FUNDAMENTAL STUDY ON THE ACIDIC STEEL MAKING

YASUSHI KOJIMA and KŌKICHI SANO

Department of Metallurgy

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CONTENTS

General Introduction

Based on the theory of dilute solution introduced by C. Wagner, many works have been carried out on the relations among the concentrations of dissolved elements in the liquid iron and these relations can be estimated by the thermodynamical calculation.

But, at the reactions between the slag and liquid iron, as the components in the slag changed in great quantity and various compounds are formed by mutual reactions among the components in the slag. It is not easy to write the equation of chemical reaction in these systems.

At the experimental research in the laboratory, even if the oxides are limited to three components, the chemical formula of oxides and their thermodynamical data are not cleared up in many cases. As the slag in the practical steel making is composed of many oxides, it is the most important to clarify these reactions.

Generally, at the investigation on the chemical reactions for kinetics or equilibrium, the reaction between the vessel which packes the reaction system and the components in this system is negligible. But the reactions in the steel making processes are carried out at high temperature, and so it is unavoidable that these reactions occur between reaction system (liquid iron, slag, and atmosphere) and the vessel (refractory) which packs them. The results obtained are affected more or less by the reaction with refractory, consequently, the reactions in the steelmaking are not considered without regard to these specific characters.

Chromium is one of the most important elements that are used as a heat-resisting and corrosion-proof materials. When chromium is added into the liquid iron as an alloying elements, it is a well known fact that liquid iron-chromium alloy can scarcely be deoxidized the general treatment of deoxidation.

The experimental study on the equilibrium between the liquid iron-chromium alloy and the slag is scarcely found in the literature, and yet many questions arise in their experimental results, when we consider them from the modern thermodynamical point of view.

In this study, therefore, the relations between the liquid iron and the slag saturated with silica have been measured, and chemical formula of the components dissolved in the slag equilibrated with liquid iron, activities and the distribution coefficients have been investigated.

Chapter I. On the Equilibrium between Liquid Iron-Chromium alloy and Silica-Saturated Acidic Slag

1.1. Introduction

In steelmaking procedure, it is undoubtedly most important to clear up the redox-reactions between the oxide phase and various elements in the liquid iron-alloy, except in cases where the ore is directly treated by the reduction gases.

There has been much research on the mutual reactions of chromium, silicon and oxygen in the liquid iron, and it has been reported for the equilibrium constants and activities. The authors have tried to observe accurately these various reactions between the slag and liquid iron.

On the various elements dissolved in the liquid iron-chromium alloy equilibrated with the silica-saturated slag, their solubilities and forms of the reactions have been found in many reports, but the state of the oxide is not well-known. Even if the oxides were limitted to the three components FeO, Cr_2O_3 and SiO_2 saturated with silica, how do their structure and chemical form change with the variation in the concentration of each component?

The experiment on this system was carried out by F. Körber and W. Oelsen[1) using a resistance furnace. But it was assumed that the maintenance of the melting was too short and the stirring of the liquid iron was not sufficient at their experimental runs, and moreover the reaction could not attain equilibrium. D. C. Hilty[2) *et ali.* analyzed the structures of the inclusions in liquid iron-chromium alloy by X-ray and studied the structure of oxides, but they did not refer to the oxide phase which reacted to each other.

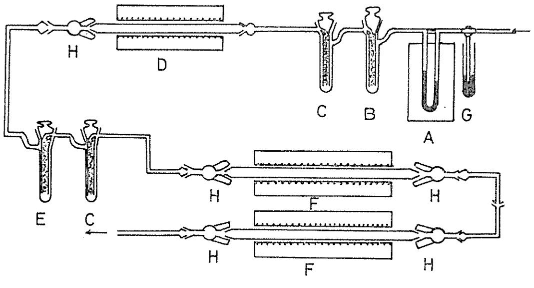
There have been a number of reports on this system. The results reported, however, do not show close agreement. For this reason, it is thought that the reactions between slag and liquid iron are too complicated, and that the viscosity of oxide phase is so high that it can not sufficiently stir. The deviation of the data is considered to be caused by the selection of the holding time, technical difficulty at the gradient of temperature in the reaction cell, the difference of sampling methods and the errors in the analytical procedure.

In addition to the above deviation in the fundamental data there are seen another differences in the method of the thermodynamical treatment, that is to say, so long as the stuctures of oxide phase reacted with liquid metal are not fully understood physically and chemically, the various reactions will not be solved definitely.

Recently, many researches[3~5) have been carried out on the molten oxide phase, —Viscosity, electrolytic dissociation and ionic mobility. Many phase diagrams of the multicomponent systems are also reported, but phase diagram for the SiO_2-Cr_2O_3-FeO system has not been made clear. The authors tried to observe quantitatively oxide phases and studied their chemical concentration in liquid metal.

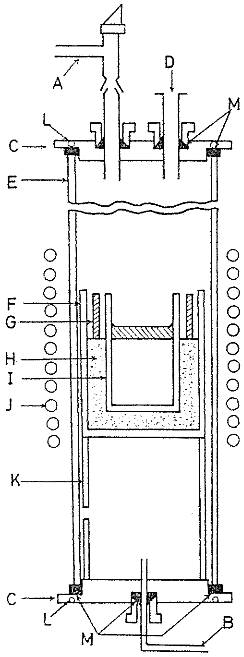
1.2. Experimental Apparatus and Procedure

Fig. 1 is a schematic diagram of the gas purifier used in all the experimental runs. Fig. 2 is a schematic section of the furnace used for the equilibrium ex-



A. Gas flow meter
B. Silica gel
C. Natronasbest
D. Cu-net furnace
E. P_2O_5
F. Mg-chip furnace
G. Hg-overflow bulb
H. Water cooling jacket

FIG. 1. Apparatus used for gas purification.



A. Gas inlet
B. Gas outlet
C. Brass cap
D. Thermocouple holder
E. Silica tube
F. High alumina protective crucible
G. Graphite tube
H. Silica powder
I. Silica crucible
J. Coil
K. High alumina stand
L. Water cooling pipe
M. Silicon rubber.

FIG. 2. Furnace used for equilibrium experiments

periments. The fused silica crucible is stamped with silica powder in the high alumina protective crucible. The powder of the purest oxide available, Fe_2O_3, Cr_2O_3 and SiO_2 were charged about 20 g in total and mixed well each other. Electrolytic iron, electrolytic chromium and ferro-33% silicon obtained by melting in the laboratory weighed about 150g in all cases. The oxides and metals were put into the crucible before heating. For the furnace atmosphere mild stream of the argon, which was purified by copper net heated 350°C, magnesium chip heated 600°C, and penta phosphoric acid and soda lime, was used.

Melting was carried out in a high frequency wave furnace keeping the pressure in the furnace 2–3 mmHg higher than that in the room. The reaction equilibrium between slag and metal phases was established at 1600°, 1650° and 1700°C. After melted for an hour, the sample was sucked at 1700°C by the fused silica tube which was 3 mm in I. D., closed its one side and bored a hole of 1.2 mm ϕ at the distance of 6 mm from the closed top, and cooled rapidly in the water. Using this tube, the metal samples were prevented from mixing with oxide and could be sucked from the center of the liquid.

As the melt solidified within 40 sec. after switching off the current, it was assmed that no significant change occurred in the slag component in the equilibrium at such a high rate of cooling.

At 1600° and 1650°C, the viscosity of the slag equilibrated with the chromium concentration less than 9% is too high to take a sample by the method of sucking, then metal and slag with the crucible were picked up from the lower part of the silica tube after taking off the brass and were quenched in the water. It took

8 sec. after switching off the current.

After cooling down the slag to the room temperature in the furnace, it was picked up from the crucible and presented for the analysis.

The temperature was measured by the platinum 5 pct. rhodium-platinum 20 pct. rhodium thermocouple protected by a silica sheath, with its hot junction touching the bottom of the crucible. The fluctuations of temperature were ±5°C at maximum. The temperature was stabilized after 20 min. from melting down the metal and slag, and from this time measurement was conducted continually till the end of the melting.

As the furnace was heated by high frequency wave, the gradient of temperature was recognized in the crucible. To hold the temperature of slag and metals uniformally, a graphite pipe was set at intermediate between the silica crucible and the protective alumina crucible. Moreover uniformity of the temperature was kept by reducing the thichness of the oxide phase as much as possible. The melting with the oxide of 3–4 mm in thickness resulted in success. The temperature of the slag was corresponded to that of the metal phase.

The metal was analysed for chromium, silicon and oxygen. Chromium was determined by redox-titration with permanganate and ferrous ammonium sulphate. The silicon and chromium of low concentration were analysed photometrically. The oxygen determinations were made by vacoum fusion apparatus using the samples about 0.5–3 g in weight in accordance with the expected concentration of oxygen. The apparatus was checked by analysing a standard sample of the N. B.S. in U.S.A.

Slags were determined both by chemical analyses for SiO_2, Fe, and Cr, and by fluorescent X-ray analyses.

1.3. Experimental Results and Discussion

The holding time of melting till the reactions attained the equilibrium was determined as follows. As the viscosity of the slag was so high and its amount was so little that the slag sample could not be taken at will, therefore, it could not be determined from these data whether the equilibrium was established completely. Then the ratios of the mixing of oxides were changed, for example, melting No. 62–8 and 62–9, or 62–21 and 62–30 as shown in Table 1. According to these analytical data, it is thought that it takes one hour to establish the equi-

TABLE 1. Results of Melting Fe-Cr System with Chromium-Silicate Slags in the Silica Crucible at the Temperatures 1600° and 1700°C.

Weight of Metals and Oxides(g)							Analysis of metals and slags (wt%)								
Sample No.	Fe	Cr	Fe-Si	Fe_2O_3	Cr_2O_3	SiO_2	O	Cr	Si	(SiO_2)	(FeO)	(Cr)	L_{Cr}	Temp. (°C)
62–8	150	23	2	0	10	10	0.0557	11.68	0.391	50.1	6.64	33.1	2.83	1700
62–9	150	23	2	4	8	8	0.0558	10.59	0.384	49.8	6.97	33.0	3.12	1700
61–21	150	2	1	8	4	8	0.0533	1.12	—	49.9	34.5	13.8	12.3	1600
62–22	150	4	1	8	4	8	0.0458	2.08	0.003	46.6	26.1	18.4	8.85	1600
62–24	150	10	1.5	4	8	8	0.0270	5.77	0.033	46.6	11.9	29.7	5.15	1600
62–27	140	21	2	1	10	8	0.0321	11.30	0.228	48.4	6.2	33.0	2.92	1600
62–28	140	25	2	2	10	8	0.0335	13.31	0.285	47.7	4.5	33.6	2.52	1600
62–30	150	0	0	0	10	8	0.0605	1.31	—	48.5	28.9	14.4	11.0	1600

librium.

As soon as the charged metal melted down, gas bubbled, the oxide being separated from the metal, flowed violently, and the fluidity of the slag was small. But as the reaction between slag and metal advanced to the equilibrium, the slag flowed mildly and the viscosity became greater.

1.3.1. Relation between the Distribution of Chromium L_{Cr} and FeO

There is no phase diagram of the three components system SiO_2-FeO-Cr_2O_3. Then, the phase diagram of the two components system of SiO_2-Cr_2O_3[6] is shown in Fig. 3. At the range of this experimental temperature Cr_2O_3 can not dissolve in SiO_2. Accoring to the results of the experiment, the concentration of FeO was negligible at a concentration of the chromium in the liquid iron of more than 10%. Therefore, these oxides must be solid or of solid solution in the phase diagrams. But in all the melting runs, the oxide phase was liquid in the range of the experimental concentration. This liquid increased its fluidity with an increase of chromic oxide and a decrease of iron oxide. The contradiction of the phase diagrams and the experimental results, however, has been elucidated as follows. Cr_2O_3 in the solution of SiO_2 is reduced to (CrO) by the chromium in the metal phase. (CrO) is increased with increasing the chromium concentration and therefore melting point of the oxide is decreased with (CrO).

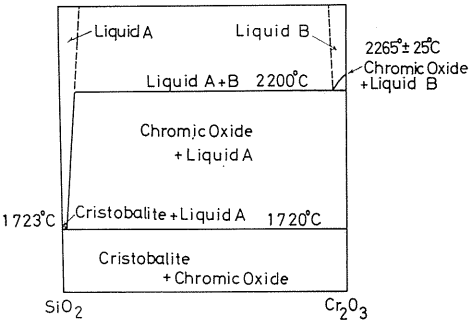


FIG. 3. Binary system of Cr_2O_3-SiO_2.

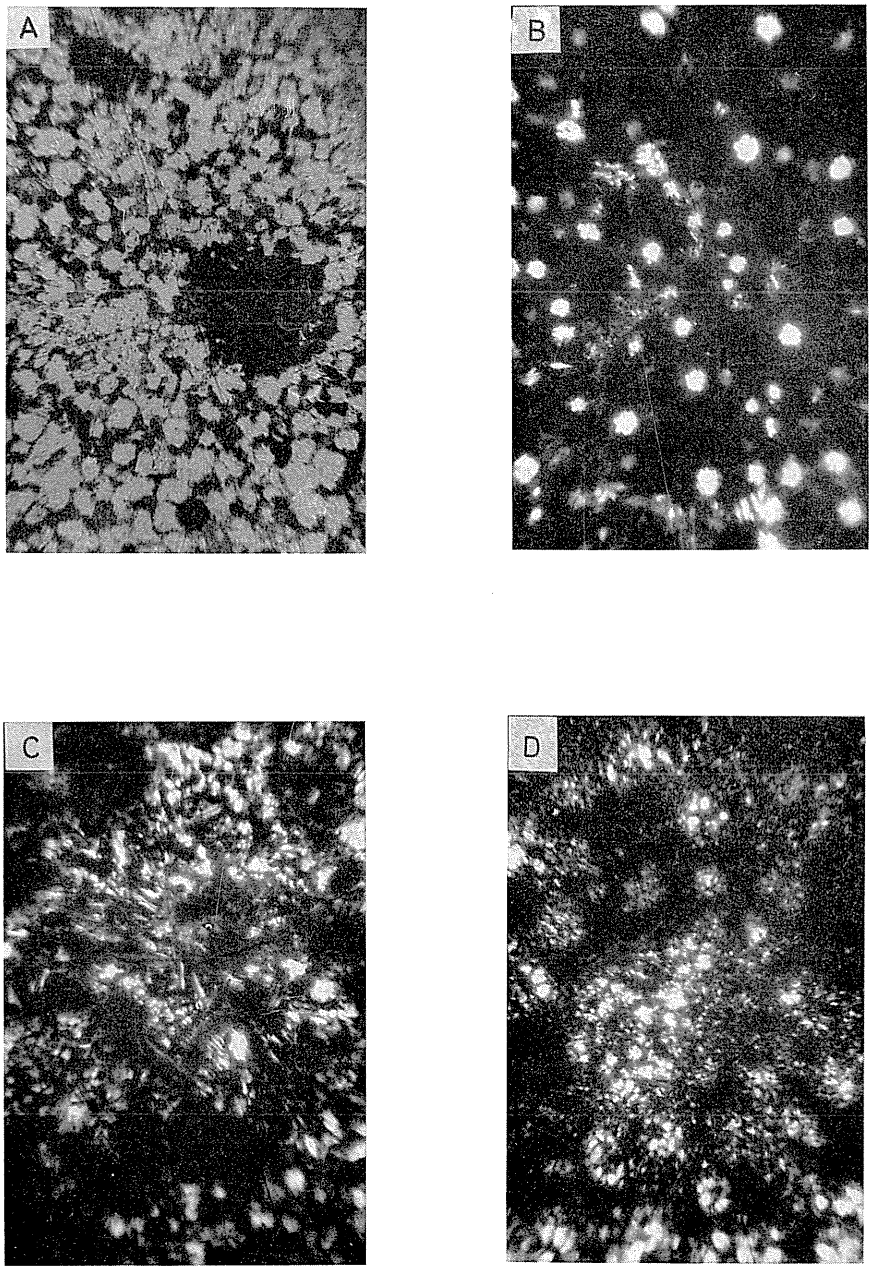
Direct adaptation of the phase diagram for the oxides equilibrated with metal is not correct.

Although chemical formula of every kind of the oxide equilibrated in the slag could not be decided in this experiment, in order to understand if Cr_2O_3 dissolved in the silicate slag and reacted with other components, or a part of Cr_2O_3 isolated in the solution and remained as solid independently of the reaction, a slice of the slag was measured microscopically, the results of which are shown in Photo 1.

The isolated chromic oxide was increased with that of chromic oxide, but recrystalization of the slag cooled in the furnace was observed in all over the section. Then it is concluded that chromic oxide has dissolved at the experimental condition and the prevailing elucidation was proved correct.

The relation between the distribution of chromium L_{Cr} (weight per cent of the chromium concentration in the slag and metal) and the concentration of iron oxide in the slag is shown in Fig. 4. The relation between L_{Cr} and FeO was independent of temperatures 1600°, 1650° and 1700°C. This has been studied in many reports.

The relation between L_{Cr} and FeO was represented by W. J. Lapitzki[7] as follows;



A. Sampling No. 62-1, (× 100). B. Sampling No. 62-3, (× 400)
C. Sampling No. 62-6, (× 400). D. Sampling No. 62-8, (× 400)

PHOTO. 1. Aspects of slags under microscope.

$$(\mathrm{Cr})/[\mathrm{Cr}] = 0.136\sqrt{(\mathrm{FeO})^3} \qquad (1\text{-}1)$$

In which ( ) denotes the concentration in oxide phase and [ ] the concentration in metal.

K. Tesche[8] obtained the following relation.

$$(\mathrm{Cr})/[\mathrm{Cr}] = 0.75(\mathrm{FeO}) \qquad (1\text{-}2)$$

As the relation was obtained at the decarburization process with oxygen, it can not be compared with the present work.

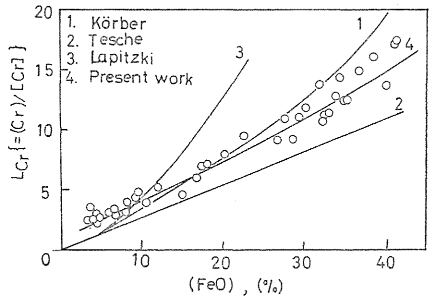


FIG. 4. Relations between the distributions of chromium and FeO in the silica-saturated acidic slag.

F. Körber and W. Oelsen represented the relation at the concentration of FeO less than 20% asfollows;

$$(\mathrm{Cr})\cdot[\mathrm{Fe}]/[\mathrm{Cr}]\cdot(\mathrm{FeO}) = 34 \qquad (1\text{-}3)$$

In the present work, the authors obtained the following empirical formula in the range of the concentration $4\% < (\mathrm{FeO}) < 17\%$.

$$(\mathrm{Cr})/[\mathrm{Cr}] = 0.260(\mathrm{FeO}) + 1.4 \qquad (1\text{-}4)$$

and $17\% < (\mathrm{FeO})$

$$(\mathrm{Cr})/[\mathrm{Cr}] = 0.390(\mathrm{FeO}) \qquad (1\text{-}5)$$

The W. J. Lapitzki's relation must have been obtained in the basic slag. Because if the empirical formula obtained by him were to be applicable for the acidic slag, the oxide of chromium must be Cr_2O_3 at the high chromium concentration. Such an oxide phase, however, is not to be recognized in the acidic slag as above described.

