Equilibrium between Liquid Iron and Fe_tO Containing Solid Solution

Mitsutaka Hino, Kenji Takahashi, Tsuneo Itoh, Ichiro Kikuchi and Tetsuya Nagasaka

Mitsutaka Hino is a Professor and Tetsuya Nagasaka is Associate Professor at
the Department of Metallurgy, Graduate School of Engineering, Tohoku University
Aoba-yama 02, Sendai 980-8579, Japan
Tel & Fax: +81-22-217-7306
E-mail: takahino@material.tohoku.ac.jp

Kenji Takahashi was a former Graduate Student at
the Graduate School of Engineering, Tohoku University,
now Chubu Electric Power Company, Japan

Tsuneo Itoh was a former Graduate Student at
the Graduate School of Engineering, Tohoku University,
now Shibukawa Works, Daido Steel Co. Ltd., Shibukawa 377-0007, Japan

Ichiro Kikuchi was a former Graduate Student at
the Graduate School of Engineering, Tohoku University,
now Kokan Mining Co. Ltd., Fukuyama 721-0914, Japan

Abstract

Oxidation and reduction are utilized in the refining process of iron and steel. Therefore, the most important thermodynamic property is the activity of Fe_tO in slag and especially in refractories, which contact with liquid iron and steel. It is well known that refractories easily form solid solution with Fe_tO, so that molten iron and steel would react with Fe_tO in the refractories, non-metallic inclusion and slag coexisted in the iron and steel production process. In the present work, reaction of molten steel with solid oxide phase will be discussed based on the activity of the constituents in MnO-Fe_tO and $Fe_tO{\cdot}Cr_2O_3$-Fe_tO solid solutions by way of examples of Fe_tO containing solid solution.

INTRODUCTION

Manganese is one of the very variable deoxidizer in steelmaking. It is, therefore, very important to investigate the equilibrium between dissolved Mn and O for assessing the yield of manganese in deoxidation process. A great number of studies[1-24)] have been reported on the equilibrium between Mn and O, where the manganese content in liquid iron has been less than 2-3 mass%. Most of the investigators considered that the deoxidation product was a pure MnO. However, the equilibrium oxide phase is not a pure MnO but a MnO-Fe_tO solid solution on this condition. As the result, the reported data have not been in agreement with each other. The reason of discrepancy caused by kinds of their crucibles.

Therefore, the previous reported studies were assessed in consideration of the activities of constituents in MnO-Fe_tO solid solution in the present work based on our previously proposed data[25] concerning Mn-O equilibrium in liquid iron, which was investigated in melts containing up to 24 mass % Mn at a pure MnO saturation.

Similarly, reliable thermodynamic information on the dissolved Cr-O equilibrium in liquid iron is necessary for the precise control of Cr in liquid stainless steel processing. A huge number of studies[22,24,26-55] have been reported concerning the Cr and O equilibrium relation, where the chromium content in liquid iron has been up to 50 mass %. The present authors[56] has also observed the Cr-O equilibrium relation in molten high chromium alloy steel. It is also well known that the liquid Fe-Cr alloy is in equilibrium with Cr_2O_3 or $FeO{\cdot}Cr_2O_3$, which depends on the Cr content in the metal[1]. $FeO{\cdot}Cr_2O_3$ has relatively wide solid solution range from approximately 70mass% Cr_2O_3 in Fe_tO-Cr_2O_3 binary, almost stoichiometric composition at pure Cr_2O_3 saturation, to 40mass% Cr_2O_3 coexisted with liquid Fe_tO-Cr_2O_3 slag[57-59]. Therefore, the activities of Cr_2O_3 and $FeO{\cdot}Cr_2O_3$ should decrease from unity at Cr_2O_3 saturation with decreasing Cr content in metal.

In the present study, therefore, the Cr-O equilibrium relation was assessed in the low Cr alloy steel, where Fe_tO containing $FeO{\cdot}Cr_2O_3$ solid solution was formed as coexisted oxide phase, based on our previously proposed data on Cr-O equilibrium[56] as well as Mn-O equilibrium[25].

EXPERIMENTS

In the present work, a high frequency induction furnace was used for heating and melting sample[25,56]. MnO and Cr_2O_3 crucibles were manufactured in the laboratory. The experimental temperatures were 1823K, 1873K and 1923K. Temperature measurement was conducted by an infrared radiation pyrometer, which was calibrated against the melting temperatures of iron, nickel and copper under hydrogen atmosphere.

The schematic diagram of experimental apparatus is shown in **Fig.1**. The experimental procedure was as follows. After a MnO or Cr_2O_3 crucible containing pre-melted 90g of Fe-Mn or Fe-Cr alloy was set as shown in Fig.1, Ar-H_2 gas mixture was introduced in the reaction tube and then the sample was melted. After that, the atmosphere was changed to pure Ar and the sample was held during constant period at constant temperatures. A MnO or Cr_2O_3 crucible was set in a MgO outer crucible. The space between the MgO outer crucible and MnO or Cr_2O_3 crucible was filled with pure MnO or Cr_2O_3 powder in order to avoid the dissolution of MgO into MnO or Cr_2O_3 crucible.

The equilibrium measurement between dissolved Mn and O or Cr and O in liquid iron was conducted by suction sampling with a quartz tube. In some experimental runs, the melt was also quenched in the reaction tube by switching off the power and impinging Ar on the surface of sample. It was confirmed in preliminary experiments that the equilibrium was reached after 60 min when the sample was melted at a constant temperature, so that the metal specimen was held for 90min in the all of the experiments.

