20	5.06	5	3.3010	2.5969
E-37	4.97	5	3.3010	2.6038
E-117	5.04	9	3.0458	2.3433
E-118	4.99	8	3.0969	2.3988
E-127	4.96	7	3.1549	2.4594
E-130	5.04	7	3.1549	2.4525
E-131	5.01	9	3.0548	2.3459
E-132	5.02	8	3.0969	2.3962

(1) The solubility and activity coefficient of carbon

The solubility of carbon at each temperature is shown in Fig. 9. The determined values of carbon have an approximately linear relation within the range of the experimental temperatures. The solubility of carbon is shown in the following equation:

$$C\% = 1.33 + 2.59 \times 10^{-3} \times t^{\circ}\text{C}.$$

Table 6 Experimental results at 1425°C

Heat No	C %	Q% $\times 10^{-4}$	$\log K_3$	$\log K_4$
E-71	5.30	7	3.1549	2.4306
E-73	5.26	9	3.0458	2.3248
E-75	5.26	7	3.1549	2.4339
E-76	5.27	6	3.2218	2.5000
E-77	5.22	7	3.1549	2.4372
E-78	5.21	9	3.0458	2.3288
E-79	5.29	9	3.0458	2.3223
E-80	5.27	9	3.0458	2.3239
E-81	5.24	8	3.0969	2.3777
E-82	5.31	6	3.2218	2.4468

Fig. 9 Effect of temperature on the solubility of carbon in molten iron.

A part of other experimental results is shown in Fig. 9. The results of the present work lie between those by Matoba and Banya⁽²⁾ by and Chipman et al. The equilibrium relation in carbon-saturated molten iron can be expressed as follows:

The phases of gas and molten iron were in the equilibrium state and the gaseous composition seemed to have a Boudouard equilibrium composition. Therefore, the activity coefficient of carbon can be calculated from a combination of Boudouard equations and Matoba and Banya's equations in the dilute solution. When an ideal line of the carbon activity is assumed from Henry's law to be $f_c = a_c/C\%$, the following formulae will be given:

$$\left. \begin{aligned} C(g) + CO_2 &= 2CO \quad (\text{Boudouard equilibrium}) \\ \log K_1 (= P_{CO}^2/P_{CO_2}) &= -8,405/T + 8.820 \end{aligned} \right\} \quad (1)$$

(6) Matoba and Banya: *Tetsu To Hagane*, **43** (1957), 790.

(7) J. Chipman et al: *Trans. of ASM*, **44** (1952), 1215.

(8) J.A. Kichener et al: *Trans. of Faraday Soc.*, **48** (1952), 608.

(9) S. Matoba and S. Banya: The Japan Society for the Promotion of Science, The Nineteenth Committee (Steelmaking) - The recommended values on equilibrium between carbon and oxygen (1960).

Table 7 Summary of experimental results.

Temp. C	C %	O %	C% $\times$ O%	of from eq. (6)	of from eq. (10)	f_c
1200	4.44	0.00064	0.0028	0.0833	0.0847	6.82
1250	4.57	0.00066	0.0030	0.0822	0.0835	6.89
1300	4.70	0.00068	0.0032	0.0811	0.0820	6.99
1350	4.83	0.00070	0.0034	0.0800	0.0809	7.06
1400	4.97	0.00072	0.0036	0.0789	0.0800	7.11
1450	5.09	0.00074	0.0038	0.0778	0.0789	7.19
1500	5.22	0.00076	0.0040	0.0767	0.0781	7.24
1550	5.35	0.00078	0.0042	0.0756	0.0773	7.28

From equation (1) or (2), we obtain

$$f_c = K_1/K_2 \times \text{C}\%.$$

The activity coefficient of carbon f_c in carbon-saturated iron can be calculated from the above equation by substituting the solubility of carbon in the formula already given. The function of temperature is expressed by the following equation:

$$\log f_c = -847/T + 2.055 - \log (\text{C}\%),$$

where C% is the solubility of carbon at $T^\circ\text{K}$.

Table 7 shows the results calculated at the representative temperatures.

(2) The oxygen content and the activity coefficient of oxygen in carbon-saturated iron

It is extremely difficult to determine the exact oxygen content in carbon-saturated iron in the light of sampling and analytical accuracy. The analytical results of the samples in which the precipitation of graphite was suppressed as much as possible are shown in Tables 3~6.

The equilibrium equation for oxygen in carbon-saturated iron is expressed by

Values of $\log K_3$ in this experiment are shown in Tables 3~6, and the relation between these values and $1/T$ is shown in Fig. 10. In all the cases, the oxygen content is very low, and the values ranging from 0.0005 to 0.0009 % are within the analytical error of ± 0.0002 %.