Assuming that the chemical formula of the oxide of chromium is represented as follows;

$$x(\mathrm{FeO}) + [\mathrm{Cr}] \rightleftarrows x[\mathrm{Fe}] + (\mathrm{CrO}_x) \qquad (1\text{-}6)$$

$$K_1' = [\mathrm{Fe}]^x(\mathrm{Cr})/(\mathrm{FeO})^x[\mathrm{Cr}] \qquad (1\text{-}7)$$

From eq. (1-7),

$$x \log L_{\mathrm{Fe}} = \log L_{\mathrm{Cr}} - \log K_1' \qquad (1\text{-}8)$$

where,

$$L_{\mathrm{Cr}} = (\mathrm{Cr})/[\mathrm{Cr}], \text{ and } L_{\mathrm{Fe}} = (\mathrm{FeO})/[\mathrm{Fe}] \qquad (1\text{-}9)$$

In order to determine x, one can estimate it accurately by calculation, using the activities of every kind of elements in eq. (1-8). But the activities of these components are not well-known. The authors assumed that the activity coefficient of oxide of chromium was equal to the activity coefficient of chromium in liquid metal, when the oxide phase was equilibrated with the metal phase. Calculation

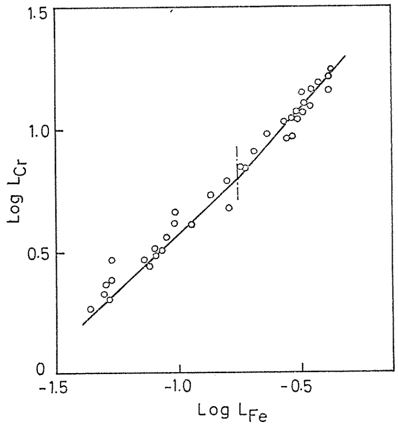


FIG. 5. The reaction $(CrO_x)+x[Fe] \rightleftarrows [Cr]+x(FeO)$ in the silica-saturated acidic slag at various temperatures.

of eq. (1-8), however, was made approximately with the concentration of every kind of components.

The relations between log L_{Fe} and log L_{Cr} were obtained and shown in Fig. 5.x can be obtained from the tangent of the line in Fig. 5.

$x=1.33$, concentration of FeO more than 17%

$x=1.00$, concentration of FeO less than 17%

The concentration of FeO in the silica-saturated acidic slag is about 17% weight per cent, when the rate of the mole fraction $N_{FeO}/N_{Cr_2O_3}$ is equal to 1.

The conclusion was made from the above results as follows. The oxide of chromium changes its chemical formula from Cr_3O_4 to CrO at the concentration of FeO=17%, where the mole fraction rate of metallic oxides is equal to 1. Then K_1' can be calculated from eq. (1-8).

$K_1'=43$

1.3.2. Relation between Chromium and Oxygen

When a solute distributes itself between two immiscible solvents at a constant temperature, its concentration rates in the two phases are constant. This conclusion is an obvious one from the kinetic standpoint, for at equilibrium the number of solute molecules crossing any given area of the interface from the first solvent to the second in unit time must be proportional to the concentration in the first solvent, and equal to the number of solute molecules crossing the same area in unit time to the opposite direction. From the thermodynamic stanpoint, the chemical potential of the solute in a dilute solution in the first solvent may be expressed as follows;

$$\mu_A=\mu_A^{\circ}+kT\ \ln\ c_A \tag{1-10}$$

and in the second solvent as;

$$\mu_B=\mu_B^{\circ}+kT\ \ln\ c_B \tag{1-11}$$

Where, c: equilibrium concentrations

Since the two chemical potentials must be equal, following equation can be given;

$$K=c_B/c_A=\varepsilon^{-(\mu_B^{\circ}-\mu_A^{\circ})/kT}=\varepsilon^{-\Delta\mu/kT} \tag{1-12}$$

which is Nernst's distribution law.

Assuming that chromium is distributed in the slag and metal phase according to Nernst's law at the low chromium concentration, the distributions of chromium in the liquid iron-chromium alloy and acidic slag should be in the relation of the function of first order, but there is no relation of first order between them as shown in Fig. 6. Nernst's law can not be applied to this system. Therefore, the mutual reaction between other solutes in the system, and Cr, O and Si, or dissociation and ionization of chromic oxide in the slag must be considered. But these phenomena could not be fully understood, and therefore it was assumed that the reaction of chromium between the oxide phase and metal phase took place in accordance with the following equations.

$$\begin{array}{lc}
\text{Oxide phase} & (CrO_x)_s \\
 & K_2' \ \downarrow\uparrow \qquad K_3' \\
\text{Metal phase} & [CrO_x]_m \rightleftarrows [Cr] + x[O]
\end{array}$$

$$K_2' = (CrO_x)_s/[CrO_x]_m \tag{1-13}$$

$$K_3' = [Cr][O]/[CrO_x]_m \tag{1-14}$$

neglecting $[CrO_x]_m$ in eqs. (1–13) and (1–14)

$$K_4' = (K_2'/K_3') = (CrO_x)_s/[Cr][O]^x \tag{1-15}$$

Assuming that (CrO_x) equilibrated with the concentration of chromium in the metal phase less than 3% does not change in its chemical components, x becomes constant. The concentration of (CrO_x) is substituted for (Cr) in eq. (1–15).

As shown in Fig. 7 the relation of chromium distribution in the two phases can be figured by two lines with aboundary at the 3 per cent chromium. At first the authors studied the chromium concentration less than 3 per cent.

The concentration of silicon was so low at the experimental condition that the effect of silicon on the solubility of oxygen was neglected. As (Cr) was obtained by analytical results, (CrO_x) was calculated by using eq. (1–16).

$$(CrO_x)_s = \{(52.01 + 16x)/52.01\} \cdot (Cr) \tag{1-16}$$

Therefore,

$$\log(CrO_x)_s = \log(Cr) + C_1 \tag{1-17}$$

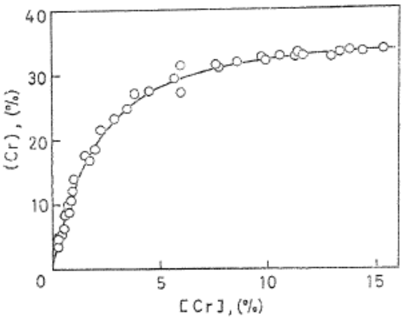


FIG. 6. Distributions of chromium in liquid iron-chromium alloy and acidic slag.

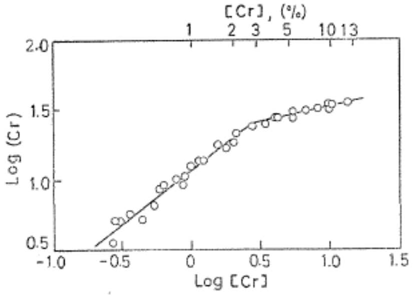


FIG. 7. Distributions of chromium in the liquid iron and silica-saturated acidic slag.

where,

$$C_1 = \log(52.01 + 16x)/52.01 \tag{1-18}$$

Tangent of the line does not change, when (CrO_x) is substituted with (Cr). This line was obtained by the experimental results with the calculation method of least squares.

$$\log(Cr) = 0.7243 \log[Cr] + 1.060 \tag{1-19}$$

From eqs. (1–15) and (1–17),

$$\log K_4' = \log(Cr) + C_1 - \log[Cr] - x \log[O] \tag{1-20}$$

Substituting eq. (1–19) into eq. (1–20)

$$0.2757 \ \log[Cr] = -x\log[O] + C_2 \tag{1-21}$$

Where,

$$C_2 = C_1 - \log \ K_4' \tag{1-22}$$

The relations between log [Cr] and log [O] are shown in Fig. 8.

Consideration has been allowed for CrO_x in the oxide phase. The solubility of oxygen and oxide was studied in the liquid Fe-Cr system by D. C. Hilty[2]. H. Sakao and K. Sano[9] studied the activity and solubility of oxygen in the liquid Fe·Cr system, and considered chemical formula of the oxide equilibrated with metal phase.

They reported that the oxide existed in the chemical formula of $Fe_yCr_{3-y}O_4$ corresponding with the concentration of chromium as $[Cr]<3\%$, $y=1$, $3\%<[Cr]<9\%$, $y=0.67$, and $[Cr]>9\%$, $y=0$.

Generally, metallic oxide dissolves in liquid SiO_2 and yields metallic ion. Therefore, it is thought that the oxide of iron and chromium ionizes and has a quality of complex oxide as described above. The molecular form of CrO_x in the silicate slag has been determined as to the following three kinds of oxides.

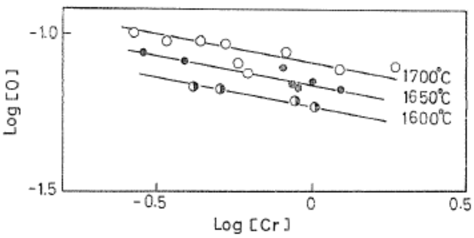


FIG. 8. Relation between the solubility of oxygen and the concentration of chromium in liquid iron-chromium alloy at various temperatures.

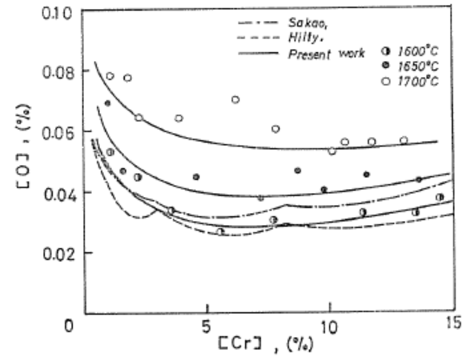


FIG. 9. Solubility of oxygen in iron-chromium alloy equilibrated with the silica-saturated acidic slag at various temperatures.

Oxides	x	A
CrO	1.00	-0.276
Cr_3O_4	1.33	-0.207
Cr_2O_3	1.50	-0.184

Where, A: $0.2757/x$ and tangent in Fig. 8.

As seen in Fig. 8, the relations between [Cr] and [O] show parallel lines and it is concluded that CrO_x has a constant chemical formula and is independent of experimental temperatures. Tangent A obtained from Fig. 8 is about -0.20. This shows that the oxide of chromium is Cr_3O_4. Then eq. (1-21) is rewritten as follows;

$$\log[Cr] = -0.207 \log[O] + C_2 \tag{1-23}$$

K_4' is obtained by combining equations.

Temperatures	1600°C	1650°C	1700°C
K_4'	695	552	458

The relation between equilibrium constant ant and temperature is represented as;

$$\log K_4' = 6679/T - 0.724 \tag{1-24}$$

In the range of the chromium concentration more than 3%, the solubility of oxygen was affected with silicon. The solubility of oxygen is shown in Fig. 9. This will be dicussed in the later section.

1.3.3. Relation between Silicon and Chromium

The relation between silicon and chromium in the metal phase is discussed in many reports. D. C. Hilty[2][10] expressed the relation using the equilibrium constants approximately as;

$$K_5 = [Cr]a^2_{SiO_2}[Si]^{1.75} \cdot a_{Cr_3O_4}, \quad [Cr] > 10\% \tag{1-25}$$

H. Sakao and K. Sano[11] calculated this relation by using the following reaction.

$$(Cr_3O_4) + 2[Si] \rightleftarrows 3[Cr] + 2(SiO_2) \tag{1-26}$$

But this calculation was performed under a condition that the Cr_3O_4 is a solid. Accordingly in the present study, eq. (1-26) should not be used. The equilibrium constant was obtained by using the following equation;

$$(CrO_{2x}) + x[Si] \rightleftarrows x(SiO_2) + [Cr] \tag{1-27}$$

$$K_5' = [Cr]/[Si]^x(Cr) \tag{1-28}$$

and substituted weight per cent for activities. The calculation was carried out as described in the former section. x was obtained from the relation between log L_{Cr}^{-1} and log [Si] at various temperatures. In the range of chromium concentration more than 5%, x was 0.538 independently of the temperatures.

In order to obtain the function of chromium and silicon, the relation between L_{Cr} and [Cr] must be fully understood.

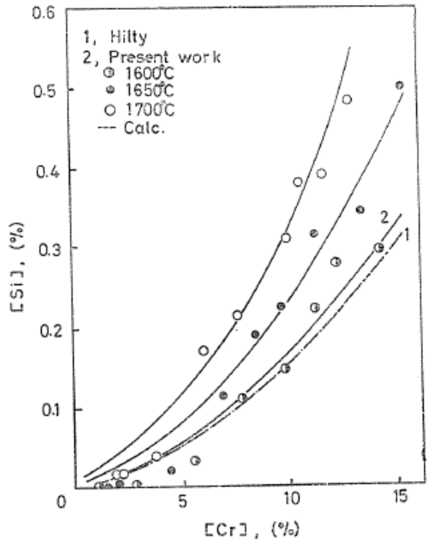


FIG. 10. Solubility of silicon in liquid iron-chromium alloy equilibrated with the silica-saturated acidic slag at various temperatures and calculated value derived from the equation $K' = [Cr]/[Si]^{0.538} \cdot (Cr)$.

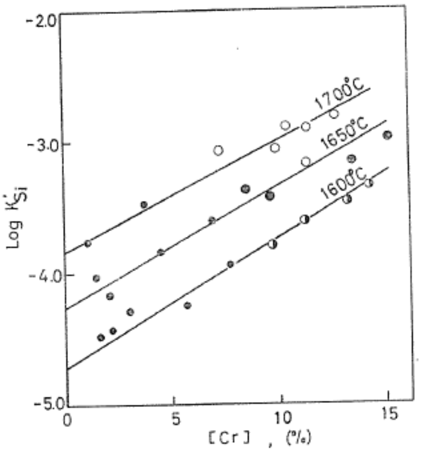


FIG. 11. Effect of chromium concentration on K'_{Si}, small dots are calculated from the concentration of silicon using not any experimental data, but the line in Fig. 10 and oxygen concentration.

Distribution function of chromium was independent of the temperature, and dependent on chromium. L_{Cr} was obtained corresponding to the [Cr] and the values obtained were substituted in eq. (1-28).

K'_5 at the chromium concentration more than 5% was obtained as follows:

Temperatures	1600°C	1650°C	1700°C.
K'_5	0.810	0.688	0.565

Therefore,

$$\log K'_5 = 5738/T - 3.179 \tag{1-29}$$

The relation between silicon and chromium is shown in Fig. 10.

1.3.4. Deoxidation Constant of Silicon and $f_O^{(Cr)}$

The equilibrium constant between silicon and oxygen in the liquid Fe-Cr alloy equilibrated with silica-saturated slag was obtained from the relations [Si]-[Cr] and [O]-[Cr]. The solubility of silicon was obtained from eq. (1-28), in which x was 0.75 at the chromium concentration less than 3% and 0.538, more than 3%, and the oxygen content was obtained from the result of the experiment. The result is shown in Fig. 11.

The deoxidation reaction is represented as follows:

$$(SiO_2)_{sat.} \rightleftarrows [Si] + 2[O] \tag{1-30}$$

and equilibrium constant of this reaction is;

$$K_{Si} = a_{Si} \cdot a_O^2 / a_{SiO_2} \tag{1-31}$$

Where a_{Si} and a_O are the activities of silicon and oxygen respectively which are chosen in the standard state as infinite dilute solution, and a_{SiO_2} is activity of pure silica in the standard state. In the present work, as the slag is saturated with silica,

$$a_{SiO_2} = 1$$

Then, eq. (1–30) is;

$$K_{Si} = a_{Si} \cdot a_O^2 \tag{1-32}$$

The activities of silicon and oxygen are represented respectively as follows;

$$a_{Si} = f'_{Si} \cdot f_{Si}^{(O)} \cdot f_{Si}^{(Cr)} \cdot [Si] \tag{1-33}$$

$$a_O = f'_O \cdot f_O^{(Si)} \cdot f_O^{(Cr)} \cdot [O] \tag{1-34}$$

Where $f_x^{(y)}$ is the interaction parameter which is the effect of y element on the activity of element x.

There have been many reports on the various interaction parameters in eqs. (1–33) and (1–34).

f'_{Si} was studied by Matoba *et ali.*[12] as follows:

$$\log f'_{Si} = (3910/T - 1.77)[Si] \tag{1-35}$$

$$(1570° \sim 1680°C, \ 0 \sim 3\%\ Si)$$

f'_{Si} was calculated by using $\varepsilon'_{Si} = 3.4 (\varepsilon'_{Si} = \partial \ln f'_{Si} / \partial N_{Si})$ obtained by J. Chipman[13] as:

$$\log f'_{Si} = 0.029[Si] \tag{1-36}$$

$f_O^{(Si)}$ and $f_{Si}^{O)}$ were obtained by Gokcen and Chipman[14] and their empirical equations were represented as:

$$\log f_O^{(Si)} = 0.12[Si] - 0.38[Si]^{0.5} \tag{1-37}$$

$$\log f_{Si}^{(O)} = (0.21 - 0.33[Si]^{-0.5})[O] \tag{1-38}$$

They were obtained also by Matoba *et ali.* at the same condition as that in which they obtained eq. (1–35).

$$\log f_O^{(Si)} = -0.137[Si] \tag{1-39}$$

$$\log f_{Si}^{(O)} = -0.24[O] \tag{1-40}$$

At low oxygen content the error was few when calculation was carried out whichever with eqw. (1–37), (1–38) or (1–39), (1–40).

As $f_{Si}^{(O)}$ is smaller than other interaction parameters, neglect of it causes no error in the calculation.

f'_O was obtained by H. Sakao and K. Sano[15] and is represented as:

$$\log f'_O = (-1750/T + 0.76)[O] \tag{1-41}$$

$$(1550° \sim 1650°C)$$

f'_O can be also neglected when the oxygen content is low.

$f_{Si}^{(Cr)}$ was calculated by using the data obtained by D. C. Hilty[10]. The value of $f_{Si}^{(Cr)}$ is represented as:

$$\log f_{Si}^{(Cr)} = -0.003[Cr] \tag{1-42}$$

$f_O^{(Cr)}$ is obtained by H. Sakao and K. Sano[9] at 1600°C as follows:

$$\log f_O^{(Cr)} = -8.01N_{Cr} + 5.82 \cdot N_{Cr}^{1.2}, \quad N_{Cr} < 0.3 \tag{1-43}$$

But its dependency on temperature is not well-known. $f_O^{(Cr)}$ is ten times greater than f'_{Si} and $f_{Si}^{(Cr)}$.

If the values of the dependency on temperature of $f_O^{(Cr)}$ are great, equilibrium constant K_{Si} yields a great error, even when the other interaction parameters could be obtained accurately.

$f_O^{(Cr)}$ was also obtained by Chen and Chipman[16] at 1595°C and Chipman recalculated this value and reprted as:

$$\log f_O^{(Cr)} = -0.041[Cr] \tag{1-44}$$

This value is considerably greater than that obtained by Sakao and Sano and also by Turkdogan[17] at the temperature range of 1565°~1660°C, but his data did not refer to the dependency on temperature.

Average value was represented as:

$$\log f_O^{(Cr)} = -0.064[Cr] \tag{1-45}$$

This equation agrees with the value obtained by Sakao and Sano at low chromium concentration, but the difference between Turkdogan and Sakao and Sano was increased with an increase of the chromium concentration.

As the great discrepancy between them was recognized at 1600°C, the relations between $f_O^{(Cr)}$ and chromium concentration as well as $f_O^{(Cr)}$ and temperature had to be studied before calculation of K_{Si}.

In order to obtain $f_O^{(Cr)}$, calculation is carried out as follows. $K_{Si}/(f_O^{(Cr)})^2$ is obtained from eq. (1-32) to calculate all terms except $f_O^{(Cr)}$.

The relation between $\{\log K_{Si} - 2\log f_O^{(Cr)}\}$ and [Cr] was obtained at various experimental temperatures.

When the chromium concentration becomes infinite dilution, $f_O^{(Cr)} = 1$, therefore, $\{\log K_{Si} - 2\log f_O^{(Cr)}\} = K_{Si}$, when $[Cr] = 0$.