A inert gas impulse melt - infrared spectroscopic analysis (LECO) was applied to oxygen quantitative analysis in the quenched sample. In case of Mn-O equilibrium experiment, a Sn bath was used to suppress the gettering effect by manganese vapor in oxygen analysis. A high-frequency induction coupled plasma spectroscopic analysis (ICP) was used for Mn and Cr quantitative analysis in quenched sample. In some cases, cross section of MnO and Cr_2O_3 crucibles was analyzed by EPMA and XRD.

RESULTS AND DISCUSSION

1. Mn-O Equilibrium Relation in Molten Low Manganese Alloy Steel

Figure 2 shows the concentration relation between dissolved Mn and O at different temperatures obtained in the present work. Our previous results[25)] up to 25 mass % were also plotted for the comparison. Dotted lines denote the Mn-O equilibrium extrapolated from the relation in the higher manganese concentration region. A considerable discrepancy is recognized between the present results and the extrapolated ones especially at lower manganese concentration. It is concluded from Fig.2 that the activity of MnO at the interface of MnO crucible was not unity because of the formation of solid solution with Fe_tO[10)], when the manganese concentration in iron held in the MnO crucible was less than a few mass %.

In order to confirm this, the extent of Fe_tO solid solubility in the cross section of MnO crucible at 1873K and Fe-1.8 mass % Mn alloy, the lowest manganese content in the present work, was measured by EPMA. The result is illustrated in **Fig.3**, and the Fe_tO concentration decrease with the distance from metal- crucible interface. About 6.5 mass % Fe_tO was dissolved in the MnO crucible at the interface in this heat. It is, therefore, recognized from the quantitative analysis that the activity of MnO(s) is less than unity in the experiments when less than 2 - 3 mass % Mn containing iron is melted in a MnO crucible.

2. Discussion on the Activity of MnO(s) in Fe_tO-MnO Solid Solution

Because it was made clear from the experimental result in the present work that Fe_tO dissolved in a solid MnO crucible in case of melting lower Mn containing iron, the activity of MnO in Fe_tO-MnO solid solution was estimated in each heat.

The equilibrium chemical reaction between solid MnO and Fe_tO is represented by Eq.(1).

$$Fe_tO(s) + Mn(l) = MnO(s) + tFe(l) \tag{1}$$

$$K_1 = \{ a_{MnO(s)} \cdot a^t_{Fe(l)} \}/\{ a_{Fe_tO(s)} \cdot a_{Mn(l)} \} \tag{2}$$

Since both of Fe_tO-MnO solid solution and molten Fe-Mn alloy are considered almost as ideal solution from their phase diagrams, Eqs.(3) and (4) are satisfied and the equilibrium constant, K_1, is expressed by Eq.(5) if all standard states of activities were their pure substances.

$$N_{MnO(s)} + N_{Fe_tO(s)} = 1 \qquad \text{(in } Fe_tO\text{-MnO solid solution)} \tag{3}$$

$$N_{Mn(l)} + N_{Fe(l)} = 1 \qquad \text{(in molten Fe-Mn alloy)} \tag{4}$$

$$\begin{aligned} K_1 &= \{ N_{MnO(s)} \cdot N^t_{Fe(l)} \}/\{ N_{Fe_tO(s)} \cdot N_{Mn(l)} \} \\ &= \{ N_{MnO(s)} (1 - N_{Mn(l)}) \}/\{ (1 - N_{MnO(s)}) N_{Mn(l)} \} \end{aligned} \tag{5}$$

where, N denotes the mole fraction of component. As t is considered to be nearly unity in Eq.(5), the activity of MnO can be expressed as a function of manganese content in liquid iron and be shown by Eq.(6).

$$a_{MnO(s)} = N_{MnO(s)} = K_1 \cdot N_{Mn(l)}/\{1 - N_{Mn(l)} + K_1 \cdot N_{Mn(l)} \} \tag{6}$$

The value of standard free energy change of Eq.(1) can be referred from many literatures, and the data recommended after Turkdogan[2)] shown by Eq.(7) is utilized in the present paper.

$$\Delta G_1^o = -RT \ln K_1 = -113600 + 11.59T \quad \text{(J)} \tag{7}$$

The relation between activity of MnO in Fe_tO-MnO solid solution and mole fraction of dissolved Mn in liquid iron is drawn as in **Fig.4** from Eqs.(6) and (7). It is clear from Fig.4 that the activity of MnO becomes less than unity with decreasing Mn content. In addition to this, mol % Mn is approximated by mass % Mn, and furthermore the activity of MnO is estimated to be unity when Mn concentration exceeds 4 -5 mass %.

3. Equilibrium Relation between <u>Mn</u> and <u>O</u> in Deoxidation of Liquid Iron

Generally speaking, manganese deoxidation of liquid iron is conducted within a few mass % Mn. The activity of MnO(*s*) is less than unity in this case, because $Fe_tO(s)$ dissolves into solid MnO(*s*) as above-mentioned. This has, therefore, to be considered exactly when the equilibrium relation between <u>Mn</u> and <u>O</u> in deoxidation of liquid iron is discussed.