From the above results it can be said that the oxygen content in carbon-saturated iron is not greatly influenced by temperature. This will be further discussed after establishing the sampling and analytical methods with a higher accuracy. A statistical arrangement of the results in Fig. 10 gives the following equation:

$$\log K_3 (= P_{\text{CO}}/\text{O}\%) = 613/T + 2.775.$$

The above equation shows that the oxygen content in carbon-saturated molten iron increases slightly with the rise of temperature.

The relation between the gaseous phase and the oxygen content in molten iron can be calculated from

equations (1) and (2) as the gaseous phase corresponds to Boudouard's equilibrium.

$$\log K_4 (= P_{\text{CO}_2}/P_{\text{CO}} \times \text{O}\%) = 9,018/T - 6.045 \quad (4)$$

The activity coefficient of oxygen can be calculated from equation (4) and Matoba and Banya's experimental equation (5) in the dilute solution:

$$\log K_5 (= P_{\text{CO}_2}/P_{\text{CO}} \times a_o) = 8,718/T - 4.762 \quad (5)$$

where $f_o = a_o/\text{O}\%$.

$$\log f_o = \log K_4 - \log K_5 = 300/T - 1.283 \quad (6)$$

The activity coefficient calculated from the above equation is shown in Table 7.

(3) The equilibrium product [C %] [O %]

The relation between carbon and oxygen in carbon-saturated molten iron is expressed as follows:

$$\log K_7 = P_{\text{CO}}/\text{C}\% \times \text{O}\% \quad (7)$$

The values of $\log K_7$ obtained from the experiment are tabulated in Tables 3~6. The relation between $\log K_7$ and $1/T$ is graphically shown in Fig. 11, from which the following equation will be obtained as the value of equation (7):

$$\log K_7 (= P_{\text{CO}}/\text{C}\% \times \text{O}\%) = 1,239/T + 1.771. \quad (8)$$

As reported in many works, the equilibrium product [C %] [O %] is usually 0.00025 at 1600°C at lower

Fig. 10 Relation between $\log K_3$ and temperature.

Fig. 11 Relation between $\log K_7$ and temperature.

carbon concentrations in the iron melt, but this experiment shows the value of 0.0043 by extrapolation. The activity coefficient of oxygen can be solved from Matoba and Banya's equation in the dilute solution.

$$\log K_8 (= P_{\text{CO}}/f_c \times \bar{C}\% \times f_o \times \bar{O}\%) = 1.160/T + 2.003, \quad (9)$$

where $K_7/K_8 = f_c f_o$.

$$\text{Accordingly, } f_o = K_7/f_c \times K_8 \quad (10)$$

The values of f_o calculated by substituting f_c in Table 5 in the above equation are shown in Table 5.

IV Conclusion

The relation between carbon and oxygen in carbon-saturated molten iron is measured in the temperature range of 1323~1520°C. The results obtained are summarized as follows:

- (1) The solubility of carbon is expressed as follows:

$$\bar{C}\% = 1.33 + 2.59 \times 10^{-3} \times t \text{ } ^\circ\text{C}.$$

- (2) The equilibrium relations between carbon and oxygen in carbon-saturated molten iron are expressed by the following equations;

$$\log K_3 (P_{\text{CO}}/\bar{O}\%) = 613/T + 2.775.$$

$$\log K_4 (= P_{\text{CO}_2}/P_{\text{CO}} \times \bar{O}\%) = 9,018/T - 6.045.$$

$$\log K_7 (= P_{\text{CO}}/\bar{C}\% \times \bar{O}\%) = 1,239/T + 1.711.$$

- (3) The equations for the activity coefficients of carbon and oxygen in carbon-saturated molten iron are defined as follows:

$$\log f_c = -847/T + 2.055$$

$$- \log \{1.33 + 2.59 \times 10^{-3} (T - 273)\}.$$

$$\log f_o = 300/T - 1.283.$$

- (4) The oxygen contents in carbon-saturated molten iron are considerably lower than those of previous works. Accordingly, the equilibrium product $[\bar{C}\%] \times [\bar{O}\%]$ is not very large and the activity coefficient is not very low.

- (5) In regard to the sampling of carbon-saturated molten iron, it is necessary to further investigate the method to suppress the precipitation of graphite by solidifying as quickly as possible. As there is no reliable analytical method to determine such a low oxygen content as shown in this experiment, it is desired that an analytical procedure for determination of the oxygen content up to 0.0001% within the experimental error of 0.00005% be established.