In the term $\{\log K_{Si} - 2\log f_O^{(Cr)}\}$, $-\log f_O^{(Cr)}$ varies according to an increase of chromium concentration.

$f_O^{(Cr)}$ is shown in Table 2. It is well understood that $f_O^{(Cr)}$ is decreased with increasing of the temperature.

$$-\log f_O^{(Cr)} = (369/T - 0.137)[Cr] - 0.0024[Cr]^{1.75} \tag{1-46}$$

This value is in good agreement with Sakao's at 1600°C.

The equilibrium constant for oxygen and silicon in the liquid iron-chromium alloy was calculated by using all the terms of interaction parameters as described

TABLE 2. The values of $f_O^{(Cr)}$ at various chromium concentrations and temperatures.

%Cr	1.0	2.0	3.0	4.0	5.0	6.0	7.0	8.0	9.0	10.0	12.0	14.0	Temp. (°C)
$-\log f_O^{(Cr)}$	0.06	0.11	0.16	0.21	0.26	0.30	0.34	0.38	0.42	0.46	0.53	0.60	1600
	0.06	0.10	0.15	0.19	0.24	0.27	0.31	0.34	0.38	0.41	0.47	0.53	1650
	0.05	0.09	0.13	0.17	0.21	0.24	0.27	0.30	0.33	0.36	0.41	0.46	1700

above.

The results obtained are as follows:

Temperatures	1600°C	1650°C	1700°C.
$\log K_{Si}$	-4.72	-4.26	-3.82

$$\log K_{Si} = -33210/T + 13.01 \tag{1-47}$$

1.5. Conclusions

The various reactions between the liquid iron-chromium alloy and the slag saturated with silica were studied. The results are summarized as follows.

1) From the relation between L_{Cr} and L_{Fe}, oxide of chromium dissolved in the silicate slag with its component nearly equal to that of CrO at concentration of FeO less than 17%.

At the concentration of FeO more than 17%, the redox-reaction between chromium and iron in the two phases is represented as;

$$4(FeO)+3[Cr]=(Cr_3O_4)4[Fe]$$

2) The distribution of Chromium between two phases and the solubility of oxygen were measured and the equilibrium constant at the chromium concentration less than 3% was determind as follows;

$$\begin{array}{l}(CrO_{1.33})_{slag}\\ \quad\downarrow\uparrow\\ [CrO_{1.33}]_{metal}\rightleftarrows[Cr]+1.33[O]\\ K_2' = (CrO_{1.33})/[CrO_{1.33}]\\ K_3' = [Cr]\cdot[O]^{1.33}/[CrO_{1.33}]\\ K_4' = (K_2'/K_3') = (CrO_{1.33})/[Cr]\cdot[O]^{1.33}\\ \log K_4' = 6679/T - 0.724\end{array}$$

3) The equilibrium data for silicon and chromium with acidic slag showed that the following chemical reaction occured in two phases at the chromium concentration more than 5%.

$$\begin{array}{l}(CrO_{1.07})+0.538[Si]\rightleftarrows[Cr]+(SiO_2)\\ K_5' = [Cr]/[Si]^{0.538}\cdot(CrO_{1.07})\\ \log K_5' = -5738/T - 3.179\end{array}$$

4) The effects of both the concentration of chromium and the temperature on

$f_O^{(Cr)}$ are expressed by the following empirical formula.

$$\log f_O^{(Cr)} = -(369/T - 0.137)[Cr] + 0.0024[Cr]^{1.75}$$

The equilibrium constant between silicon and oxygen in the liquid Fe-Cr system was calculated at 1600°, 1650° and 1700°C. The relationship between the equilibrium constan K_{Si} and the temperature is as follows:

$$\log K_{Si} = -33210/T + 13.01$$

Chapter II. Equilibrium between FeO-MnO-SiO$_2$ Slags and Molten Iron

2.1. Introduction

Silicon and manganese are the important elements as the deoxidation reagent in the steelmaking practice. There have been a number of reports on the deoxidation reaction of these elements. The equilibrium constants reported, however, do not show good agreement among themselves. And the study for the co-deoxidation with silicon and manganese are scarcely found in the literatures.

The equilibrium between iron containing silicon and manganese and acidic slags saturated with silica has been investigated by Körber and Oelsen[18]. Hilty

TABLE 3. Comparison of Experimental conditions

Worker			Present work	Körber *et ali.*[1]	Schenck *et ali.*[20]	Hilty & Crafts[19]	Bell[21]
Heat. Furnace			High freq. wave	Graphite resist.	High freq. wave	High freq. wave	Pt-resist.
Atmosphere			Ar	N_2	—	Ar	N_2
Measure. Temp.			PtRh 5% -PtRh 20%	Optical pyro.	Optical pyro.	Pt-PtRh(13%)	Pt-PtRh(13%)
Crucible			SiO_2	SiO_2	SiO_2	SiO_2, MgO, Al_2O_3	MgO, SiO_2
Holding Time			1 hr	10-60 min	—	15 min-6 hr	1.5-2 hr
Fluctuation of temperature			± 5°C	± 20°C	± 5°C	± 5°C	± 5°C
Wheight of metal and slag			150 g, 20 g	80 g, 20 g	400 500 g, 2-3 g ?	6.7 kg	50 g, ?
Exp. Temp.			1550°-1650°C	1530°-1680°C	1530°-1730°C	1550°-1650°C	1550°C
Quality of slag.			SiO_2 sat.	SiO_2 sat.	SiO_2 sat.	SiO_2 unsat.	SiO_2 unsat.
Sampling method	metal		sucktion	casting	sucktion	sucktion	sucktion
	slag		cooling in fur.	casting	spoon	cooled iron bar	cooled iron bar
Analytycal method	iron	O	vacuum fusion	FeO chemical analysis	vacuum fusion	vacuum fusion	vacuum fusion
		Si	photometry	gravimetric	photometry	photometry & gravimetric	photometry
		Mn	photometry	titration	titration	spectrum anal.	titration
	slag		X-ray fluorescent & Chem. anal.	chem. anal	chem. anal.	chem. anal.	chem. anal.

and Crafts[19] also have been studied on the redox-reaction of the silicon and manganese using iron-manganese-silicate slags not saturated with silica in a rotating crucible furnace. They are listed in Table 3. When the experimental investigation of the equilibrium between liquid iron and the slag unsaturated with silica has been carried out, the reaction between the refractroy and the slag is unavoidable, so that experimental results are effected more or less by this reaction. Thermodynamical data to calculate these effects quantitatively have not cleared up by this time. On the contrary. when the slag were saturated with refractory, the consideration did not need on this reaction.

Thermodynamical consideration has been reported on various systems of the slags by Richardson[22] and Chipman[24]. As the chemical structures of the silicate slags are very complex, thermodynamical considerations for these slags are, however, not easy in case of the steelmaking practice. However, in the most cases, as the molten iron is derectly contacted with the slag, it is considered that the most important thing is theremodynamical treatment to be done by combining both phases.

Present chapter has been studied on the activity of MnO and FeO in the slags saturated with silica, and on the equilibrium constants among silicon, manganese and oxygen in the liquid iron.

The authors have reported the data on the equilibrium constant between silicon and oxygen in the liquid iron, chromium alloys in chapter 1, with discussions on the interaction parameters of various elements dissolved in the liquid.

Because the effect of the manganese on the activity coefficient of silicon is small, it had been neglected by other workers. But the value of $f_{\mathrm{Si}}^{(\mathrm{Mn})}$ calculated from the equilibrium constant between silicon and oxygen in the liquid iron equilibrated with the slags saturated with silica is not so small as compared with the other interaction parameters. Thus it was concluded that the interaction parameter $f_{\mathrm{Si}}^{(\mathrm{Mn})}$ should not be neglected for the calculation of the equilibrium constant K_{Si}.

2.2. Experimental Apparatus and Procedure

Experimental apparatus and procedures were described in detail in the previous chapter. Its outline, therefore, was described in this chapter.

The fused silica crucible was stamped with silica powder into the high alumina protective crucible. About 20 g of the powder of the purest available oxides, Fe_2O_3, MnO_2 and SiO_2 were well mixed and charged. Electrolytic manganese, electrolytic iron and ferro-silicon (33% Si) obtained by melting in the authors' laboratory were weighed about 150g, in all cases. Then the oxides and metals were put into the crucible before heating. Atmosphere in the furnace was mild stream of the argon gas which was purified by the copper net heated at 350°C, magnesium chip heated at 600°C, phosphorous pentoxide and soda lime.

Melting was carried out in a high frequency induction furnace keeping the pressure in the furnace 2-3 mmHg higher than the atmosphere of the room. The reaction equilibrium between slag and metal phases was established at 1550°, 1600° and 1650°C. After melted for an hour, the sample was sucked up and quenched in water by the fused silica tube of 3 mm in inner diameter, closed one end and bored a hole of 1.2 mmϕ at the distance of 6 mm from the closed end. Using this tube, the metal samples were prevented perfectly from mixing with oxide slags and could be sucked from the centre of the liquid.

As the melt solidified within 40 sec. after switching off the power current, it was assumed that no significant change occurred in the slag composition during solidification at such a high cooling rate. Slag was separated from metal after cooling down to the room temperature in the furnace and used for the analysis.

Temperature was measured by the platinum 5 pct. rhodium-platinum 20 pct. rhodium thermocouple protected by a silica sheath, with its hot junction touching the bottom of the crucible. The fluctuation of temperature was ± 5°C at most. The temperature was stabilized after 20 minutes from melting down the metals and slags and from this time careful temperature control was conducted continuously till the end of the melting.

The metal was analysed for manganese, silicon and oxygen. Manganese and silicon were detemined photo-metrically. The oxygen determination was made in a vacuum fusion apparatus. The composition of the slags was determined by the methods of chemical analysis and by fluorescence of X-ray analysis.

2.3. Results

In Figs. 12, 13 and 14, the relations among the concentration of silicon, manganese and oxygen were shown at 1550°, 1650° and 1650°C, respectively and compared with that of Körber and Oelsen.

As the viscosity of the slag decreased with increasing manganese oxide in the slags saturated with silica, and the crucible was eroded violently by the re-

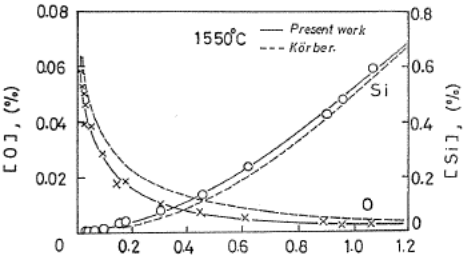


FIG. 12.

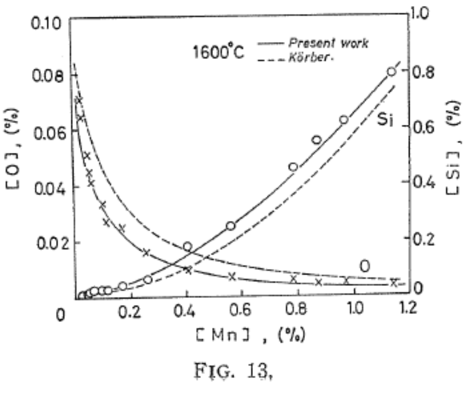


FIG. 13.

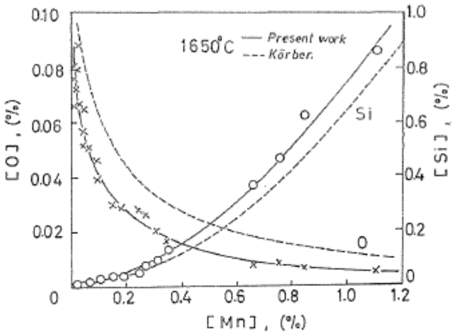


FIG. 14.

Figs. 12, 13 and 14. Relation between the solubility of oxygen and manganese, and concentration of silicon and manganese, in the liquid iron equilibrated with FeO-MnO-SiO_2 slag saturated with silica at 1550°, 1600° and 1650°C, respectively.

action with such slags, the continuance of the melting became difficult for a long time.

When the temperature was raised above 1680°C, the melting became impossible because of the melting point of fused silica.

The relations between silicon and manganese, oxygen ahd manganese have been already reported by Körber and Oelsen. It was considered that the melting and holding time by them was too short to establish the equilibrium, and especially the analytical values of oxygen of the sample quenched in the copper mould were higher than that of sucked sample. Generally, it is considered that sampling by casting is not a suitable for the oxygen determination. Therefore, it came to the conclusion that the values obtained by Körber and Oelsen were lacking in the accuracy.

When manganese was below 0.2 per cent, the silicon concentration became less than 0.05 per cent in all experimental runs. As the silicon was determined photometrically, the relative errors were rapidly increased to 10-50% for less than 0.05% Si due to the hindrance by coloured ions of Fe^{3+} and approaching of the Si contents to the lower limit of silicon determination by the present method.

Contents of manganese oxide and iron oxide in the slags saturated with silica were shown in Fig. 15. Körber and Oelsen concluded in their report that the ratio of oxygen content in the liquid iron to iron oxide in the slag was constant; $(\mathrm{FeO})_{\mathrm{slag}}/[\%\mathrm{O}]=\mathrm{const.}$, but this relation was not proved from the present experimental data. It seemed that the ratio had the tendency to increase slightly with an decreasing of the iron oxide as discussed in the later section.

Körber and Oelsen assumed that the silica concentration was 50% at the slags saturated with silica, and then the summation of the manganese oxide and iron oxide, therefore, was equal to 50%. And they showed the relation between the concentration of MnO and FeO and manganese in the liquid iron without any correction as to the change of the saturation point of SiO_2. At the present work, silica content in the slag are 51 ± 2% in all experimental runs, and it was recognized that the silica content had the tendency to increase slightly with an increasing the manganese oxide. The concentration of both oxides, therefore, are shown in Fig. 15 separately.

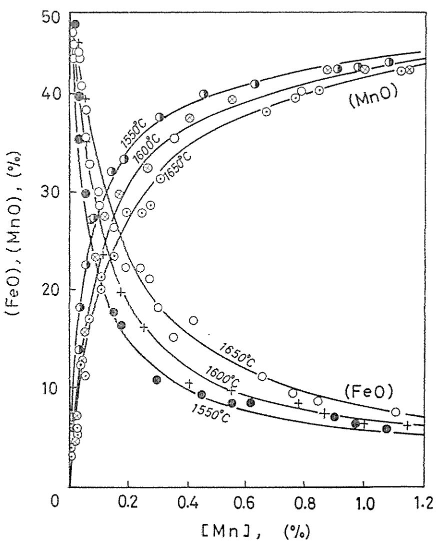


FIG. 15. Relation getween weight per cent MnO and FeO in the acidic slags saturated with silica and the concentration of manganese in the liquid iron.

The summation of the analytical values of all components in the slags is 101 ± 1.5%. As the mixing of metals are not found in the slag, it was considered that the reason of the excess summation is caused by analytical errors.

2.4. Discussion

2.4.1. Effects of Manganese on the Equilibrium between Silicon and Oxygen

The equilibrium of the deoxidation reaction with silicon in the liquid iron is presented as the following equation.

$$(SiO_2) \rightleftarrows [Si] + 2[O] \tag{2-1}$$

$$K_{Si} = a_{Si} \cdot a_O^2 / a_{SiO_2} \tag{2-2}$$

where a_{Si} and a_O are the activities of silicon and oxygen, respectively, based on the standard state at infinite dilute solution, and a_{SiO_2} is the activity of silica based on the standard state at pure silica.

Using Wagner's[24] equation, the activities of both the elements can be expressed by substituting for the interaction parameters of the coexisting elements in the liquid iron as following equations.

$$a_{Si} = f_{Si} \cdot [Si] = f'_{Si} \cdot f_{Si}^{(O)} \cdot f_{Si}^{(Mn)} \cdot [Si] \tag{2-3}$$

$$a_O = f_O \cdot [O] = f'_O \cdot f_O^{(Si)} \cdot f_O^{(Mn)} \cdot [O] \tag{2-4}$$

At the present work, as the slag was saturated with silica, then $a_{SiO_2} = 1$. The equilibrium constant K_{Si}, therefore, can be calculated using the following equation.

$$\begin{aligned} K_{Si} &= a_{Si} \cdot a_O^2 \\ &= f'_{Si} \cdot f_{Si}^{(O)} \cdot f_{Si}^{(Mn)} \cdot \{f'_O \cdot f_O^{(Si)} \cdot f_O^{(Mn)}\}^2 \cdot K'_{Si} \end{aligned} \tag{2-5}$$

where,

$$K'_{Si} = [Si] \cdot [O]^2 \tag{2-6}$$

The relation between the equilibrium constant K'_{Si} and manganese content at 1550°, 1600° and 1650°C, respectively are shown in Fig. 16. When manganese concentration becomes less than 0.2 per cent, the relative error of analytical value of silicon content becomes larger as described in the former section. Therefore, the calculation of K'_{Si} was not carried out in this range at the present work.

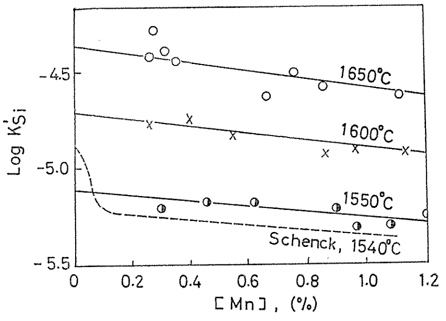


FIG. 16. Effects of the manganese concentration on the deoxidation constant K'_{Si} in the liquid iron at the temperatures of 1550°, 1600° and 1650°C.

Schenck *et ali.*[20] have studied the equilibrium between slag and liquid iron in the silica crucible at 1540°C, and they have reported on the relation between K'_{Si} and the manganese content that K'_{Si} was rapidly increased with a decreasing manganese concentration as shown in Fig. 16. When manganese become less than 0.1 per cent, the concentration of silicon as described above is so small that K'_{Si} lacks in accuracy for such a low manganese concentration range. It is considered with more propriety that the values of K'_{Si} were calculated with the high silicon concentration at the manganese concentration more than 0.2 per cent, and were extrapolated linearly to the range of low manganese concentration.

K'_{Si} is decreased silightly with an increasing of the manganese concentration.

The interaction parameters used in equation (2-5) have been reported by many workers.

Reliable values are summarized as follows:

$$
\begin{aligned}
\log f'_{Si} &= (3910/T - 1.77)\cdot[Si] && (2\text{-}7)^{12)}\\
&= 0.108[Si] && (2\text{-}7')^{13)}\\
\log f_{Si}^{(O)} &= -0.24[Si] && (2\text{-}8)^{12)}\\
&= \{0.21 - 0.33[Si]^{0.5}\}\cdot[O] && (2\text{-}8')^{14)}\\
\log f'_{O} &= (-1750/T + 0.76)\cdot[O] && (2\text{-}9)^{15)}\\
\log f_{O}^{(Si)} &= -0.173\cdot[Si] && (2\text{-}10)^{12)}\\
&\ -0.167\cdot[Si] && (2\text{-}10')^{25)}\\
&\ -0.125\cdot[Si] && (2\text{-}10'')^{26)}\\
\log f_{O}^{(Mn)} &= 0 && (2\text{-}11)^{13)27)}
\end{aligned}
$$

In addition to these values, f'_{Si} was obtained by many workers.

The interaction parameter defined as, $\varepsilon_{Si}^{Si} = d \ln \gamma_{Si}/d N_{Si}$ which was calculated from mole fraction instead of weight percentages has been reported as follows at 1600°C, respectively.