The activity of MnO(*s*) was assessed precisely as follows using our equilibrium constant and interaction parameter reported in our previous study[25)].

Namely, the following value was obtained from our previous experimental results.

$$\mathrm{MnO}(s) = \underline{\mathrm{Mn}} + \underline{\mathrm{O}} \tag{8}$$

$$\log K_8 = \log \{ h_{Mn} \cdot h_O / a_{MnO(s)} \} = -11900/T + 5.10 \quad (1823\mathrm{K}<T<1923\mathrm{K}) \tag{9}$$

Where, *h* and *a* denote Henrian activity and Raoultian activity of component, respectively. Taylor and Chipman[60)] reported the following value on oxygen distribution between molten iron oxide and liquid iron.

$$\mathrm{Fe}_t\mathrm{O}(l) = t\mathrm{Fe}(l) + \underline{\mathrm{O}} \tag{10}$$

$$\Delta G_{10}^o = -RT \ln (a^t_{Fe(l)} \cdot h_O / a_{Fe_tO(l)}) = 117700 - 49.83T \quad \text{(J)} \tag{11}$$

Combination of Eqs.(8) to (13) give us Eq.(15) as the equilibrium constant of Eq.(14).

$$\mathrm{Fe}_t\mathrm{O}(s) = Fe_tO(l) \tag{12}$$

$$\Delta G_{12}^o = -RT \ln \{ a_{Fe_tO(l)} / a_{Fe_tO(s)} \} = 33470 - 20.30T \text{ [61)]} \quad \text{(J)} \tag{13}$$

$$\mathrm{Fe}_t\mathrm{O}(s) + \underline{\mathrm{Mn}} = \mathrm{MnO}(s) + t\mathrm{Fe}(l) \tag{14}$$

$$\log K_{14} = \log [a_{MnO(s)} \cdot a^t_{Fe(l)} / \{ a_{Fe_tO(s)} \cdot h_{Mn} \}] = 4005/T - 1.44 \tag{15}$$

$a_{MnO(s)}$ is expressed by Eq.(16) derived from Eq.(15) with the same derivation as avobe-mentioned in the former chapter.

$$a_{MnO(s)} = N_{MnO(s)} = 1 - 1/\{1 + K_{14} \cdot f_{Mn} \cdot [\%Mn]\} \quad (16)$$

f_{Mn} in Eq.(16) is represented by Eq.(17) from our previous results[25].

$$\log f_{Mn} = 3.43\ e_O^{Mn} \cdot [\%O] = -0.121[\%O] \quad (17)$$

The equilibrium relation between <u>Mn</u> and <u>O</u>, shown by solid lines, in consideration of assessment of MnO(*s*) activity in the present work is compared with that, shown by dotted lines, in case of unit activity of MnO(*s*) in Fig.2. Both agree with our previous experimental values when Mn concentration is greater than 4 mass %. However, the relation based on unit activity of MnO(s) deviates from the present experimental points with decreasing Mn content for Mn concentration less than 4 mass %.

The reasonable agreement of the assessed equilibrium relation in this study with the results reported in the literature for Mn concentrations less than 1 mass % makes clear that the activity of MnO(*s*) is not unity at equilibrium, even if MnO crucible was used in the experiment.

4. Equilibrium Relation between <u>Mn</u> and <u>O</u> in Liquid Iron Coexisted with Fe_tO-MnO Slag

The relation between <u>Mn</u> and <u>O</u> equilibrated with MnO(*s*) has been discussed in the present paper. It is clear from the phase diagram of Fe_tO-MnO system[10] shown in **Fig.5** that the equilibrium oxide phase changes from solid solution to liquid at steelmaking temperature with increasing Fe_tO content. In other words, liquid iron equilibrates with liquid Fe_tO-MnO slag when dissolved Mn content is less than a given concentration. Therefore, it is very important to estimate the relation between <u>Mn</u> and <u>O</u> in liquid iron equilibrated with liquid slag in manganese deoxidation process.

The relation between <u>Mn</u> and <u>O</u> in equilibrium with MnO(*l*) is expressed by Eq.(18), and the equilibrium constant is estimated as Eq.(19) by combining Eq.(9) obtained in our previous work[25] with Eq.(21) for the free energy of fusion of MnO(*s*) reported by Schenck *et al*.[61].

$$\mathrm{MnO}(l) = \underline{\mathrm{Mn}} + \underline{\mathrm{O}} \quad (18)$$

$$\log K_{18} = \log \{ h_{Mn}\ h_O / a_{MnO(l)} \} = -9610/T + 3.97 \quad (19)$$

$$\mathrm{MnO}(s) = \mathrm{MnO}(l) \quad (20)$$

$$\Delta G_{20}^{o} = -RT \ln (a_{MnO(l)} / a_{MnO(s)}) = 43920 - 21.64T \quad \text{(J)} \quad (21)$$

Since the activity of MnO(*l*) will also deviate from unity in this case, it is estimated by Eq.(19) in the same manner as Eq.(16).

$$\mathrm{Fe}_t\mathrm{O}(l) + \underline{\mathrm{Mn}} = \mathrm{MnO}(l) + t\mathrm{Fe}(l) \quad (22)$$

$$\log K_{22} = \log [a_{MnO(l)} \cdot a_{Fe(l)}^{t} / \{ a_{Fe_tO(l)} \cdot h_{Mn} \}] = 3290/T - 1.23 \quad (23)$$

$$a_{MnO(l)} = N_{MnO(l)} = 1 - 1/\{1 + K_{22} \cdot f_{Mn} \cdot [\%\ Mn]\} \quad (24)$$

Where, Eq.(23) representing the equilibrium constant of Eq.(22) is derived from a combination of Eqs.(11) and (19) obtained in the present work.