J. Chipman *et ali.*[28)	10–12
J. Chipman *et ali.*[29)	13
Matoba *et ali.*[12)	37
A. M. Samarin *et ali.*[26)	17

Niwa *et ali.*[30) pointed out that the value of f'_{Si} reported by Matoba *et ali.* is greatly different from the others. Also, Niwa *et ali.* carefully considered the heat of mixing of Fe-Si system measured by Körber[31) and Chipman[32), and they concluded that the f'_{Si} was independed on the temperature.

Niwa *et ali.* have suggested the reason that Matoba *et ali.* had not considered following side reaction, when SiO_2 is equilibrated with the gas mixture of H_2-H_2O under their experimental condition.

$$SiO_2(s) + H_2(g) \rightleftarrows SiO(g) + H_2O(g) \qquad (2\text{-}12)$$

By Richardson[33), standard free energy for this reaction is given as,

$$\Delta G_T = 127{,}100 - 45.07T \qquad (2\text{-}13)$$

P_{SiO} is, therefore, increased with the increasing of pressure of H_2 gas and temperature.

Niwa *et ali.* have calculated the pressure P_{SiO} under Matoba's experimental conditions, and they came to conclusion the interaction parameter ε_{Si}^{Si} is equal to 10. The value calculated by Niwa *et ali.* come to a good agreement with that of Chipman[28][29].

In the present work, there is no H_2 gas in the furnace, then SiO is produced by the following reaction:

$$2SiO_2 \rightleftarrows 2SiO + O_2 \qquad (2\text{-}14)$$

The equilibrium constant of equation (2–14) has been given by Darken[34] and Richadson[35] as follows:

$$\log K = 79{,}500/T + 25.58 \qquad (2\text{-}15)$$

It can be neglected at the present work, because the value of P_{SiO} is small.

On the above reason it is better to use the value of f'_{Si} obtained by Chipman[29] than that of Matoba[12].

As theoxygen concentration is low, $f_{Si}^{(O)}$ and f'_O is so small. The equilibrium constant could be obtained within experimental error, when calculation was carried out using whichever values described above.

Under the experimental condition, the equilibrium constant could be calculated within experimental error, using whichever interaction coefficient $f_O^{(Si)}$ obtained by Matoba *et ali.*[12] Gekcen *et ali.*[25] or Samarin *et ali.*[26]

Thus, the interaction coefficients of the equations (2–7′), (2–8), (2–9), (2–10) and (2–11) were used in the following calculation.

Rewriting equation (2–5), following equation is obtained:

$$\log f_{Si}^{(Mn)} = \log K_{Si} - \log f'_{Si} \cdot f_{Si}^{(O)} \cdot \{f'_O \cdot f_O^{(Si)} \cdot f_O^{(Mn)}\}^2 \cdot K'_{Si} \qquad (2\text{-}16)$$

By substituting the various interaction coefficient considered above into equation (2–16), $f_{Si}^{(Mn)}$ can be obtained corresponding to the concentration of manganese. Second terms of the right side of the equation (2–16) is equal to zero. Then at the infinite dilute concentration of manganese, $\log f_{Si}^{(Mn)}$ is equal to zero.

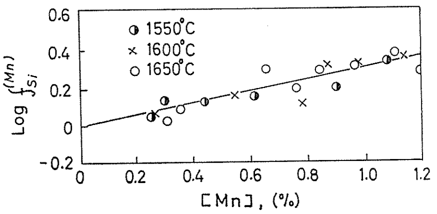


FIG. 17. Values of the effects of manganese concentration on the activity coefficients of silicon in the liquid iron.

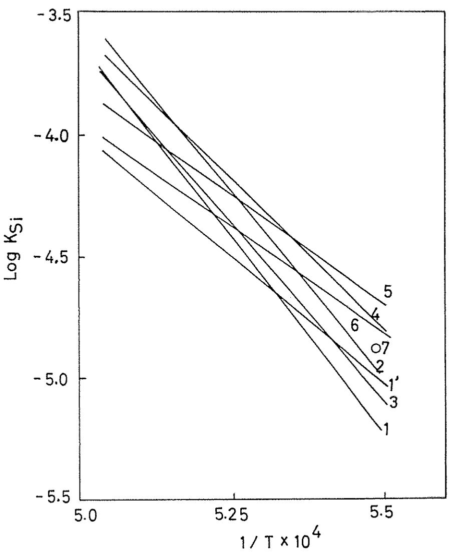


FIG. 18. Effects of temperature on the equilibrium constants. (Numbers in Fig. 18 are listed in Table. 4)

TABLE 4. Equilibrium Constant of Silicon and Oxygen

Investigater	Reaction & equ. const.	function of temperature.	See Fig. 18.
Gokcen & Chipman[14)]	$(SiO_2)_{sat}+2H_2=\mathbf{Si}+2H_2O$ $H_2+\mathbf{O}=H_2O$	$\log K_{Si}=-29150/T+11.01$	2
Matoba *et ali.*[12)]	〃	$\log K_{Si}=-30720/T+11.76$	3
Present work	$(SiO_2)_{sat}=\mathbf{Si}+2\,\mathbf{O}$ $K_{Si}=a_{Si}\cdot a_0^2$	$\log K_{Si}=-33210/T+13.01$ $\log K_{Si}=-23100/T+7.59$	1 1′
Körber & Oelsen[18)] (recalculated by Gocken & Chipman)	$K''_{Si}=[Si]\cdot(FeO)^2$ $K'_{Si}=[Si]\cdot[O]^2$	$\log K''_{Si}=-19057/T+11.101$ $\log K'_{Si}=-26050/T+9.51$	4
Schenck & Wiesner[20)]	$K'_{Si}=[Si]\cdot[O]^2$ $(FeO\cdot SiO_2)$	$\log K'_{Si}=19050/T+5.750$	5
Hilty & Craft.[19)]	$K'_{Si}=[Si]\cdot[O]^2$	$\log K'_{Si}=-18050/T+5.10$	6
Bell.[21)]	$K'_{Si}=[Si]\cdot[O]^2$	$K'_{Si}=1.3\times10^{-5}$	7

The values of interaction parameter $f_{Si}^{(Mn)}$ are shown in Fig. 17. $f_{Si}^{(Mn)}$ is a function of only the concentration of manganese and not of temperature.

The relation between K_{Si} and temperature is shown together with those of the other investigators in Fig. 18 and in Table 4.

The equilibrium constant K_{Si} is in a good agreement with that obtained in 18–8 stainless steel but is inconsistent with that of Fe-Cr reported in the previous section.

It is considered that the discrepancy between other reports and the present work is due to the difference in the experimental process, and the experimental errors which are affected by the coexisting elements in the liquid iron.

2.4.2. Activity of Iron Oxide in the Slag Saturated with Silica

Generally, the activity of iron oxide in the slag is defined in the relation with the oxygen concentration in the liquid iron equilibrated with the slag. At the constant temperature, oxygen concentration in the liquid iron equilibrated with wustite (the solubility of oxygen) is represented as $[O]_{sat.}$, then, the activity of iron oxide in the slag composed of various oxides can be calculated by the following equation;

$$a_{FeO}=[O]_{obs.}/[O]_{sat.} \tag{2-18}$$

where $[O]_{obs.}$ refers to the oxygen concentration in the liquid iron equilibrated with slag composed of various oxides.

If there are some elements which increase or decrease the activity of oxygen in the liquid iron, the calculation must be carried out using the activity instead of weight per cent of oxygen.

It is well known that such elements as carbon, silicon and chromium decrease the activity of oxygen. When the effects of such elements is negligibly small, the activity of iron oxide can be obtained approximately using the concentration of oxygen in liquid iron equilibrated with the slag.

Sakao and Sano[15] have reported that the activity of oxygen decreased with an increasing oxygen content. $[O]_{sat.}$ has to be, consequently, represented by the activity of oxygen as follows:

$$[O]_{.sat} = f'_O \cdot [O]_{sat.} \tag{2-19}$$

$[O]_{sat.}$ has been obtained by Taylor and Chipman[36] and given as a function of temperature as follows;

$$\log [O]_{sat.} = -6320/T + 2.734 \tag{2-20}$$

and f'_O was obtained by Sakao and Sano asdescribed above section.

The activity of iron oxide can be calculated from the values of oxygen concentration equilibrated with the slag at any temperature.

The relation between the activity of iron oxide in the system FeO-MnO-SiO_2 saturated with silica and the mole fraction of iron oxide is shown in Fig. 19.

Schuhmann and Ensio[37] has made the slag of FeO-SiO_2 contacting to γ-iron in the temperaure range of 1258°-1407°C, and under the mixing gas of CO and CO_2 into the reaction cell. They obtained a_{FeO} from the ratio CO/CO_2. Using a_{FeO} obtained by them at 1315°C, Turkdogan and Pearson[38] recalculated a_{FeO} at the condition $N_{FeO}+N_{SiO_2}=1$, (actually, the slag contained Fe_2O_3) and showed the relation between a_{FeO} and N_{FeO}. From the result, a_{FeO} showed the negative deviation from Raoult's law at lower mole fraction of iron oxide.

Schuhmann and Ensio calculated a_{FeO} as a function of temperature and showed γ_{FeO} is equal to 0.81 in the slag saturated with silica by extrapolating the temperature to 1530°C.

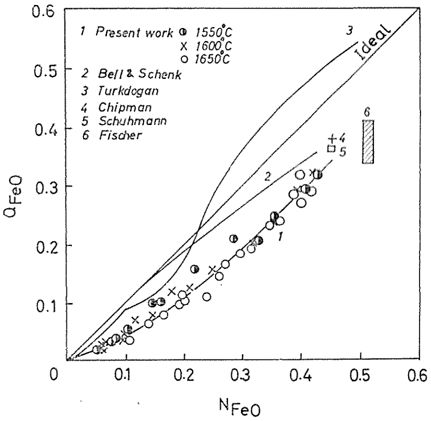


FIG. 19. Relation between the activity of iron oxide and the mole fraction of FeO in the slags, FeO-MnO-SiO_2 saturated with silica.

Bell, Murad and Carter[39] carried out thier experiment in the MgO crucible, and equilibrated the liquid iron with the slag containing FeO, MnO and SiO_2 (MgO was contained less than 13% in the slag). They also obtained the activities of the oxides in the slag.

Fischer and Ende[40] studied on the distribution of oxygen equilibrating the liquid iron and the slag containing FeO, CaO and SiO_2 and calculated a_{FeO} in the slag saturated with silica, and reported that γ_{FeO} was distributed from 0.8 to 0.9 in the temperature range of 1530°-1700°C, and γ_{FeO} was decreased slightly with increasing of temperature.

Gokcen and Chipman[14] studied on the equilibrium between liquid iron and the mixing gas of H_2 and H_2O. a_{FeO} in the slags saturated with silica was obtained from the eqilibrium data between silicon and oxygen at the temoerature, 1600°C. Then they reported that γ_{FeO} is equal to 0.83.

Bell[21] studied on the eqilibrium between the slag cotnaining FeO, MnO, MgO and SiO_2 and liquid iron, he obtained also that γ_{FeO} is equal to 0.87.

Schenck *et ali.*[20] tried their experiment in the silica crucible, and they reported a_{FeO} in the slags saturated with silica containing FeO, MnO and SiO_2 at 1540°C. Their result came to a good agreement with that of Bell.

These results are summarized and shown in Fig. 19. As shown in Fig. 19, there is a great discrepancy among the results of Turkdogan[38], Bell[21] and Schenck[20] and present works regarding the activity of iron oxide which can be easily obtained. It is thought that the differences among these results were caused by the other reason and not due to the difference in the methcd of the experimental run. When the concentration of iron oxide comes to 50%, that is, the slag becomes to two component system, γ_{FeO} is distributed between 0.8 and 0.9 except the results of Turkdogan.

It is not clear why the activity of iron oxide obtained by Turkdogan is different from the other values at the high iron oxide content. For this reason, it is thought that there may be an error in the result obtained by Schuhmann, which is used as the basis of the calculation by Turkdogan, or in the process of the calculation by Turkdogan. The slag used by Bell in his experiment contains some Al_2O_3. Our knowledge for these silicate is too poor to discuss the effects of Al_2O_3 on the activity of iron oxide. Except the present work, as it is not evident what sort of interaction parameter is used to calculate the activity of oxygen, we can not compared them accurately.

2.4.3. Activity of Manganese Oxide in the Slag Saturated with Silica

There are many reports regarding the deoxidation reaction by manganese. Generally, the equilibrium constant of this reaction in the system FeO-MnO slag is called as manganese constant and is presented as follows:

$$K_{Mn} = a_{MnO}/a_{FeO} \cdot a_{Mn} = N_{MnO}/N_{FeO} \cdot [Mn] \qquad (2\text{-}21)$$

By Gero, Winkler and Chipman[41], K_{Mn} was obtained as a function of the temperature as follows:

$$\log K_{Mn} = 6440/T - 2.95 \qquad (2\text{-}22)$$

Recently Gunji and Matoba[27] reported the following equations.

$$FeO(s) + [Mn] = MnO(s) + [Fe] \qquad (2\text{-}23)$$

$$\log K_{Mn}(s) = 6980/T - 2.91 \qquad (2\text{-}24)$$

$$\Delta F^\circ = -31{,}930 + 13.27T \qquad (2\text{-}25)$$

$$FeO(l) + [Mn] = MnO(l) + [Fe] \qquad (2\text{-}26)$$

$$\log K_{Mn}(l) = 6440/T - 2.83 \qquad (2\text{-}27)$$

$$\Delta F^\circ = -29{,}470 + 12.95T \qquad (2\text{-}28)$$

In the present work, the reaction between manganese and oxygen in the liquid iron equilibrated with the slag saturated with silica is presented as follows:

$$[\mathrm{Mn}] + [\mathrm{O}] = (\mathrm{MnO}) \qquad (2\text{-}29)$$

$$K_{\mathrm{Mn-O}} = a_{\mathrm{MnO}}/a_{\mathrm{Mn}} \cdot a_{\mathrm{O}} \qquad (2\text{-}30)$$

where a_{MnO} is the activity of manganese oxide by the Raoult's law and a_{Mn} and a_{O} are the activities of manganese and oxygen by the Henry's law, respectively.

Even if $K'_{\mathrm{Mn-O}}$ is obtained as a function of the concentration of manganese oxide, and the activity of manganese oxide is calculated by extrapolating to one mole fraction of manganese oxide, the values of $K'_{\mathrm{Mn-O}}$ should be lacking in accuracy, as there is always a great quantity of SiO_2 in the silica slag.

$K'_{\mathrm{Mn-O}}$ can be calculated from K_{Mn} and thermodynamical data. Chipman[42] has calculated $K'_{\mathrm{Mn-O}}$ combining K_{Mn} obtained by Geor Winkler and Chipman as a function of temperature with the ratio $[\mathrm{O}]/(\mathrm{FeO})$ obtained by Taylor and Chipman as a function of temperature as follows:

$$\log K'_{\mathrm{Mn-O}} = 12{,}760/T - 5.68 \qquad (2\text{-}31)$$

As $K'_{\mathrm{Mn-O}}$ by Chipman[42] has been calculated without using the activity, Adachi *et ali.*[43] recalculated $K'_{\mathrm{Mn-O}}$ using new thermodynamical data and interaction parameters and the following equation was obtained.

$$\log K_{\mathrm{Mn-O}} = 13{,}470/T - 6.045 \qquad (2\text{-}32)$$

Equation (3-31) has a good agreement with equation (3-32) within experimental temperature range. If there is no elements which affects on the activity of manganese in the liquid iron, concentration can be directly substituted for the activity in the calculation.

At the present work, the effect of silicon on the activity of manganese can not be neglected in the calculation.

$$a_{\mathrm{Mn}} = f'_{\mathrm{Mn}} \cdot f^{(\mathrm{O})}_{\mathrm{Mn}} \cdot f^{(\mathrm{Si})}_{\mathrm{Mn}} \cdot [\mathrm{Mn}] \qquad (3\text{-}33)$$

where f'_{Mn} and $f^{(\mathrm{O})}_{\mathrm{Mn}}$ were obtained by Ōtani *et ali.*[44] and Gunji *et ali.* and they are equal to 1, respectively.

The authors already obtained $f^{(\mathrm{Mn})}_{\mathrm{Si}}$ above, then $f^{(\mathrm{Si})}_{\mathrm{Mn}}$ can be obtained using the equation introduced by Wagner.

$$e^3_2 = (\mathrm{M}_2/\mathrm{M}_3) \cdot e^2_3 \qquad (3\text{-}34)$$

therefore,

$$\log f^{(\mathrm{Si})}_{\mathrm{Mn}} = 0.550[\mathrm{Si}] \qquad (3\text{-}35)$$

and a_{O} has been obtained in the prvious section. a_{MnO}, therefore, can be calculated using $K_{\mathrm{Mn-O}}$, a_{Mn} and a_{O}.

The relation between activity of manganese oxide and mole fraction is shown

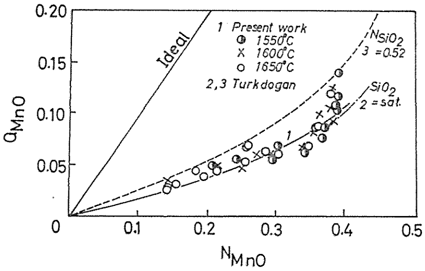


FIG. 20. Relation between the activity of manganese oxide and the mole fraction of MnO in the slags, FeO-MnO-SiO$_2$ saturated with silica.

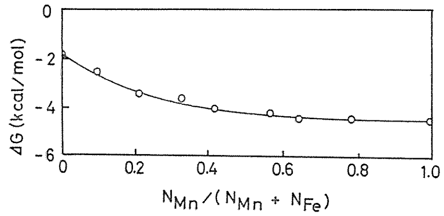


FIG. 21. Gibbs free energy of formation of ternary oxide slags, FeO-MnO-SiO$_2$ saturated with silica, per mole of oxide at 1600°C.

in Fig. 20. In addition to it, the relations between them at various silica concentration obtained by Turkdogan[45] are also shown in Fig. 20. As shown in Fig. 20, activity of manganese oxide in the slags saturated with silica is independent of the temperature, and is dependent on the concentration of manganese oxide.

Turkdogan obtained a_{MnO} using the following equation,

$$a_{MnO} = K_{Mn} \cdot a_{FeO} \cdot [Mn] \tag{3-36}$$

As discussed in the previous section on the activity of iron oxide, it has been recognized that the values obtained by Turkdogan are different from those of others. And if the calculation is carried out directly using the concentration of manganese in substitution for the activity, fairly big error is introduced by the coexistence of silicon.

a_{MnO} obtained by the authors showed a good agreement with that by Turkdogan and this meant that a_{MnO} was not affected by the other oxides in the slag. Or it is thought that this agreement is due to the cancellation of errors in the calculation which arise from the error of a_{FeO} and neglecting the activity coefficient of manganese.

Free energy of mixing of FeO, MnO and SiO$_2$ in the slags saturated with silica can be calculated using the activities of iron oxide and manganese oxide obtained above.

As for the binary systems, FeO-SiO$_2$ and MnO-SiO$_2$, free energy of mixing has been reported by Richardson and his group[46].

Solubility of silica in the slags saturated with silica is obtained from the analytical values, then ΔG_B of the binary system FeO-SiO$_2$ and MnO-SiO$_2$ can be obtained from their data. Using the activities of iron oxide and manganese oxide which are calculated from the equilibrium constants, ΔG_T of the ternary system FeO-MnO-SiO$_2$ saturated with silica can be calculated and is shown in Fig. 21.

ΔG_T is decreased with an increasing concentration of manganese oxide, and is in accord with ΔG_B of the binary system MnO-SiO$_2$.