The relation between Mn and O in liquid iron equilibrated with solid and liquid Fe_tO-MnO slag is estimated by Eqs.(9) and (19) and is shown in **Fig.6**. It is understood from Fig.6 that the equilibrium oxide phase changes from liquid to solid in the vicinity of 0.2 - 0.7 mass % Mn at steelmaking temperature. The previously reported results are also shown in Fig.6 for the comparison. Ivanchev *et al.*[21], Janke and Fischer[22] and Demitrov *et al.*[24] measured the equilibrium using solid MnO, and the other investigators[3,4,5,10,11,15,16] did the same under the presence of liquid slag. These experimental results, except for the results after Hilty and Crafts[5] and Dimitrov *et al.*[24], are in good accord with the present estimated relation between Mn and O.

5. Cr-O Equilibrium Relation in Molten Low Chromium Alloy Steel

The formation of $FeO{\cdot}Cr_2O_3$ was detected at the metal-Cr_2O_3 crucible interface by EPMA and XRD after the present experiment. Therefore, it was concluded that the present experimental works were performed on condition that the activity of Cr_2O_3 was less than unity. And there is a possibility of smaller activity of $FeO{\cdot}Cr_2O_3$ than unity, because $FeO{\cdot}Cr_2O_3$ easily forms solid solution with Fe_tO[57-59] as shown in **Fig.7**.

Figure 8 shows the equilibrium relation between Cr and O concentrations at different temperatures observed in the present work together with other literature values[22,24,26,56]. The equilibrium relation in the present work is compared in Fig.8 with that in unit activity of $Cr_2O_3(s)$, which has been obtained as follows in our previous study[56].

$$Cr_2O_3\,(s) = 2\,\underline{Cr} + 3\,\underline{O} \tag{25}$$

$$\Delta G^o_{25} - RT \ln K_{25} = 693000 - 308.21T\ (\mathrm{J}) \tag{26}$$

$$\log K_{25} = \log\,(h^2_{Cr} \cdot h^3_O / a_{Cr_2O_3(s)}) = -\,36200/T + 16.1 \quad (1823\mathrm{K} < T < 1923\mathrm{K}) \tag{27}$$

$$e^{Cr}_O = -\,123/T + 0.034 \quad (\text{mass \% Cr} < 46,\ 1823\mathrm{K} < \mathrm{T} < 1923\mathrm{K}) \tag{28}$$

The present results obtained for Cr concentration less than 7 mass % did not agree with our previous equilibrium relation estimated by Eqs.(27) and (28). This means that the equilibrium oxide phase would not be pure solid Cr_2O_3 in the present work.

Hino *et al.*[62] have determined the free energy of formation of $FeO{\cdot}Cr_2O_3$ as Eqs.(29) and (30).

$$Fe(s) + 1/2\ O_2(g) + Cr_2O_3(s) = FeO{\cdot}Cr_2O_3(s) \tag{29}$$

$$\Delta G^o_{29} = -\,RT \ln [\,a_{FeO\cdot Cr_2O_3(s)} / \{\,a_{Fe(s)} \cdot P^{1/2}_{O_2} \cdot a_{Cr_2O_3(s)}\,\}]$$

$$= -\,307600 + 66.82T\ (\mathrm{J}) \tag{30}$$

The free energy of dissolution of $O_2(g)$ in liquid iron is given by Eq.(32)[1].

$$1/2\ O_2(g) = \underline{O} \tag{31}$$

$$\Delta G^o_{31} = -RT \ln (h_O / P^{1/2}_{O_2}) = -118100 - 2.39T \text{ (J)} \quad (32)$$

Combination of Eqs.(25) to (32) with the free energy for conversion of the standard states of Fe activities from solid to liquid[63] gives us Eqs.(33) and (34).

$$FeO{\cdot}Cr_2O_3(s) = Fe(l) + 2\,\underline{Cr} + 4\underline{O} \quad (33)$$

$$\Delta G^o_{33} = -RT \ln \{ a_{Fe(l)} \cdot h^2_{Cr} \cdot h^4_O / a_{FeO\cdot Cr_2O_3(s)} \}$$

$$= 898800 - 386.37T - 2.79\times10^{-21}T^7 \text{ (J)} \quad (34)$$

In the same manner, one can get the following relations.

$$3\,Fe(l) + 4\,Cr_2O_3(s) = 3\,FeO{\cdot}Cr_2O_3(s) + 2\,\underline{Cr} \quad (35)$$

$$\Delta G^o_{35} = -RT \ln [a^3_{FeO\cdot Cr_2O_3(s)} \cdot h^2_{Cr} / \{ a^3_{Fe(l)} \cdot a^4_{Cr_2O_3(s)} \}]$$

$$= 75600 - 73.74T + 8.37\times10^{-21}T^7 \text{ (J)} \quad (36)$$

When the activities of both oxide phases are unity, liquid iron is equilibrates with Cr_2O_3 and $FeO{\cdot}Cr_2O_3$. In this limiting case, the equilibrium constant of Eq.(35) can be simplified as Eq.(37).