2.5. Conclusions

The equilibrium between the molten iron and the slags containing FeO, MnO and saturated with silica was studied in the SiO_2 crucible at 1550°, 1600° and 1650°C. The results obtained are summarized as follows:

1) The equilibrium constant for the deoxidation of silicon in the molten iron containing less than 1.2% manganese is given as,

$$\log K_{Si} = -23{,}100/T + 7.59$$

2) The effect of manganese on the activity coefficient of silicon was examined. The activity coefficient $f_{Si}^{(Mn)}$ is a function of only the concentration of manganese and not of temperature. The experimental results are presented by equation:

$$\log f_{Si}^{(Mn)} = 0.281 \cdot [Mn]$$

3) The activity of iron oxide in the slag, $FeO\text{-}MnO\text{-}SiO_2$ system, was determined using the following relation.

$$a_{FeO} = (a_O)_{obs.}/(a_O)_{sat.}$$

The activity of iron oxide is independent of temperature, and dependent on the concentration of iron oxide. It shows negative deviation from the Raoult's law.

The activity coefficient of iron oxide (γ_{FeO}) in the binary slags $FeO\text{-}SiO_2$ saturated with SiO_2 obtained by extrapolating the concentration of manganese oxide to zero came to a good agreement with the values reported in the literature.

4) The activity of manganese oxide in the ternary slags was obtained. It has defined as follows:

$$K_{Mn-O} = a_{MnO}/a_{Mn} \cdot a_O$$

The true equilibrium constants of K_{Mn-O} were calculated using the value of $K_{Mn} = a_{MnO}/a_{FeO} \cdot [Mn]$ obtained by Chipamn. The activities of oxygen and manganese were calculated from the interaction parameters of the elements dissolved in the liquid iron.

The effects of silicon on the activity coefficient of manganese, $f_{Mn}^{(Si)}$, were estimated using the Wagner's equation. The result is expressed as a function of silicon concentration in the liquid iron as follows:

$$\log f_{Mn}^{(Si)} = 0.550 \cdot [Si]$$

The activity of manganese oxide is independent of temperature, and dependent on the concentration of manganese oxide in the slag saturated with silica. It showed negative deviation from Raoult's law in the same way as the iron oxide.

Chapter III. Deoxidation with Silicon and Manganese in the Liquid Iron-Chromium Alloy and Equilibrium between Silica-Saturated Slag and Liquid Iron

3.1. Introduction

Following the previous study on the equilibrium between silicon and oxygen in the liquid iron, the authors tried to solve the relations among silicon, oxygen and manganese in the liquid iron-chromium alloy in the silica crucible.

In the liquid iron-chromium alloy equilibrated with the slags saturated with silica, these relations were already investigated by Körber and Oelsen[1]. Many questions in the method of their calculation, however, could be found from the modern thermodynamical point of view. For an example, the calculation was carried out only by using the concentrations of dissolved elements but not by using the activity. And also, it was assumed experimentally that the keeping time for equilibration was too short and the method of the analysis seemed not so suitable.

The authors have reported previously on the equilibrium between silicon and oxygen in the liquid iron-chromium alloy and in the liquid iron-manganese alloy. In both the cases, the equilibrium values were measured with experimental works, which were carried out equilibrating with the slags saturated with silica. The results obtained experimentally on the relations of the concentrations of silicon, oxygen and manganese in the liquid Fe-Cr alloys were compared with the calculated values which were obtained by using the thermodynamical function introduced by Wagner[24].

On the thermodynamical consideration for the reactions in the steelmaking practice, it was important that the relations of the concentrations for these dissolved elements were clearly known. As the molten iron was contacted directly with the slag phase, it was, moreover, important that the thermodynamical consideration had to be done for these systems by analysing the reactions between iron and slag in the molten state. But, the components in the slag changed in great quantity and its chemical formula in the slag, especially the ionic structure of the silicate slag was very complex and was changed corresponding with its concentration.

How does the change of ionic structure of oxide at the molten state influence on the equilibrium constants? It is difficult to solve this question only based on the thermodynamical consideration.

Even if its calculation was incomplete in the concentrated solution, quantitative relation among dissolved elements in the dilute liquid iron could be evaluated by applying the thermodynamical equation introduced by Wagner. But, these thermodynamical treatments for oxides in the slag, even if the oxides were limited to three components, could be carried out only using the Gibbs-Duhem equation[47][48] and was impossible for the multi-component system.

Because of the above reasons, it was considered that one of the most important work at the present time was to obtain these fundamental data by the experiments.

In the previous chapters, the authors have discussed how the activities of iron and manganese oxides were changed corresponding to the concentration in the silica-saturated ternary system, FeO, MnO and SiO_2. In the present work, they studied how the activities of iron and manganese oxide are changed by addition of chromic oxide to this ternary slag, and how they react each other. Also they discussed the method of the thermodynamical treatment to be combined with the dissolved elements in liquid iron and the oxide phases for the various metallic oxides in the slags saturated with silica.

3.2. Experimental Apparatus and Procedure

Experimental apparatus and procedures were described in detail in the previous chapter. Only the outline, therefore, was described in this chapter. Apparatus was composed with the high frequency induction furnace and gas purifier.

The fused silica crucible was stamped with silica powder into the high alumina protective crucible. The powder of the purest oxides available, Fe_2O_3, MnO_2, Cr_2O_3 and SiO_2 were charged about 20 g in total and mixed well each other. Electrolytic iron, electrolytic manganese, electrolytic chromium and ferro-72 pct. silicon obtained by melting in the authors' laboratory were weighed about 150 g in all cases. The oxides and metals were put into the crucible before heating. For the furnace atmosphere, mild stream of the argon purified by the copper net heated at 350°C, magnesium chip heated at 600°C, pentaphosphoric acid and soda lime, was used.

Melting was carried out keeping the pressure in the furnace 2–3 mmHg higher than that in the room.

The reaction equilibrium between slag and metal phases was established for an hour at 1550°, 1600° and 1650°C. At the end of the melting, the thickness of the slag phases was 2–4 mm. To hold the temperature of slag and metals uniformly a graphite pipe was set at intermediate between the silica crucible and the protective alumina crucible.

The temperature was measured by the platinum 5 pct. rhodium-platinum 20 pct. rhodium thermocouple protected by a silica sheath 8 mm O. D, with its hot junction touching the bottom of the crucible. Temperature was stabilized after 20 min. from the melting down the metal and slag, and from this time measurement was conducted continuouslly till the end of the melting.

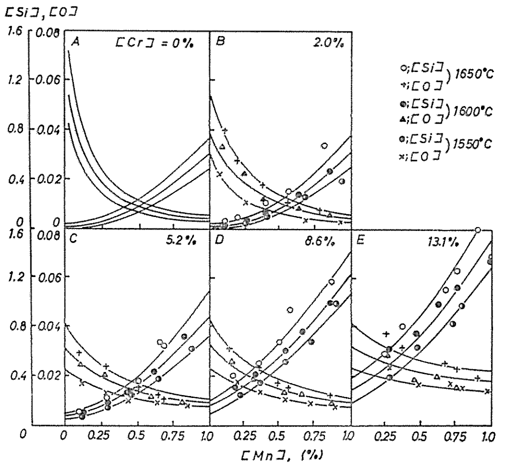
The sample of metal was sucked by fused silica tube which was 3 mm in I. D., one closed end and bored a hole of 1.2 mmϕ at the distance of 6 mm from the closed end, and cooled rapidly in the water. After sampling the metal, the furnace was switched off the current immediately. The metal and slag were cooled down to the room temperature in the furnace. As the melt solidified within 40 sec. after switching off the current, it was assumed that no significant change occurred in the slag component in the equilibrium at such a high rate of cooling.

The oxygen determination was carried by a vacuum fusion at 1750°C. Silicon and manganese were determined photometrically and chromium was analysed by redox-titration with permanganate and ferrous ammonium sulphate.

Slags were determined both by chemical analyses for SiO_2, Fe, Mn and Cr, and by flourescent X-ray analyses.

3.3. Experimental Results

The relations among the concentration of silicon, manganese and oxygen at various chromium concentrations were shown in Figs. 22-B–E, at 1550°, 1600° and 1650°C, respectively. The authors have shown this relation in the previous chapter, which was obtained in the chromium-free liquid iron and showed it in Fig. 22-A to be compared with the present work.



A) In the liquid chromium-free alloy

B)-E) In the liquid Fe-Cr alloy equilibrated with acidic slag saturated with silica.

FIG. 22. The effect of the concentration of manganese on the solubilities of silicon and oxygen.

The controlling of the concentration of chromium was difficult, because it changed according to the oxygen, manganese and silicon contents at the initial condition of the melting down the metals. Although chromium concentration could not be attained accurately at will, from the result of the analysis of the chromium, its concentration was deviated within ± 0.5% from the mean value. However, the concentrations of oxygen at 2.0% Cr, and of silicon at 13% Cr were changed violently themselves with variation of a little amount of chromium. In addition to the experimental errors, when the calculation was carried for these data, the effect of the chromium concentration, therefore, had to be considered carefully.

The viscosity of the slag FeO-CrO-SiO_2 systems, especially slag equilibrated with chromium concentration of 2-3%, was so high that the slag could not be sufficiently stired at the experimental temperature range. The viscosity was abruptly decreased with increasing of MnO in the slag. Increasing manganese and chromium in the liquid iron, fluidity of the slag became small, and the crucible was eroded violently by the reaction with the slag. The continuance of the melting was difficult for a long time.

The results of the analysis for slag showed that the contents of each oxide were as follows at the range of the exprimental temperature: SiO_2: 50 ± 2%, FeO: 5-20%, MnO: 5-40%, Cr (as metallic Cr): 2-20%.

When the concentration of the chromium was less than 5.2%, the concentrations of iron and manganese oxide were affected with the temperature. But in the range of more than 8.6% Cr, this effect of the temperature was not recognized from the analytical data.

3.4. Discussion

3.4.1. Equilibrium between Silicon and Oxygen

The authors have already studied on the equilibrium between silicon and oxygen in the liquid iron-chromium alloy and liquid iron-manganese alloy in the previous chapters. In those chapters, the interaction parameters for the coexistent various elements were discussed and obtained from the experimental data. In the present work, the authors studied equilibrium between silicon and oxygen in the liquid iron-chromium-manganese alloy. By combining both liquids above described the calculated values were compared with the experimental values.

The activities of silicon and oxygen were calculated by using interaction parameters of other dissolved elements, chromium, manganese, silicon and oxygen by using the equation introduced by Wagner as follows:

$$a_{Si} = f'_{Si} \cdot f_{Si}^{(O)} \cdot f_{Si}^{(Mn)} \cdot f_{Si}^{(Cr)} \cdot [Si] \quad (3\text{-}1)$$

$$a_O = f'_O \cdot f_O^{(Si)} \cdot f_O^{(Mn)} \cdot f_O^{(Cr)} \cdot [O] \quad (3\text{-}2)$$

In the previous chapters, the authors calculated the equilibrium constant in the liquid Fe-Cr alloy as

$$\begin{aligned} K_{Si} &= a_O \cdot a_{Si}^2 \\ &= f'_{SS} \cdot f_{Si}^{(O)} \cdot f_{Si}^{(Cr)} \cdot \{f'_O \cdot f_O^{(Si)} \cdot f_O^{(Cr)}\}^2 \cdot K'_{Si} \quad (3\text{-}3) \end{aligned}$$

$$\log K_{Si(Fe\text{-}Cr)} = -33{,}210/T + 13.01 \quad (3\text{-}4)$$

and also estimated the equilibrium constant in the liquid iron-manganese alloy as

$$\begin{aligned} K_{Si(Fe\text{-}Mn)} &= a_{Si} \cdot a_0^2 \\ &= f'_{Si} \cdot f_{Si}^{(O)} \cdot f_{Si}^{(Mn)} \cdot \{f'_O \cdot f_O^{(Si)} \cdot f_O^{(Mn)}\}^2 \cdot K'_{Si} \quad (3\text{-}5) \end{aligned}$$

$$\log K_{Si(Fe\text{-}Mn)} = -23{,}100/T + 7.59 \quad (3\text{-}6)$$

therefore, the equilibrium constant in the liquid iron-chromium-manganese alloy can be evaluated from the activities of oxygen and silicon which are shown in the eqs. (3-1) and (3-2).

$$K_{Si(Fe\text{-}Cr\text{-}Mn)} = a_{Si} \cdot a_O^2 \quad (3\text{-}7)$$

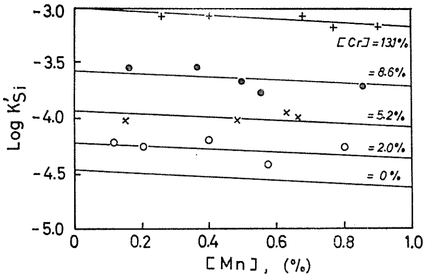


FIG. 23. The effect of the concentration of manganese on the deoxidation constants K'_{Si} at 1650°C.

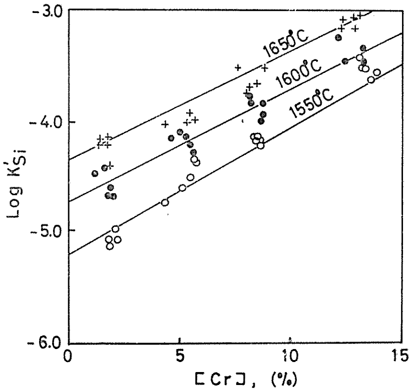


FIG. 24. The effect of the concentration of chromium on the deoxidation constant K'_{Si}. The lines in Fig. 24 are obtained from the manganese-free liquid iron-chromium alloy.

The interaction parameters in eqs. (3–1) and (3–2) were all used in eqs. (3–3) and (3–5) and these values were already reported by many workers and the authors discussed those all interaction parameters in previous chapters.

The relation between the concentration product $K'_{Si} = [Si] \cdot [O]^2$ and manganese content at 1650°C are shown in Fig. 23. As seen in Fig. 23, K'_{Si} is increased with increasing of the chromium in the liquid iron and is slightly decreased with increasing of manganese at constant chromium concentration. The relation between log K'_{Si} and [Mn] shows paralle lines to that in chromium-free solution, approximately.

Neglecting the effect of [Mn] on K'_{Si}, the relation between K'_{Si} and [Cr] is shown in Fig. 24. Though the effect of manganese is not shown clearly from Fig. 24, this relation is good agreement with that in the liquid iron-chromium formerly obtained by the authors'.

Calculating the activities of silicon and oxygen described above, the relations between the equibrium constant $K_{Si(Fe\text{-}Cr\text{-}Mn)}$ and [Cr] are shown in Fig. 25. $K_{Si(Fe\text{-}Cr\text{-}Mn)}$ is increased with increasing of [Cr] to be compared with $K_{Si(Fe\text{-}Cr)}$ for the respective temperature.

For these deviations, the various reasons are thought. These are considered to be caused by the errors in the interaction parameters, and by the fact that the system is not dilute solution for thermodynamical calculation with Wagner's equation. In both the cases, there were technical difficulties in the experimental runs. Thus, one of the methods of the reliable calculation to obtain the relation between [Si] and [O] is as follows. If [Mn] is less than 1%, K'_{Si} can be expressed as the function of only chromium concentration. Therefore, the relation between the concentration of [Si] and [O] can be obtained.

Even if [Cr] is given, [Mn], however, can not be known form this relation. For this problem, they will discuss in the latter section.

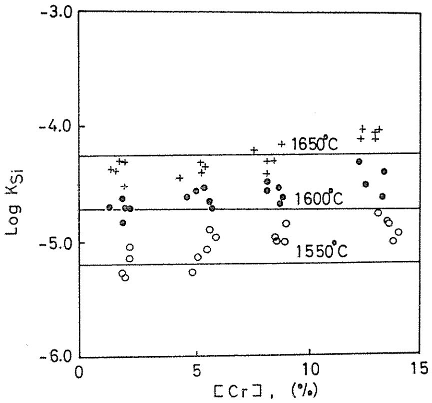


FIG. 25. Relation between the equilibrium constant K_{Si} and the concentration of chromium. The lines in Fig. 25 are obtained from the manganese-free liquid iron-chromium alloy.

3.4.2. Activity of Iron Oxide

In this section, the authors will discuss on the relation between oxygen in the liquid iron and iron oxide in the slags saturated with silica.

FeO in the slags saturated with silica was not analysed to distinguish from Fe_2O_3, but it was considered[42] that Fe_2O_3 is only few per cent of FeO. Therefore, assuming that oxide of iron in this system is entirely FeO, the calculation is carried out hereafter.

The relation between iron oxide in the slag and the concentration of oxygen in the liquid iron at 1550°, 1600° and 1650°C respectively were shown in Fig. 26-A, B and C.

As seen from Fig. 26, at constant oxygen concentration, FeO is decreased with increasing of the chromium concenttration in the liquid iron. At constant chromium concentration, if the chromium concentration is higher, FeO is less changed regardless of the big variation of oxygen concentration.

Körber and Oelsen[1] also studied on the relation between iron oxide in the slag saturated with silica and oxygen in the liquid metal. Their result of the distribution of oxygen showed the constant value as seen in Fig. 26-B, and was independent of chromium concentration. Their result is different from the present work.

The tendency described above was shown clearly with increasing of the tempreature, that is to say, FeO is hardly change with abrupt decreasing of oxygen.

In previous chapter, the authors showed that the activity of iron oxide could be calculated by the following equation.

$$a_{FeO} = (a_O)_{obs.}/(a_O)_{sat.} \tag{3-8}$$

where $(a_O)_{obs.}$ refers to the activity of oxygen in the liquid iron-chromium alloy equilibrated with slag composed with the multi-component system, and $(a_O)_{sat.}$ refers to the activity of oxygen in the liquid iron equilibrated with wustite at the same temperature. $(a_O)_{sat.}$ can be calculated by combining the solubility of oxygen studied by Taylor *et ali.*[36] with the activity coefficient obtained by Sakao

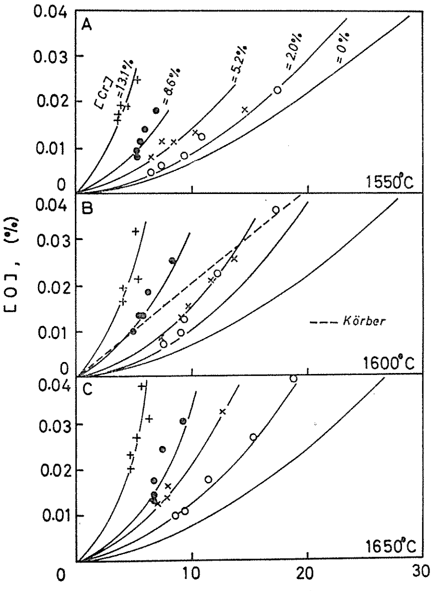


FIG. 26. Relation between the solubilities of oxygen in the liquid Fe-Cr-Mn alloys and the concentration of iron oxide in the acidic slag saturated with silica.

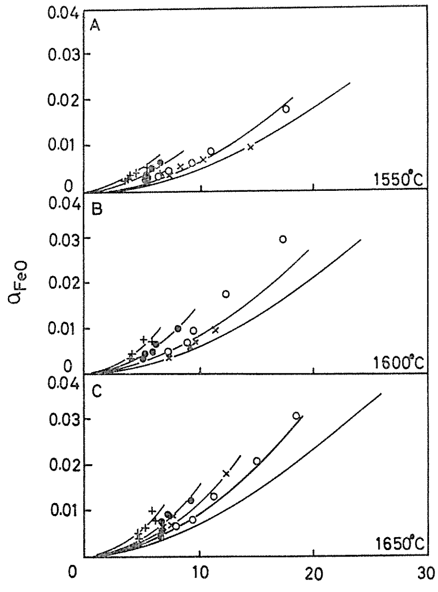


FIG. 27. Relation between the activities of oxygen in the liquid Fe-Cr-Mn alloys ann iron oxide.

et al.[15].

In this way at any temperature and concentration, the activity of (FeO) can be calculated from the activity of oxygen in liquid iron equilibrated with multi-component slag. The method of the calculation for the activity of oxygen was shown in detail in former section 3.4.1.

The relation between the activity of oxygen and the concentration of iron oxide (weight per cent) was shown in Fig. 27-A, B and C. (Cr) in the slag was increased with constant distribution rate with increasing of [Cr] in liquid iron. When (MnO) is equal to zero, the maximum concentration of (FeO) is decreased with increasing of (CrO) in the slag. With increasing of chromium in liquid metal, the solubility of oxygen is slightly increased, but a_O became very small. The effect of chromium concentration on the relation between a_O and (FeO) for 2% [Cr] and 5.2% [Cr] is scarcely distinguishable among themselves at 1550° and 1600°C, but it can be done at 1650°C.

The following tendency can be seen for all experimental run. a_O at constant (FeO) was increased with increasing of [Cr] in liquid metal.

If the ratio of [O] and (FeO) is a constant independent of [Cr] as shown by Körber and Oelsen, the relation between a_O and concentation of (FeO) must be given against the authors' result. Therefore, a_O at constant (FeO), is abruptly decreased with increasing of [Cr] in liquid metal. Generally, as the activity of a component in slag was given as a function of its mole fraction, this relation was shown to be compared with other results in Fig. 28.

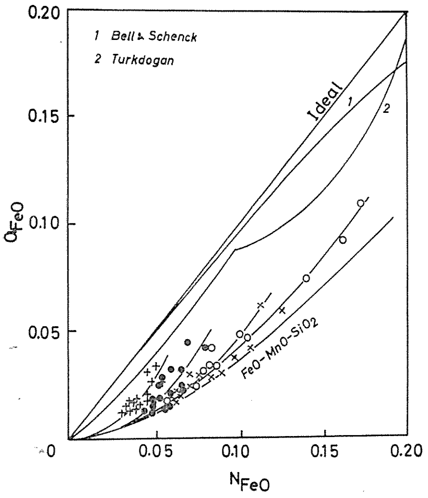


FIG. 28. The activity of iron oxide in the acidic slag saturated with silica calculated from the equation (3-8).

If the result obtained by Körber *et ali.* is correct, a_{FeO} should be fallen down to a remarkable degree from other works as seen in Fig. 28. As the authors will discuss in the latter section for the distribution of chromium, a contradiction is occurred between the negative deviation from Raoult's law and the experimental result, therefore, it comes to the conclusion that their result is not correct.

The relation between activity and mole fraction is independent of the temperature and dependent on [Cr]. a_{FeO} can be written as a function of dissolved components in the slag as follows:

$$a_{FeO} = \gamma'_{FeO.} \cdot \gamma^{(Mn)}_{FeO} \cdot \gamma^{(Cr)}_{FeO} \cdot N_{FeO} \qquad (3\text{-}9)$$

where

$\gamma^{(Mn)}_{FeO}$ and $\gamma^{(Cr)}_{FeO}$ refer to the interaction parameters which are effects of manganese oxide and chromium oxide on a_{FeO} in the slag, respectively. The result showed that a_{FeO} was increased with increasing of [Cr] in liquid metal at constant concentration of (FeO). Increasing [Cr] concentration in the liquid metal, (CrO) is increased and (MnO) is decreased in the slag. However, it is not evident that the increase of a_{FeO} is to be caused by the increasing of $\gamma_{FeO}^{(Mn)}$ with decreasing of (MnO) in the slag or the increase of $\gamma_{FeO}^{(Cr)}$ with increasing of (CrO) in the slag.

Generally it is considered that the silicate slag shows electrolytic dissociation, that is,

$$SiO_2 + 2MeO \rightleftarrows SiO_4^{4-} + 2Me^{2+} \qquad (3\text{-}10)$$

By Reichardson, *et ali.*[49], SiO_2 is net structures in the liquid state. Dissolving the metal ion into the liquid, the chemical bond of silica net is cut off and the molecule is decomposed from polymer to monomer. By decomposition of silicate, viscosity, electric conductivity and etc. were varied.

Dukelow, *et ali.*[5] studied the electre-chemical measurement for oxide phase of the $FeO\text{-}MnO\text{-}SiO_2$ system, and reported that the current efficiency at constant SiO_2 was scarcely changed with the variations of (FeO) and (MnO). This result shows that electrolytic quality of (FeO) resembles to (MnO), therefore, it is considered that $\gamma_{FeO}^{(Mn)}$ is close to unit. Viscosity of silicate slag is slightly decreased with (CrO) whereas it is very much decreased with (MnO) and (FeO). Thus, it is considered that the ability of cutting off the chemical bond of SiO_2 net by (CrO) is less, that is, (CrO) has a less ionization tendency than (MnO) and (FeO).

Increasing chromous ion in the silicate slag:

$$Fe_2SiO_4 + 2Cr^{2+} \rightleftarrows Cr_2SiO_4 + 2Fe^{2+} \qquad (3\text{-}11)$$

Fe^{2+} increases to give electrons to chromium. As Fe^{2+} is increased in the slag, it comes to the conclusion that a_{FeO} is increased. That is to say, it is assumed that a_{FeO} depended on the concentration of Fe^{2+} in the silicate slag.

It is very interesting to combine physical properties such as current efficiency, viscosity, etc. with the reaction between slag and metal. The experimental results are so few that it can not quantitatively discuss here, but the authors can assume much facts based on such electrochemical data in the present step.

3.4.3. Relation between the Distribution of Chromium L_{Cr} and FeO

The distribution of chromium which was a ratio of weight per cent of (Cr) in slag and [Cr] in liquid metal was studied by many workers[1][7][8] as a function of (FeO). That is to say, L_{Cr} is dependent on the oxygen in the liquid metal.

The redox reaction between iron and chromium is represented as a following equation:

$$x(FeO) + [Cr] \rightleftarrows x[Fe] + (CrO_x) \qquad (3\text{-}12)$$

where, as the oxide of the chromium changes its chemical formula with chromium concentration in the liquid iron, it is expressed as CrO_x in this report.

Equilibrium constant for eq. (3–12) can be presented as follows:

$$K_{Cr} = a_{Fe}^{x} \cdot a_{CrO_x} / a_{FeO}^{x} \cdot a_{Cr} \qquad (3\text{-}13)$$

For the calculation of equilibrium constant, it is almost unknown how the activity of metal and especially oxide are givin in each phase. Calculation of eq. (3-13) is, therefore, difficult and disadvantageous. For the simpler calculation, the equilibrium constant K'_{Cr} was directly calculated by using the weight per cent substituted for activity in eq. (3-13). Rewriting eq. (3-13), K'_{Cr} is calculated with the following equation:

$$K'_{Cr} = (Cr)/(EeO)^{x}[Cr] = L_{Cr}/(FeO)^{x} \qquad (3\text{-}14)$$

In eq. (3-14), x was changed with the concentration of chromium in the liquid iron. The relation between L_{Cr} and (FeO) is affected with the value of x. In the previous chapters, the authors reported that x was equal to 1, if the concentration of (FeO) in the slag saturated with silica was less than 17%, and was equal to 1.33 at the concentration more than 17%. Lapitzki[7] also reported that x is equal to 1.5 in the basic slag.

The relation between L_{Cr} and (FeO) was shown in Fig. 29. The full line in Fig. 29 was shown for this relation obtained previously in the liquid Fe-Cr solution free from manganese.

By the addition of [Mn] to liquid Fe-Cr alloy, (MnO) was increased in the silicate slag, and distribution coefficient of chromium was decreased as seen in Fig. 29. For instance, by addition of manganese to the liquid of 2% Cr, the diminution of L_{Cr} was bigger than by that of (FeO). Then L_{Cr} in Fe-Cr-Mn showed the lower value than that in Fe-Cr solution. This results show that L_{Cr} was affected by the concentration of (MnO).

It was reported by Körber *et ali.* that the relation between L_{Cr} and (FeO) was in dependent of the concentration of (MnO) and constant. This is approximatlely inagreement with the relation between L_{Cr} and (FeO) in Fe-Cr solution obtained by the authors. In the liquid Fe-Cr-Mn alloy, the results obtained by them, however, are doubtful. If the activities of these components are approximately equal to their concentration in eq. (3-14), the relation between L_{Cr} and (FeO) in eq. (3-14) should be expressed by a function of the first order. a_{FeO} was much affected by [Cr] as discussed in the former section 3.4.2. Then, it could not be considered that the relation between L_{Cr} and (FeO) obtained from eq. (3-14) became

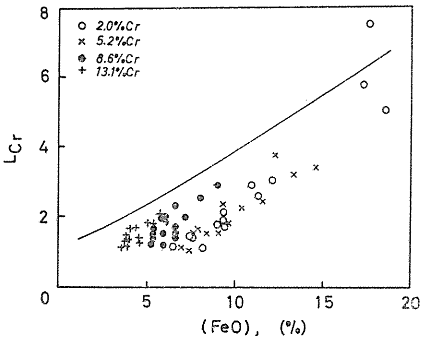
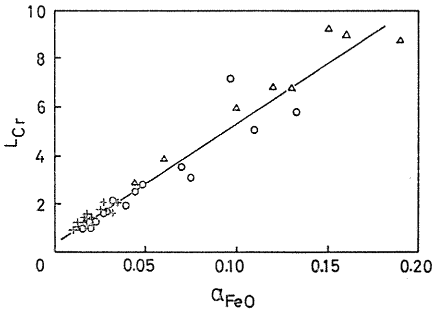


FIG. 29. Relation between chromium distribution and iron oxide. The line in Fig. 29 shows the chromium distribution in the manganese-free liquid Fe-Cr alloy and marks represent the same as in Fig. 26.



△: Distrbiution of chromium in the manganese-free system.

○, +: The same as in Fig. 26.

FIG. 30. Relation between the distribution of chromium and the activity of iron oxide

a function of the first order. Therefore, the redox equilibrium constant represented as eq. (3–14) is suitable for the calculation in the liquid Fe-Cr alloy, but if the another oxide such as (MnO) was contained in the slag, eq. (3–14) can not be employed for the calculation.

In the former section, the authors calculated the activity of (FeO) in the slag saturated with silica. Then, the relation between L_{Cr} and a_{FeO} was obtained by using the following equation:

$$K''_{Cr} = L_{Cr}/a_{FeO} \tag{3-15}$$

If the equilibrium is established between liquid metal and slag, L_{Cr} should be a linear function of a_{FeO}, assuming that the activity coefficients of chromium in the both phases were approximately equal to each other at any concentration. This relation is shown in Fig. 30. The relation in liquid Fe-Cr obtained previously was recalculated with activity of (FeO) substituted for the concentration and also shown in Fig. 30. As seen in Fig. 30, it is well understood that the relation between L_{Cr} and a_{FeO} is a linear function regardless of the coexistence of (MnO) and was expressed approximately by the empirical equation as

$$L_{Cr} = 54.8 \cdot a_{FeO} + 0.38 \tag{3-16}$$

Therefore, the calcualtion for L_{Cr} must be done by using a_{FeO} instead of (FeO).

Recalculating the results obtained by Körber *et ali.* for eq. (3–15), L_{Cr} is not a linear function of a_{FeO}, but distributed in the wide region depending on the concentration of [Cr]. Therefore, if it is assumed that the ratio of [O] and (FeO) obtained by them is correct, L_{Cr} should not be a linear function of a_{FeO}, and in reverse way if L_{Cr} is a linear function of a_{FeO}, the former assumption should be wrong. Because the keeping time of melting was too short to attain the equilibrium for the reaction with their experimetal condition, it is considered that eq. (3–14) was in a good agreement with the experimental values by chance, or experimental value has so many errors that L_{Cr} can be expressed by such a simple function of (FeO).

As L_{Cr} has a linear relation with a_{FeO}, it is assumed that x in eq. (3–12) is approximately equal to 1, and the chemical formula of oxide of chromium is (CrO) the same as in the previous chapter.

3.4.4. Relation between the Distribution of Manganese L_{Mn} and FeO

The relation between the distribution of manganese L_{Mn} and (FeO) was studied by many workers1)7)27)41)43)45), but there is a few data in FeO-MnO-SiO$_2$ system, and only one for FeO-CrO-MnO-SiO$_2$ system by Körber *et ali.*

Generally, the deoxidation constant for manganese is represented by

$$(FeO) + [Mn] \rightleftarrows (MnO) + [Fe] \tag{3-17}$$

$$K'_{Mn} = (Mn)/(FeO) \cdot [Mn] \tag{3-18}$$

but in the multi-component slag, especially containing chromium as the present work, activities were varied at the constant (FeO), so that K'_{Mn} in eq. (3–18) does not give a constant value. The activity of a componentt in the slag was almost unknown. Therefore, the equation for the equilibrium constant should be calculated with the slag containing less components as possible. At the present work, the deoxidation constant was calculated by appling the following equaion:

$$[Mn] + [O] \rightleftarrows (MnO) \qquad (3\text{-}19)$$

$$K'_{Mn\text{-}O} = (MnO)/[Mn]\cdot[O] \qquad (3\text{-}20)$$

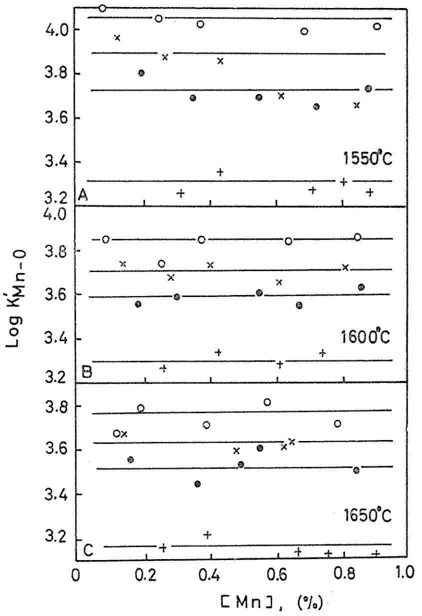


FIG. 31. Relation between the concentration of manganese and deoxidation constant of manganese $K'_{Mn\text{-}O}$

The relation between $K'_{Mn\text{-}O}$ and the concentration of manganese is shown in Fig. 31-A, B and C at 1550°, 1600° and 1650°C, respectively.

When [Cr] is a constant comcentration, $K'_{Mn\text{-}O}$ is given as a constant value, independing of [Mn] at the respective temperatures. And $K'_{Mn\text{-}O}$ was decreased with an increasing of [Cr] and slightly decreased with increasing of temperature.

The equilibrium constant in eq. (3-20) was rewritten by substituting each concentrations with the activities.

$$K_{Mn\text{-}O} = a_{MnO}/a_{Mn}\cdot a_O \qquad (3\text{-}21)$$

It was reported that the effect of chromium on the activity of oxygen is great to be compared with other alloying elements. Employing activity coefficients and rewriting eq. (3-21) as

$$K_{Mn\text{-}O} = \gamma_{MnO}\cdot(MnO)/f_{Mn}\cdot[Mn]\cdot a_O$$
$$(\gamma_{MnO}/f_{Mn})\cdot\{(MnO)/[Mn]\cdot a_O\} \qquad (3\text{-}22)$$

because activity coefficient of (MnO) and [Mn] were not evident. Neglecting these activity coefficients, eq. (3-22) can be rewritten advantageously as follows:

$$K''_{Mn\text{-}O} = (MnO)/[Mn]\cdot a_O \qquad (3\text{-}23)$$

The deviation of $K''_{Mn\text{-}O}$ was happened to be caused by the variation of the activity coefficients of (MnO) and [Mn] which were affected by the coexistent elements in the liquid iron and slag.

When $K''_{Mn\text{-}O}$ was obtained as the function of chromium concentration, a convex curve was drawn with increasing of chromium concentration, and $K''_{Mn\text{-}O}$ was decreased with increasing of [Mn]. From Fig. 31, $K_{Mn\text{-}O}$ can be calculated with $K'_{Mn\text{-}O}$ and $K''_{Mn\text{-}O}$ by interpolating [Mn] and [Cr] to zero, respectively.

The difference of $K''_{Mn\text{-}O}$ from $K_{Mn\text{-}O}$ is (γ_{MnO}/f_{Mn}). Activity coefficient of manganese can be obtained by applying interaction parameters reported already.

Then, γ_{MnO} is possible to calculate from $K_{Mn\text{-}O}$ and f_{Mn}, but includes in itself the errors which summed up the experimental error, the errors from interaction parameters and the error of $K_{Mn\text{-}O}$ by interpolating. It comes to the conclusion, therefore, that the thermodynamical consideration and theoretical treatment in the equation might be no meaning by employing γ_{MnO} obtained from the above calculation.

Each concentration can be calculated by eq. (3–22), but the calculation was complexed and unadvantageous. The most convenient equation to obtain the concentration is eq. (3–23) or (3–24) substituting a_{FeO} by (FeO),

$$K''_{Mn\text{-}O} = (MnO)/[Mn] \cdot a_{FeO} = L_{Mn}/a_{FeO} \qquad (3\text{-}24)$$

The relation between the distribution of manganese and a_{FeO} was shown in Fig. 32, and was represented approximately by the empirical equation as,

$$L_{Mn} = (5.37 \times 10^7/T - 2.63 \times 10^4)a_{FeO} \qquad (3\text{-}25)$$

At any chromium concentration, Körber *et ali.* reported that L_{Mn} was a linear function of (FeO). As discussed in the former section 3.4.2., a_{FeO} was affected strongly by coexistent chromium.

Because K'_{Mn} was changed with the variation of a_{FeO}, it is, therefore, concluded that the result obtained by Körber *et ali.*—L_{Mn} was a simple function of (FeO)—was not correct. As discussed above, (γ_{MnO}/f_{Mn}) was not accurately equat to 1. Assuming it approximately equat to 1, L_{Mn} is a simple function of a_{FeO}, but this relation become more inaccurate with increasing of the temperature, and the maximum relative error of K''_{Mn} is calculated about 30%. If this error is distributed equally to three components, it must be 10% at maximum for each component and is slightly bigger than an experimental error.

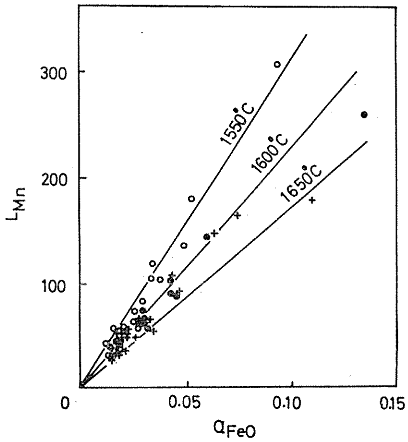


FIG. 32. Relation between the distribution of manganese and the activity of iron oxide.

It is considered that the values obtained from eq. (3–24) is enough for the estimation of the concentrations of these components.

3.4.5. Relation between Silicon and Manganese

The redox reaction between silicon and manganese is represented as follows:

$$(SiO_2)_{sat.} + 2[Mn] \rightleftarrows 2(MnO) + [Si] \qquad (3\text{-}26)$$

$$K'_{Si\,Mn} = (MnO)^2 \cdot [Si]/[Mn]^2 \qquad (3\text{-}27)$$

or

$$K_{Si,Mn} = a^2_{MnO} \cdot a_{Si}/a^2_{Mn} \qquad (3\text{-}28)$$

As discussed in the previous section the ratio $(a_{\mathrm{MnO}}/a_{\mathrm{Mn}})$ can be easily obtained, but it is impossible to calculate the activities of each component individually. The relation between [Si] and [Mn], therefore, can not be calculated from eq. (3–28).