$$K_{35} = \exp(-\Delta G^o_{35} / RT) = h^2_{Cr} / a^3_{Fe(l)} \quad (37)$$

Assumed that the effects of oxygen on the activities of Fe and Cr in Fe-Cr-O melt are negligible due to the small equilibrium concentration of oxygen[1], the Cr content satisfying Eq.(37) can be calculated from its activity in Fe-Cr binary melt. Andersson[64] assessed the thermodynamic properties of Fe-Cr system in 1988 and proposed the excess free energy term for liquid phase as Eq. (38), so that the value of $a_{Fe(l)}$ can be calculated at any composition of liquid Fe-Cr alloy and temperature.

$$G^{ex}_{liquid} = N_{Cr}(1 - N_{Cr})(-14400 + 6.65T) \text{ (J)} \quad (38)$$

Combination of Eqs.(36) to (38) gives us the Cr contents in liquid iron coexisted with Cr_2O_3 and $FeO{\cdot}Cr_2O_3$ at 1823, 1873 and 1923K as 6.31, 6.82 and 7.24 mass %, respectively. If Cr concentration in metal is lower than this critical Cr content, equilibrium oxide phase should be $FeO{\cdot}Cr_2O_3$. This equilibrium relation between $\underline{Cr}$ and $\underline{O}$ coexisted with pure $FeO{\cdot}Cr_2O_3$ can be calculated by Eqs.(28) and (34) based on unit activity of $FeO{\cdot}Cr_2O_3$. The result is represented by dotted lines in Fig.8. It is obvious that the present observed results deviate downward from this relation. It means that $FeO{\cdot}Cr_2O_3$ formed at the metal-crucible interface is not stoichiometric compound due to the dissolution of Fe_tO into $FeO{\cdot}Cr_2O_3$ when the iron contained less than 7 mass % Cr is melted in a Cr_2O_3 crucible at steelmaking temperature.

Therefore, it is necessery to estimate the activities of $Fe_tO(l)$, $Cr_2O_3(s)$ and $FeO{\cdot}Cr_2O_3(s)$ in $FeO{\cdot}Cr_2O_3$ solid solution. The activities of $Fe_tO(l)$ and $Cr_2O_3(s)$ were calculated by Eqs.(11),

(27) and (28). The activity of $FeO{\cdot}Cr_2O_3(s)$ is evaluated with Eq.(40) which is derived by combining Eqs. (11), (26) with (34).

$$FeO(l) + Cr_2O_3(s) = FeO{\cdot}Cr_2O_3(s) \qquad (39)$$

$$\Delta G^o_{39} = -RT \ln [\, a_{FeO\cdot Cr_2O_3(s)} / \{ a_{FeO(l)} \cdot a_{Cr_2O_3(s)} \}]$$

$$= -88100 + 28.33T + 2.79\times10^{-21}T^7 \ \text{(J)} \qquad (40)$$

The each estimated activity at 1873K is shown in **Fig.9**. It is seen from Fig.9 that the activities of $Cr_2O_3(s)$ and $FeO{\cdot}Cr_2O_3(s)$ become definitely smaller than unity as Cr concentration in liquid iron decreases from 7 mass %. The equilibrium relation between dissolved <u>Cr</u> and <u>O</u> at low Cr content in liquid iron can be estimated by Eqs.(28) and (34) taking the change of activity of $FeO{\cdot}Cr_2O_3(s)$ shown in Fig.9 into account,. The result was drawn in **Fig.10** together with the present experimental results. The experimental results are in good accord with the present estimated relation between dissolved <u>Cr</u> and <u>O</u> for Cr concentrations less than 7 mass%.

SUMMARRY

The equilibrium relation between dissolved <u>Mn</u> and <u>O</u> in liquid iron coexisted with Fe_tO-MnO solid solution was omeasured at 1823 - 1923K using a MnO crucible. And also the equilibrium relation between dissolved <u>Cr</u> and <u>O</u> in liquid iron coexisted with $FeO{\cdot}Cr_2O_3$ solid solution was observed at the same temperatures using a Cr_2O_3 crucible. The following results were obtained.

(1) The activity of MnO in Fe_tO-MnO solid solution equilibrated with Mn containing liquid iron can be expressed as a function of dissolved Mn content in the liquid iron.

(2) The relation between dissolved <u>Mn</u> and <u>O</u> which were equilibrated with Fe_tO-MnO(*l* or *s*) slag is in good agreement with the previous experimental reports, when appropriate correction for MnO activity is applied.

(3) The present experimental results are also in good accord with the present estimated relation between dissolved <u>Cr</u> and <u>O</u> equilibrated with $FeO{\cdot}Cr_2O_3$ solid solution, when appropriate correction for $FeO{\cdot}Cr_2O_3$ activity is applied.

ACKNOWLEDGEMENTS

The authors wish to thank former undergraduate students at Tohoku University Mr. Y. Tominaga (now Japanese Patent Office, Ministry of International Trade and Industry) and Mr. M. Kimoto (now graduate student at Tohoku University) for their experimental assistance. Special thanks are also due to the great help given by Yoshizawa Lime Ind. Co. (Tochigi, Japan) for the processing of Cr_2O_3 crucible. The present work was financially supported in part by the Ministry of Education, Science, Sports and Culture, and the Iron and Steel Institute of Japan (ISIJ).