It is not easy to calculate eq. (3–28), even if the system was composed with FeO, MnO and SiO_2. Rewriting eq. (3–27), Sekiguchi[50] reported the concentration of manganese as a function of silicon for this system by employing the result obtained by Körber, *et ali.* Although the activity was not used in his calculation instead of the concentrations, the discrepancy between the calculated and experimental values was small. It is considered that a good agreement among them is caused by the absence of coexistent elements which effect strongly on the activity.

In the system FeO-MnO-CrO-SiO_2, applying the concentrations instead of the activities in like manner by Sekiguchi in eq. (3–27), it is impossible to obtain the relation between [Si] and [Mn], because the concentration of (CrO) comes into eq. (3–27). It is most important to know the relation between [Si] and [Mn], and is necessary to calculate the concentration of a component at any concentration of another component.

The relation between [Si] and [Mn] at 1600°C is shown inFig. 33. The solubility of silicon in the liquid Fe-Cr-Mn alloy is increased with increasing of [Mn] and [Cr].

If the concentrations of any two elements, for example, manganese and chromium, in the liquid Fe-Cr-Mn alloy equilibrated with the slag saturated with silica are given:

(1) From Fig. 33, the concentration of silicon is obtained.

(2) Concentration of oxygen can be calculated from the equilibrium constan- of silicon and oxygen.

(3) The activity of oxygen is estimated with coexistent elements obtained from (1) and (2).

(4) Activity of FeO can be obtained.

(5) (FeO) is known from Fig. 27, and from Figs. 30 and 32, (MnO)/[Mn] and (Cr)/[Cr] are reckoned, and then concentrations of all components in the slag can be calculated.

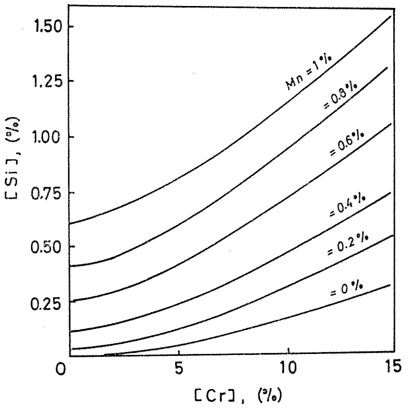


FIG. 33. Relation between the solubility of silicon and the concentration of manganese in the liquid Fe-Cr alloy at 1600°C.

3.5. Conclusions

The equilibrium between the liquid iron chromium alloy and FeO-MnO-CrO-SiO_2 slag saturated with silica was studied at 1550°, 1600° and 1650°C, respectively.

The results are summarized as follows;

(1) The equilibrium constant for the deoxidation by silicon was evaluated by using various interaction parameters, and it turned out higher than that in the

liquid iron-chromium alloy with an increasing chromium concentration. In a multi-component system, it is assumed that the deviation of the equilibrium constants is due to the errors in the experimental procedure, the errors in the interaction parameters and neglecting of all terms after the second term in the Wagner's equation.

(2) The activity of iron oxide in the slag saturated with silica was calculated with the experimental data. The result showed that the activity of iron oxide increased with an increasing of chromous oxide and a decreasing of manganese oxide. The reason for this is considered to be that Fe^{2+} in the silicate slag was increased with the ionic reaction between chromium and iron.

The activity of iron oxide was independent of temperature, and depended upon the concentrations of coexistent components. It exhibited negative deviation from Raoult's law.

(3) The distribution coefficients of chromium are affected by chromous oxide and manganese oxide and do not show good agreement with these by Körber and Oelsen.

The relation between the distribution coefficients of chromium and the activity of iron oxide was expressed approximately by the equation,

$$L_{\mathrm{Cr}} = 54.8a_{\mathrm{FeO}} + 0.38$$

(4) The distribution coefficients of manganese also do not show good agreement with those of Körber and Oelsen. The relation between the distribution coefficients of manganese and the activity of iron oxide was represented approximately by the equation,

$$L_{\mathrm{Mn}} = (5.37 \times 10^7/T - 2.63 \times 10^4) \cdot a_{\mathrm{FeO}}$$

(5) The effect of chromium and manganese on the solubility of silicon were measured and by arbitrrily choosing two elements in the molten iron, the concentrations of the other two elements and the oxides in the silicate slag can be determined.

Chapter IV. On the Activity of Iron Oxide in Silica-Saturated Slags

4.1. Introduction

When the concentration of an oxide was changed in the molten slag composed of multi-components, chemical and physical properties of the molten slag would be changed corresponding to the concentrations.

It these changes due to the change of slag compositions were quantitatively determined, the thermodynamical consideration might be easily done for the reactions in the steelmaking processes and it became possible to estimate the chemical properties of the secondary inclusions produced during the solidification of the ingot. However, the temperature is so high that the direct method to examine chemical properties of the molten state is limited with experiments are always difficult in many cases.

The authors studied the equilbrium between liquid iron and slag in order to obtain thermodynamical properties of the silicate slags. Previously, the authors have reported on the distribution of chromium between slag saturated with silica and liquid iron and also on the deoxidation constant with manganese. The distribution coefficients of chromium and the deoxidation constant with manganese were represented as a function of the concentration of iron oxide in the slag by Körber and Oelsen and the calcultiaon was accordingly carried out by employing directly the concentration up to this time. When chromous oxide or manganese oxide was dissolved in the quaternary slag, the distribution coefficients of chromium and manganese could not be clearly represented as a function of the concentration of iron oxide. The authors have shown that these distribution coefficients could be represented as a function of the activity of iron oxide instead of its concentration advantagewously in the previous chapters.

The activity of iron oxide was one of the most important and fundamental properties for the thermodynamical consideration on the relation between liquid iron and slag. Thus, the activity of iron oxide was measured in the various ternary systems saturated with silica.

The general relationship between oxygen in liquid iron and iron oxide in slags is well understood as the distribution of oxygen. There are many reports dealing with the equilibrium between oxygen in liquid iron and ternary slag FeO-CaO-SiO_2[51], and FeO-MnO-SiO_2[19][45]. And also, thermodynamical considerations on the variation in chemical properties of slags have been developed by many workers, but with many assumptions and with many problems not yet solved. The authors measured the effects of various oxides, namely, CaO, Al_2O_3, MnO and CrO, on the distribution of oxygen.

The distribution coefficient of chromium between liquid Fe-Cr alloy and the quaternary system, FeO-CaO-CrO-SiO_2 saturated with silica was measured and it was discussed whether or not the distribution of chromium by the present work could be given as a linear function of the concentration of iron oxide as shown by Körber *et ali.* or the activity of iron oxide, samely as the case of FeO-MnO-CrO-SiO_2 system reported previously by the authors.

4.2. Experimental Apparatus and Procedure

The experimental apparatus and procedure were described in detail in the previous chapter. Therefore, only the outline was described in this chapter. The apparatus was composed of a high frequency induction furnace and gas purifiers.

The fused silica crucible was stamped with silica powder into the high-alumina protective crucible. Totally about 20g of available pure oxides were charged and mixed well each other. Electrolytic iron, ferro-silicon (72%) obtained by melting in the authors'laboratory, and electrolytic alloying metal corresponding to the slag components were weighed about 150g in all cases. The oxides and metals were put into the crucible before heating.

The reaction equilibrium between slag and metal phase was established for an hour at 1600°C. After the melting, the thickness of the slag phases was 2–4 mm. To assure the uniform temperature distribution in the slag and metal a graphite pipe was set between the silica crucible and the protective alumina crucible. The temperature was measured by the thermocouple of platinum 5% rhodium-platium 20% rhodium.

The sample of the metal was sucked by fused silica tube of 3 mmφ I.D. After sampling metal, the power to heat the furnace was switched off immediately. Metal and slag were cooled down to the room temperature in the furnace.

The oxygen was determined by the vacuum fusion method at 1750°C. Silicon and manganese were determined photometrically and chromium was analyzed by redox-titration with permanganate and ferrous ammonium sulphate. Slag compositions were determined by both chemical analysis for SiO_2, Fe, Mn, Cr, Al, Ca and by fruorescent X-ray analysis.

4.3. Experimental Results

Equilibrium measurements were carried out for the two kinds of slag systems. The first was carried out on the ternary slagsFeO-MeO-SiO_2 and the second on the quaternary slag FeO-CaO-CrO-SiO_2.

The equilibrium was established in all cases at 1600°C. For the first group, the experimental results obtained are as follows.

The effects of metallic oxides (Al_2O_3, CaO, MnO and CrO) on the silica concentration in the slag saturated with silica were summarized as in Fig. 34. As shown in Fig. 34, the concentration of saturation of silica was affected particularly by the kind of oxides.

As the saturated concentration of silica was changed by the variation of added oxide as described above, when the authors discuss quantitatively on the effects of added oxides on the solubility of oxygen in the liquid iron and on the activity of iron oxide in the slag, it is, thus, unavoidable that the quantitative comparison of the effects of added each oxides was become more complex by this variation. However, it is interesting phenomena that this variation of the solubility of silica depended closely on the basicity of added oxide.

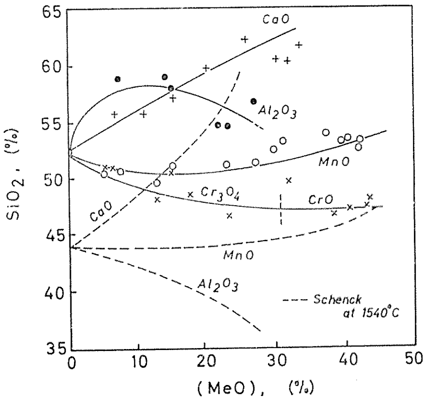


FIG. 34. The effects of various oxides on silica concentration in the silica saturated slag.

With increasing the concentration of CaO in the system FeO-CaO-SiO_2 slag, the solubility of silica increased linearly. When the slag contained CaO more than 35%, the slag became very fluid and the crucible was eroded violently by the reaction with the slag, and then the melting became impossible in this range at 1600°C. The relation obtained by Schenck *et ali.*[20] was also shown in Fig. 34. Their results on the effect of CaO on the solubility of silica showed same tendency with that obtained by the authors, but the increasing ration $\{(SiO_2)_{FeO\text{-}CaO\text{-}SiO_2} - (SiO_2)_{FeO\text{-}SiO_2}\}/(CaO)$ obtained by them was bigger than that by the authors.

When Al_2O_3 is dissolved into the binary FeO-SiO_2 slag saturated with silica, the solubility of silica was increased abruptly with increasing Al_2O_3 in the range of low Al_2O_3 concentration and on the other hand, the solubility was decreased oppositely, when Al_2O_3 concentration was more than 15%.

As seen from the phase diagram for FeO-Al_2O_3-SiO_2,[52] if the content of Al_2O_3 in this system became more than 30%, the melting point of this system becomes higher than 1600°C. Consequently, solid state mullite ($3Al_2O_3 \cdot 2SiO_2$) was isolated from the liquid slag, and homogeneous slag was not obtained, so that equilibrium experiment could not be carried under these condition. From this phase diagram, the melting point of binary FeO-SiO_2 system saturated with silica (SiO_2 contents is about 50%) was lowered by addition of Al_2O_3 and had the minimum at 20% Al_2O_3 and had the minimum at 20% Al_2O_3. The more Al_2O_3 was added into this system, the melting point of the slag became higher and higher, and the melting point became 1600°C at the concentration of Al_2O_3 of about 30%. From these reasons, it is concluded that the solubility of silica was increased with lowering the melting point of the slrg, and was decreased with raising the melting point.

From the results obtained by Schenck *et ati.*, the solubility was decreased linearly with increasing the concentration of Al_2O_3. Therefore, it was assumed that the reason of this linear decrease is caused by the fact that the slag was not sufficiently saturated with silica.

Fig. 35. shows how the solubility of oxygen in liquid iron was changed with the kind of added oxides. By adding CaO, Al_2O_3 or MnO into the binary FeO-SiO_2 slag saturated with silica, the concentration of oxygen in the liquid iron equilibrated with these ternary slag is decreased monotonously with increasing the added oxides. On the other hand, by adding chromic oxide into the slag, the oxygen concentration changed its tendency from deminution to increment with the increase of the concentration of CrO in the slag.

If the solubility of silica is not affected by the kind of added oxide, the concentration of (FeO) in the slag can be calculated from the following simple equation;

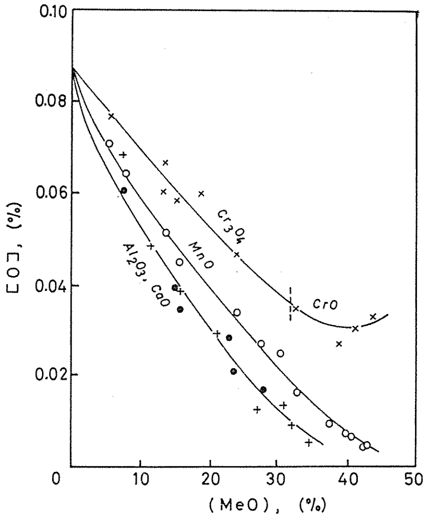


FIG. 35. The effects of various oxides in the slag on the solubility of oxygen in the liquid iron.

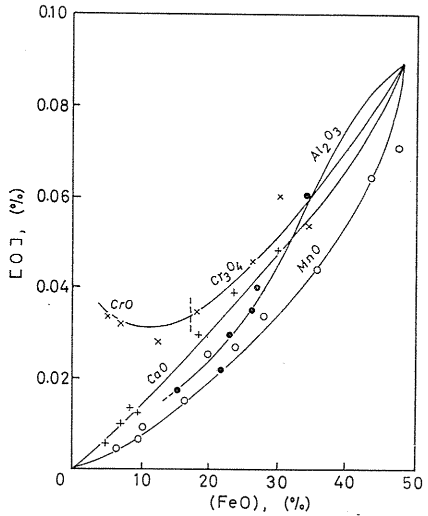


FIG. 36. The relation between the solubility of oxygen and the concentration of iron oxide in the silica saturated slag.

$$(FeO) = 48 - (MeO) \qquad (4\text{-}1)$$

If (MeO) of the horizontal axis in Fig. 35 was converted to (FeO) with the above equation, the relation between FeO and oxygen could be drawn in the same figure. However, the solubility of silica was changed as shown in Fig. 34, so that the relation beween per cent oxygen in liquid iron and FeO content in slag could not be shown in Fig. 35, only by converting the horizontal axis. The relations between FeO and oxygen in various systems were shown in Fig. 36. Because the saturation point of silica was different among the systems CaO-, Al_2O_3- and MnO-, the position of the line of MnO- system as shown in Fig. 35 moved to opposite side of the lines of CaO- and Al_2O_3- systems in Fig. 36. Difference of the influences of added oxide Al_2O_3 and of CaO could not be recognized in Fig. 35, but the difference could be clearly demonstrated in Fig. 36.

The experimental results obtained from the second group are as follows; Fig. 37 shows the relations between oxygen in liuqid iron and iron oxide in the system FeO-CaO-CrO-SiO_2 slag saturated with silica. And also, Fig. 37 indicates how this relation in FeO-CaO-SiO_2 systems, is changed by addition of the chromic oxide into this system. That is, the concentration of oxygen is changed with small change of iron oxide in the slag which contains CrO. The similar result was obtained in the system FeO-MnO-CrO-SiO_2 by the previous work. The distribution coefficient of chromium could not be simply expressed as a function of the concentration of iron oxide in slags with CaO or MnO as shown by Körber and Oelsen. The distribution coefficient of chromium in this system showed the same tendency as in FeO-MnO-CrO-SiO_2 slag obtained by the previous work and deviated lower than that of FeO-CrO-SiO_2 system.

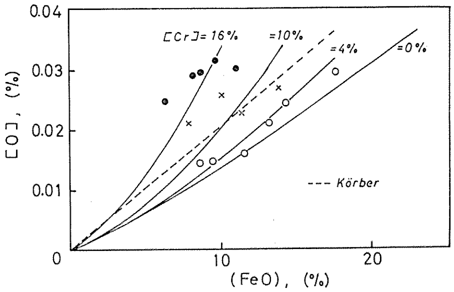


FIG. 37. The relation between the solubility of oxygen and the concentration of iron oxide in the FeO-CaO-CrO-SiO_2 system saturated with silica.

4.4. Discussion

4.4.1. The Activity of Iron Oxide in the Ternary System, FeO-MeO-SiO_2

Generally, the activity of iron oxide in the slag was estimated from the oxygen concentration equilibrated with its slag as described previous chapters.

At the present chapter, the activity of oxygen in the liquid iron equilibrated with ternary slags was calculated as follows:

FeO-Al_2O_3-SiO_2 slag

With the experimental conditions in this system, the maximum silicon concentration is about 0.15%. Therefore, the effect of silicon on the activity of oxygen is so small. Then, the activity coefficient $f_O^{(Si)}$ is neglected approximately.

$$2[Al]+3[O]\rightleftarrows(Al_2O_3)_{slag} \qquad (4\text{-}2)$$

The very small concentration of aluminum was calculated from equilibrium constant[53] of equation (4-2). Analytical results for aluminum in the molten iron also showed so small that the effect of aluminum on the activity of oxygen could be negligible. The interaction coefficient f_O' and $f_O^{(Al)}$ are ignored on the calculation.

FeO-CaO-SiO₂ slag

It was assumed that the solubility of calcium was very much small in the molten iron. Thus, the analysis was not performed for calcium. There are no reports on the effect of calcium on the activity of oxygen, and the interaction coefficient $f_O^{(Ca)}$ was neglected on this calculation. With the decrease of the concentration of oxygen, silicon is increased in the liquid iron. $f_O^{(Si)}$ was employed on the calculation to obtain the activity of oxygen in this system.
The authors have already reported on the quilibrium between silicon and oxygen in the systems, FeO-MnO-SiO_2 and FeO-CrO-SiO_2. Those reports showed in detail how to calculate the activity of oxygen.

By these means, the activity of iron oxide was obtained from the ratio of the activities of oxygen between two systems. Fig. 38 shows the relations between the activity of iron oxide and its mole fraction in the slag saturated with silica.

When the chromium concentration is increased in the liquid iron in the range of small chromium content, the oxygen is decreased by the deoxidation with chromium, and when the chromium content is 5-10%, the dissolved oxygen gives the minimum value. But if chromium concent increases more than these concentrations, the dissolved oxygen increases again. The oxygen concentration is increased due to the increment of the chromous oxide in the slag saturated with silica, in spite of the diminution of the iron oxide.

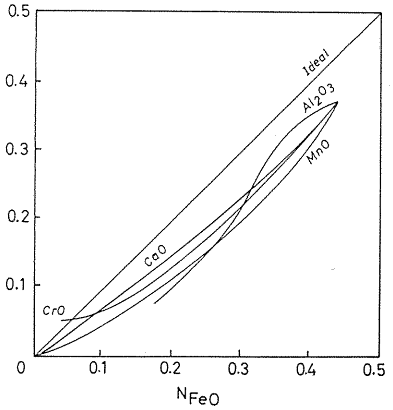


FIG. 38. The activity of iron oxide in the ternary slag saturated with silica.

Although the activity of oxygen is decreased with increasing chromium content, there are no experimental data in the range where N_{FeO} is less than 0.04. Therefore, it is not clear how much values a_{FeO} becomes.