REFERENCES

1. Steelmaking Data Sourcebook. Part I, ed. by The 19th committee on steelmaking, The Japan Society for the Promotion of Science, Gordon and Breach Science Publishers, 1988.
2. E.T.Turkdogan : Physical Chemistry of High Temperature Technology, Academic Press, 1980, p.5.
3. J. Chipman, J.B. Gero and T.B. Winkler, Trans.AIME, vol.188, 1950, p.341.
4. F. Korber and W. Oelsen, Mitt.K.W.Inst., vol.14, 1932, p.181
5. D.C. Hilty and W. Crafts, Trans.AIME, vol.188, 1950, p.425.
6. E.T. Turkdogan and J. Pearson, J.Iron Steel Inst., vol.175, 1953, p.393.
7. W. Oelsen and G. Heynert, Arch.Eisenhuttenw., vol.26, 1955, p.567.
8. K.Gunji and S.Matoba, Tetsu-to-Hagane, vol.49, 1963, p.758.
9. A. Adachi, Z. Morita and N. Hiraoka, The19th committee on steelmaking, JSPS-Tech. Report, No.4519, 1957.
10. W.A. Fischer and H.J. Fleischer, Arch.Eisenhuttenw., vol.32, 1961, p.1.
11. W.A. Fischer and H.J. Fleischer, Arch.Eisenhuttenw., vol.32, 1961, p.305.
12. H.B. Bell, J.Iron Steel Inst., vol.201, 1963, p.116.
13. B.I.Markhasev and O.G.Sidletskii, Izv.Vysshikh.Uchebn.Zavedenii, Chern.Met., No.9, 1966, p.168.
14. D.B. Caryll and R.G. Ward, J.Iron Steel Inst., vol.205, 1967, p.28.
15. W.A. Fischer and P.W. Bardenheuer, Arch.Eisenhuttenw., vol.39, 1968, p.559.
16. W.A. Fischer and P.W. Bardenheuer, Arch.Eisenhuttenw., vol.39, 1968, p.637.
17. P.M. Mathew, M.L. Kapoor and M.G. Frohberg, Arch.Eisenhuttenw., vol.43, 1972, p.865.
18. T. Uno, S. Hayashi, Y. Iguchi and J. Hirao, The19th committee on steelmaking, JSPS-Tech. Report, No.10376, 1981.
19. G.W. Healy, Trans.Met.Soc.AIME, vol.227, 1963, p.207.
20. V.P. Luzgin, A.F. Vishkarev and V.I. Yavoiskii, Izv.Vysshikh.Uchebn. Zavedenii, Chern.Met., No.9, 1963, p.20.
21. I. Ivanchev and H.B. Bell, J.Iron Steel Inst., vol.210, 1972, p.543.
22. D. Janke and W.A. Fischer, Arch.Eisenhuttenw., vol.47, 1976, p.147.
23. H. Gaye, C. Gatellier, M. Nadif, P.V. Riboud, J. Saleil and M. Faral, Rev.Metall., Cah.Inf.Tech., 1987, p.759.
24. S. Dimitrov, H. Wenz. K. Koch and D. Janke, Steel Research, vol.66, 1995, p.39.
25. K. Takahashi and M. Hino, High Temp. Mater. Proc., vol.19, 2000, p.1.
26. H.M. Chen and J. Chipman, Trans. Am. Soc. Metals, vol.38, 1947, p.70.
27. B.V. Linchevskii and A.M. Samarin, Dok. Akad. Nauk SSSR, Otd. Tekhn. Nauk, vol.89, 1953, p.701.
28. E.T. Turkdogan, J. Iron Steel Inst., vol.178, 1954, p.278.
29. J. Chipman, J. Iron Steel Inst., vol.180, 1955, p.97.
30. D.C. Hilty, W.D. Forgeng amd R.L. Folkman, Trans. AIME, vol.203, 1955, p.253.
31. H. Sakao and K. Sano, J. Jpn. Inst. Metals, vol.26, 1962, p.236.
32. Y. Kojima and K.Sano, Tetsu-to-Hagane, vol.50, 1964, p.888.
33. A. McLean and H.B. Bell, J. Iron Steel Inst., vol.203, 1965, p.123.
34. S. Matoba and T. Kuwana, Tetsu-to-Hagane, vol.51, 1965, p.163.
34. W.A. Fischer and M. Hussmann, Arch. Eisenhuttenw., vol.37, 1966, p.959.
36. J.K. Pargeter, Can. Metall. Quart., vol.6, 1967, p.21.
37. A. Adachi and N. Iwamoto, Trans. Iron Steel Inst. Jpn., vol.53, 1967, p.317.
38. H. Schenck and E. Steinmetz, Arch. Eisenhuttenw., vol.6, 1966, p.188.
39. Y. Kojima, H. Sakao and K.Sano, Arch. Einsenhuttenw., vol.39, 1968, p.187.
40. H. Schenck, E. Steinmetz and P.C.-H. Rhee, Arch. Eisenhuttenw., vol.39, 1968, p.803.
41. R.J. Fruehan, Trans. Met. Soc. AIME, vol.245, 1969, p.1215.