Generally, the relation between activity of iron oxide and mole fraction is given by the following thermodynamical equation:

$$a_{FeO}=\gamma_{FeO}\cdot N_{FeO} \qquad (4\text{-}3)$$

It is considered that the factors affecting γ_{FeO} are silicate anion and metallic cations in the slag. It is considered that one of the most important factors which governs

TABLE 5. Oxides and Ion-oxygen Attraction

Oxide	$I=2\ z/a^2$	Quality
SiO_2	3.16	acidic
Al_2O_3	1,90* 1.66**	intermediate
Cr_2O_3	1.44	intermediate
FeO	0.87	basic
MnO	0.83	basic
CaO	0.70	basic

I: Metallic ion-oxygen attaction
a: Distance of both ions
z: the value of the electronic charge
*: Co-ordination number 4, anion
**: Co-ordination number 6, cation

the chemical behaviors of those ions is the strength of the ion-oxygen attraction of an oxide. This is well known as one of the quantitative scales of the basicity. These values were summarized in Table 5[54]. From Table 5, the basic strength of the oxides in the present work are put in order as follows:

$$CaO > MnO, FeO > Al_2O_3,\ Cr_2O_3$$

The authors have reported that Cr_2O_3 is altered its chemical formula from Cr_3O_4 to CrO in the slag saturated with silica at the boundary, $[Cr]=3\%$. Although the values of Cr_3O_4 and CrO were not listed in Table 5, it is considered that the I values of both oxides are smaller than Cr_2O_3.

When Al_2O_3 dissociates electrolytically in the silicate slag and produces two Al^{3+} ions, the decrease of the oxygen solubility per ion equivalent added are rearranged as follows:

$$CaO > MnO > Al_2O_3,\ Cr_3O_4 \text{ or } CrO$$

It is concluded that the effects of added oxides on the solubility of oxygen in the liquid iron are closely related to their basicity. Although these relations are obtained qualitatively, it is, however, assumed that the relations between a_{FeO} and N_{FeO} in various systems are independent on the basicity of added oxides from Fig. 38. As the saturation point of silica was chaged with the added oxide described above, Fig. 38 was drawn without considering the variation of silica content. Namely, Fig. 38 indicated merely how a_{FeO} takes a value at the constant N_{FeO} by the kinds of co-existent added oxides.

Thus, the relations between a_{FeO} and the mole fractions of added oxides were shown in Fig. 39. When Al_2O_3 dissociated in the slag, it produces two cations with the valence of 3+. Then, in order to compare with the cations of 2+ from the other oxides, it is necessary to multiply the concentration of Al_2O_3 by three in Fig. 39.

When the added oxide dissolves in FeO-SiO_2 slag saturated with silica, the activity of iron oxide is decreased. The decreasing ratio of the activity of iron oxide is closely related with the basicity of added oxides.

Employing the strength of ion-oxygen attraction, I and mole fraction $N_{Me^{2+}}$ of an added oxide, the relation between a_{FeO} and $N_{Me^{2+}}$ can be expressed as following

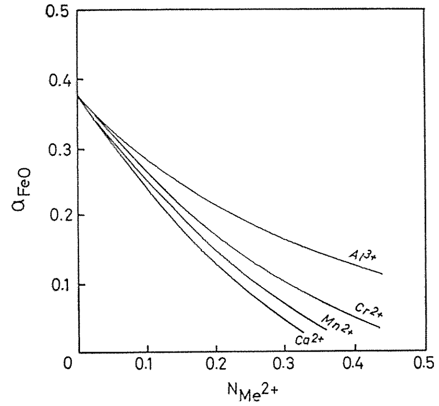


FIG. 39. The effects of cations on the activity of iron oxide. (per bivalence)

empirical equation:

$$a_{FeO} = 0.388 - (1.30N_{Me^{2+}} - 1.14N^2_{Me^{2+}})/\sqrt{I} \qquad (4\text{-}4)$$

from eqs. (4–3) and (4–4), γ_{FeO}, therefore, can be obtained as follows:

$$\gamma_{FeO} = \{0.388 - (1.30N_{Me^{2+}} - 1.14N^2_{Me^{2+}})/\sqrt{I}\}/N_{FeO} \qquad (4\text{-}5)$$

where $1/\sqrt{I}$ is equal to $a/\sqrt{2z}$, it is well understood that a_{FeO} and γ_{FeO} are closely dependent on the distance between the both ions.

If I of any oxide in the system FeO-MeO-SiO_2 slag saturated with silica is given, a_{FeO} can be obtained accurately by using eq. (4–4).

As described above, I for CrO and Cr_3O_4 are not listed in Table 5, I can be calculated oppositely from the experimental data. For CrO at the concentration of FeO less than 17 wt%, I is equal to 1.00 and for Cr_3O_4, at the concentration of FeO more than 17 wt% I is equal to 1.20, respectively.

4.4.2. On the Anions in the Slag Saturated with Silica

As described above, it is considered undoubtedly that important factor which affects on γ_{FeO} is the basicity of metallic oxide. On the other hand, it must be also considered the other factor which is the behvior of anion, namely, the desociation of silica.

Basic oxides, FeO and CaO dissociate to cations Fe^{2+}, Ca^{2+} and anion O^{2-} in the silicate melts. And acidic oxide such as SiO_2 reacts with dissociated anion O^{2-} and becomes the anion having various sizes.

At the pure state, silica has the net structure constructed as a unit of SiO_4 tetrahedron, and the chemical bond of Si-O-Si is cut off in proportion to added amount of a basic oxide, MeO into the silica; and silica decomposes from big anion to the smallest SiO_4^{4-} ion.

Fincham and Richardson[55] showed that the oxygen in the silicate melts takes only three types of chemical bond. There are doubly bonded O^0 with silicon, singly bonded O^- formed silicate ions, and free oxygen ions O^{2-}.

Toop and Samis[56] had shown that the equilibrium was established among three types of oxygen as follows:

$$2(O^-) \rightleftarrows (O^0) + (O^{2-}) \tag{4-6}$$

$$K = (N_{O^0}) \cdot (N_{O^{2-}}) / (N_{O^-})^2 \tag{4-7}$$

where (N_{O_0}), $(N_{O^{2-}})$ and (N_{O^-}) refer the mole fraction of each anions in the silicate melts.

Assuming number of moles of silica as N_{SiO_2}, numbers of silicon bond B are obtained as following equation:

$$B = 2N_{O_0} + N_{O^-} = 4N_{SiO_2} \tag{4-8}$$

and

$$(N_{O_0}) = 1/2\{4N_{SiO_2} - (N_{O^-})\} \tag{4-9}$$

numbers of basic oxides and metallic ions which combined with silicate, therefore,

$$N_{O^{2-}} = (1 - N_{SiO_2}) - 1/2 \cdot (N_{O^-}) \tag{4-10}$$

substituting eqs. (4-9) and (4-10) into eq. (4-7), the relation between equilibrium constant K and N_{O^-} can be obtained as follows:

$$4K = \{N_{SiO_2} - (N_{O^-})\}\{2 - 2N_{SiO_2} - (N_{O^-}\}/(N_{O^-})^2 \tag{4-11}$$

The actual number of moles of oxygen ion that have reacted with the silica in the melt is $(N_{O^-})/2$ moles. Hence, free energy change due to eq. (4-6) per mole of liquid silicate should be given by the equation.

$$\Delta G^{mix.}/4.575T = 1/2 \cdot (N_{O^-}) \cdot \log K \tag{4-12}$$

ΔG^{mix} for the system FeO-MnO-SiO_2 slag saturated with silica has been obtained by using the activities of FeO and MnO reported by the authors. $\Delta G^{mix.}$ in the system FeO-CaO-SiO_2 slag saturated with silica is calculated by using the activity of FeO obtained above and the activity of CaO obtained by Elliott[51]. The calculated $\Delta G^{mix.}$ are shown in Fig. 40.

For the systems FeO-Al_2O_3-SiO_2 and FeO-CrO-SiO_2, the activities of added oxides could not be obtained from the present work. Thus, $\Delta G^{mix.}$ of these systems could not be estimated. Substituting the solubility of silica and $\Delta G^{mix.}$ for eqs. (4-11) and (4-12), K and mole fraction of (O^-) can be estimated to solve the simultaneous eqs. (4-11) and (4-12). The effects of cations on mole fraction of N_{O^-} and $N_{O^{2-}}$ were shown in Fig. 41. Although N_{O^0} is not drawn in Fig. 41, N_{O^0} takes a constant values approximately and the value of N_{O^0} is nearly equal to N_{O^-} even if the kind of cation is varied in the slag. As shown in Fig. 41, mole fraction of (O^{2-}) is abruptly decreased with increasing Ca^{2+} and Mn^{2+}. It is well understood that the equilibrium constant was varied due to the variation of (O^{2-}) and independent on (O^-) and (O^0) in the slags saturated with silica.

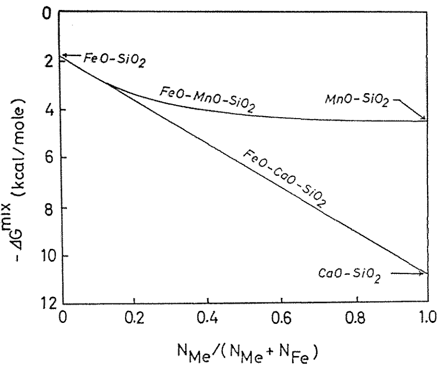


FIG. 40. Free energies change of mixing ternary slag saturated with silica.

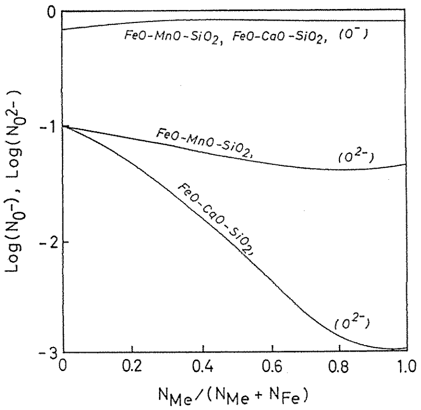


FIG. 41. The effects of cation on the concentration of (0^{2-}) and (0^-) in the silica saturated slag.

As O^{2-} is very few in the system FeO-CaO-SiO$_2$ it is considered that Ca^{2+} formed silicate such as $CaO \cdot nSiO_2$ in the slag.

If the iso-activity curve of iron oxide could be cleared over all ranges in the systems FeO-CaO-SiO$_2$ and FeO-CrO-SiO$_2$ with the aid of the Gibbs-Duhem's equation or the theory of ideal mixing approximately, the activities of Al_2O_3 and CrO might be obtained and $\Delta G^{mix.}$ also, might be obtained for these systems. Comparing ΔG^{mix} , (O^-) and (O^{2-}) for the various systems, the behaviors of anions in the slag saturated with silica will be well understood.

4.4.3. On the Distribution of Chromium

The authors have already reported on the distribution of chromium for the FeO-CrO-SiO$_2$ and FeO-MnO-CrO-SiO$_2$ slags saturated with silica. The distribution coefficient of chromium can be expressed simply as a function of concentration of iron oxide in the system, FeO-CrO-SiO$_2$, not of its activity. That is, the redox-reaction between iron and chromium is represented by the next reactions.

$$x(\mathrm{FeO}) + [\mathrm{Cr}] \rightleftarrows (\mathrm{CrO}_x) + x[\mathrm{Fe}] \qquad (4\text{-}13')$$

$$K'_{\mathrm{Cr}} = (\mathrm{Cr})/[\mathrm{Cr}] \cdot (\mathrm{FeO})^x = L_{\mathrm{Cr}}/(\mathrm{FeO})^x \qquad (4\text{-}14)$$

If the concentration of iron oxide is less than 17 wt%, x is equal to 1.00, and if the concentration is more than 17 wt%, x is equal to 1.33.

The concentration of each component in the slag could be used on the calculation instead of the activity for the case of FeO-CrO-SiO$_2$ slag. The distribution coefficient of chromium could be shown as a function of first order or 1.33 order with respect to concentration of the iron oxide.

If the calculation was carried out in the system FeO-MnO-CrO-SiO$_2$ slag with the same method as the system, FeO-CrO-SiO$_2$, the distribution coefficient became varous values according to the concentration of manganese oxide dissolved in the slag. Because the distribution coefficient is affected by the manganese oxide, it can not be expressed as a function of the concentration of iron oxide. That is, if the system is composed of the more components, the calculation becomes more complex. The equilibrium constant K'_{Cr} is no longer constant, if it is calculated with the concentration of each components.

The activities of each components in the slag are not sufficiently investigated as the case of the elements dissolved in liquid iron at present day. It is not easy to obtain the chemical activity in slag, experimentally and theoretically. The authors carried out the calculation for eq. (4–14) by using the activity of iron oxide which was obtained more easily than that of the other components as follows:

$$K''_{Cr} = L_{Cr}/a^{x}_{FeO} \tag{4-15}$$

If x is assumed to be equal to 1, the relation of eq. (4–15) can be applied for the both systems, FeO-CrO-SiO_2 and FeO-MnO-CrO-SiO_2. It is recognized that K''_{Cr} becomes almost constant. And also, if eq. (4–15) was applied, it is possible to estimate the relation between the concentrations of the both phases.

Substituting calcium oxide instead of manganese oxide, the authors measured the effects of CaO on the distribution of chromium in the system of FeO-CaO-CrO-SiO_2. To be different from manganese, calcium does not dissolve in liquid iron. Therefore, it was considered that the effects of CaO were limited only to the slag phase. When CaO was added into the slag, it was assumed that its chemical effect was only the diluting action of the other components in the slag. The distribution coefficients of chromium in this system might consequently be given as a function of iron oxide like the system FeO-CrO-SiO_2. On the other hand, if the activity of iron oxide was changed by addition of CaO, the distribution coefficients of chromium should be represented as a function of the activity of iron oxide like the system FeO-MnO-CrO-SiO_2.

The experimental results in this system showed that the relation between the distribution coefficients of chromium and the concentration of iron oxide was varied by the addition of CaO like the system FeO-MnO-CrO-SiO_2. For instance, with the constant concentration of iron oxide, distribution coefficients of chromium depended on the concentration of CaO. Namely, this result showed that the distribution could not be represented simply as a function of the concentration of iron oxide.

The relation between the activity of iron oxide and the distribution coefficient was calculated and shown in Fig. 42. Fig. 42 indicates that this relation remarkably agreed with that of both systems described above.

The relation between a_{FeO} and N_{FeO} in the FeO-CaO-CrO-SiO_2 slag is dependent in the chromium concentration in the liquid iron like the system of FeO-MnO-CrO-SiO_2.

In the dilute solution, the chemical activities of dissolved elements in the multi-components system is fairly well deduced from the activities in the simple systems by introducing the interaction parameters by C. Wagner. However, in the slag the composition of any components is not in the dilute range. From this reason, the theory of dilute solution is not always used in slag.

Let's consider how to caluclate approximately the activity of iron oxide in

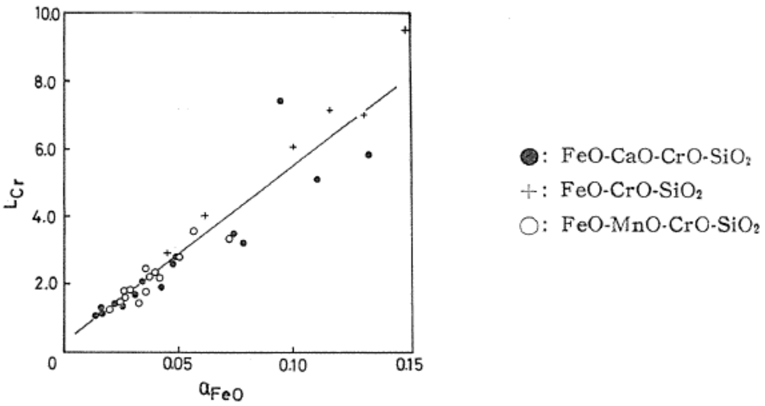


FIG. 42. The relation between the distribution of chromium and the activity of iron oxide in various systems.

the quaternary slag from the a_{FeO} in the ternary system. From Fig. 39 or eq. (4-4), the relation between a_{FeO} and the concentration of added oxide in ternary slag can be calculated. It is assumed that mole fraction of Me_1O and Me_2O in the quaternary system are N_{Me_1} and N_{Me_2}, respectively. If the activity of iron oxide in the both ternary slags is calculated for the mole fraction of $N_{Me_1}+N_{Me_2}$, a_{FeO} in the quaternary system can be obtained by the following equation:

$$a_{FeO} = (a_{FeO})_{Me_1} - \{(a_{FeO})_{Me_1} - (a_{FeO})_{Me_2}\} \times N_{Me_1}/(N_{Me_1} + N_{Me_2}) \qquad (4\text{-}16)$$

For instance, the analytical results on the FeO-MnO-CrO-SiO_2 slag at 1600°C obtained by the authors previously are as follows:

Oxide	SiO_2	FeO	(Cr)	MnO
Weight per cent	49.1	6.0	11.0	31.8
Mole fraction	0.527	0.048	0.136	0.289

From eq. (4-4), $(a_{FeO})_{Cr}=0.040$, and $(a_{FeO})_{Mn}=0.010$. If these values are substituted for eq. (4-16), $(a_{FeO})_{qua.}$ can be calculated as 0.019. On the other hand, $(a_{FeO})_{qua.}$ is obtained from the activity of oxygen in the liquid iron also, and is equal to 0.019. It is recognized that these two values showed good agreement.

$(a_{FeO})_{Ca}$ is equal to zero at 0.37 of the mole fraction of N_{CaO} in the system of FeO-CaO-SiO_2. Although $(a_{FeO})_{Ca}$ takes minus value, if $(a_{FeO})_{Ca}$ is extraporated beyond 0.37 of N_{CaO}. $(a_{FeO})_{qua.}$ in the system of FeO-CaO-CrO-SiO_2 can be calculated in the same procedure.

The solubility of silica was increased remarkably with increasing CaO in the ternary system of FeO-CaO-SiO_2. For the low chromium concentration, the silica concentration in the FeO-CaO-CrO-SiO_2 system was increased like in the system of FeO-CaO-SiO_2. For instance, at 4.0% [Cr], the solubility becomes more than 60%. The solubility becomes nearly constant at 16% [Cr], similarly as in the FeO-CrO-SiO_2 slag. It is assumed that this variation suggests the state of anions in the silicate slag. Therefore, it is concluded that anions in the quaternary slag take the similar state as in the system of FeO-CaO-SiO_2 within the low chromium concentration and they behave similarly in the system FeO-CrO-SiO_2 for the high chromium concentration.

4.5. Conclusions

The equilibrium between liquid iron and the slag saturated with silica was studied at 1600°C. The results obtained are summarized as follows:

(1) The effects of various oxides on the solubility of silica in slag are related to the melting point of its silicate.

(2) The solubility of oxygen decreases with an increase in the added oxide in FeO-SiO_2 system. It is recognized the there exist same relationships between the diminution rate of oxygen and the basicity of added oxide, defined by the strength of cation-oxygen attraction.

(3) The effects of various oxides on the activity of iron oxide are related with the basicity of added oxide. The activity of iron oxide was represented by the following empirical formula:

$$a_{\mathrm{FeO}} = 0.388 - (1.30 N_{\mathrm{Me}^{+2}} - 1.14 N^2_{\mathrm{Me}^{2+}}) / \sqrt{I}$$

(4) The equilibrium relation among three forms of oxygen in silicate melts shown by Richardson was studied for the ternary slags saturated with silica.

The concentration of (O^{2-}) was abruptly changed with the variation of cation in silica-saturated slag.

(5) The distribution coefficient of chromium was obtained for the quaternary slag of FeO-CaO-CrO-SiO_2. The results show that the distribution coefficient of chromium is affected by CaO. And it can be expressed by the activity of iron oxide, but not by the concentration of iron oxide as shown by Körber *et ali.* This fact was reported previously for the system FeO-MnO-CrO-SiO_2 by the present authors.

(6) An expedient method of calculating the activity of iron oxide in the quaertnary system can be obtained with the aid of the activity of iron oxide in ternary system. The calculated values showed close agreement with the experimental results.

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