42. K. Suzuki, S. Ban-ya and T. Fuwa, Tetsu-to-Hagane, vol.56, 1970, p.20.
43. N. Iwamoto, M. Takano, H. Kanayama and A. Adachi, Tetsu-to-Hagane, vol.56, 1970, p.727.
44. Y. Nakamura, T. Ohno and K. Segawa, Trans. Iron Steel Inst. Jpn. Suppl., vol.11, 1971, p.456.
45. P.A. Cerkasov and W.A. Fischer, Arch. Eisenhuttenw., vol.42, 1971, p.699.
46. Z. Buzek, M. Macoszek and J. Szlauer, Hutn. Listy, vol.27, 1972, p.547.
47. F.C.L. Larche and A. McLean, Trans. Iron Steel Inst. Jpn., vol.13, 1973, p.71.
48. Z. Buzek, Chemical Metallurgy of Iron and Steel, 1973, p.173.
49. Y. Nakamura and M. Uchimura, Trans Iron Steel Inst. Jpn., vol.13, 1973, p.343.
50. G.K. Sigworth and J.F. Elliott, J. Mater. Sci., vol.8, 1974, p.298.
51. E.T. Turkdogan, BOF Steelmaking, Vol.II, Iron Steel Soc.-AIME, 1975, p.160.
52. V.E. Shevchov, Izv. IUV Chernaya Met., vol.7, 1979, p.5.
53. V.S. Krasilnikov, V.I. Yacoiskii, V.P. Grigorev and A.F. Vishkarev, Izv. VUZ Chernaya Met., vol.7, 1979, p.32.
54. C.K. Kim and A. McLean, Met. Trans. B, vol.10B, 1979, p.585.
55. M. Heinz, K. Koch and D. Janke, Steel Research, vol.60, 1989, p.246.
56. T. Ito, T. Nagaska and M. Hino, Curr. Adv. Mater. Proc. Iron Steel Inst. Jpn., vol.12, 1999, p.108.
57. P.V. Riboud and A. Muan, Trans. AIME, vol.230, 1964, p.88.
58. A.D. Pelton, H. Schmalzried and J. Sticher, J. Phys. Chem. Solids, vol.40, 1979, p.1103.
59. J.R. Taylor and A.T. Dinsdale, Z. Metallknd., vol.84, 1993, p.335.
60. C.R.Taylor and J.Chipman, Trans.AIME, vol.154, 1943, p.228.
61. H.Schenck, N.G.Schmahl and A.K.Biswas, Arch.Eisenhuttenw., vol.28, 1957, p.517.
62. M.Hino, K.Higuchi, T.Nagasaka and S.Ban-ya, ISIJ Int., vol. 34, 1994, p.739.
63. A.T. Dinsdale, Calphad, vol.15, 1991, p.317.
64. J.-O. Andersson, Metall. Trans. A, vol.19A, 1988, p.627.

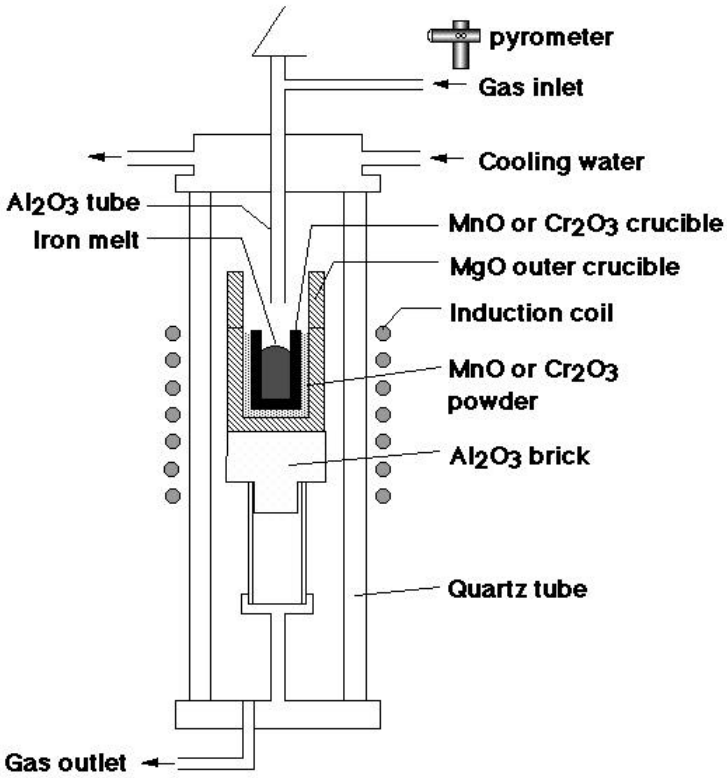

Fig.1 Schematic diagram of the experimental apparatus.

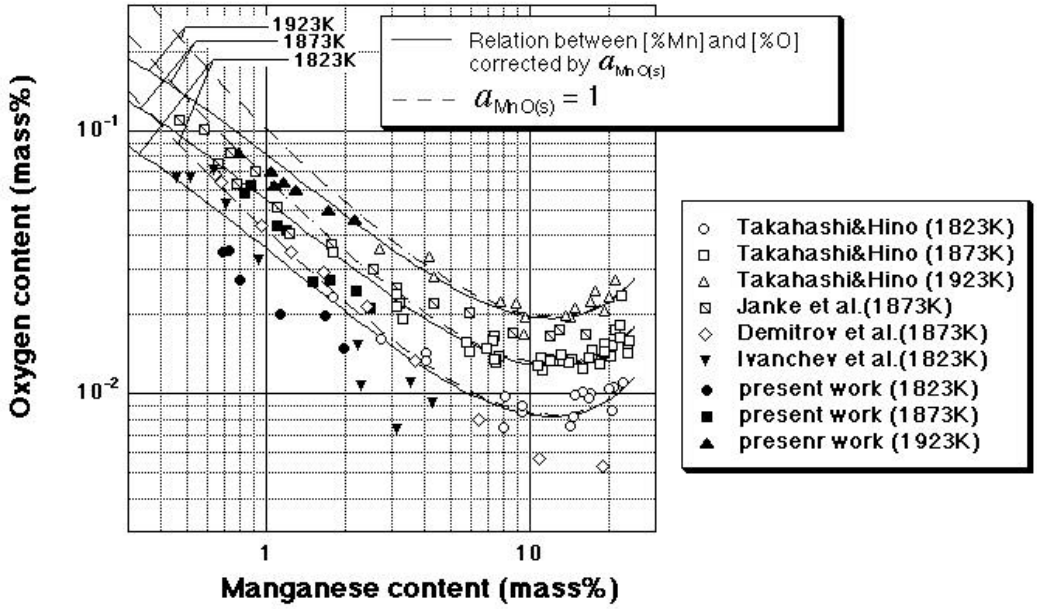

Fig.2 Relation between [%Mn] and [%O] compared with previous works.

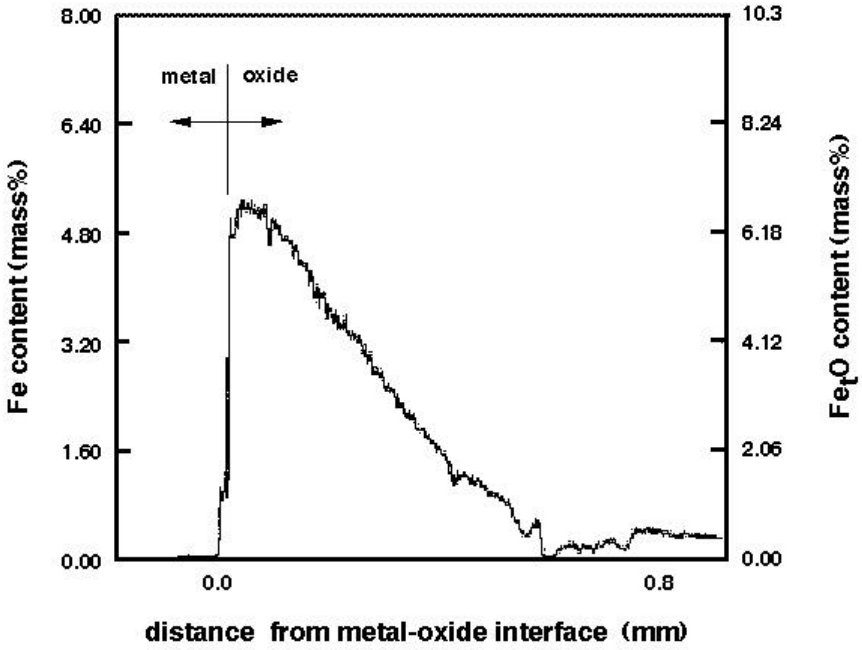

Fig. 3 Concentration profile of Fe in MnO crucible by EPMA.

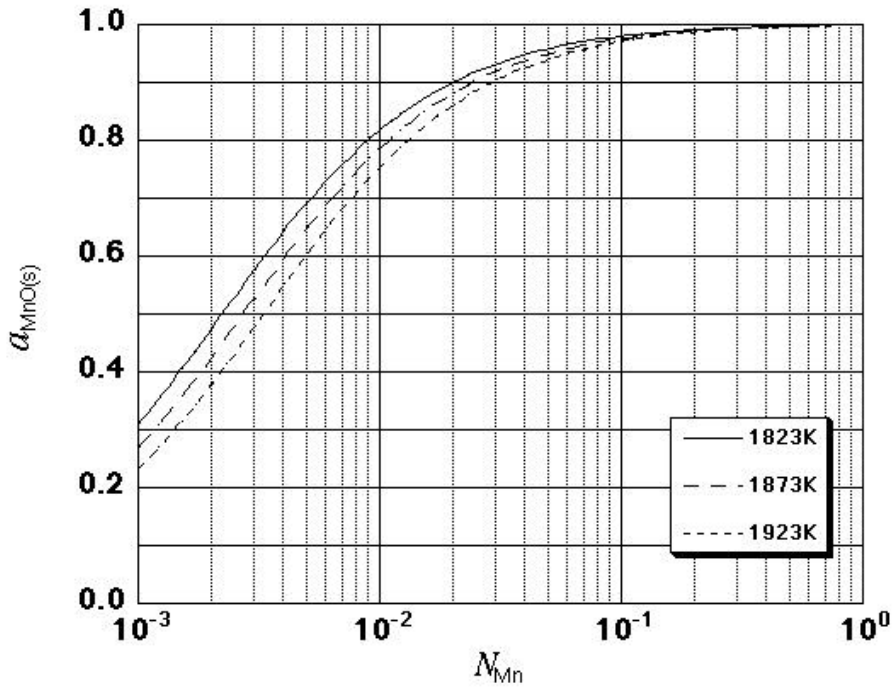

Fig.4 Activity of MnO(s) vs. N_{Mn}.

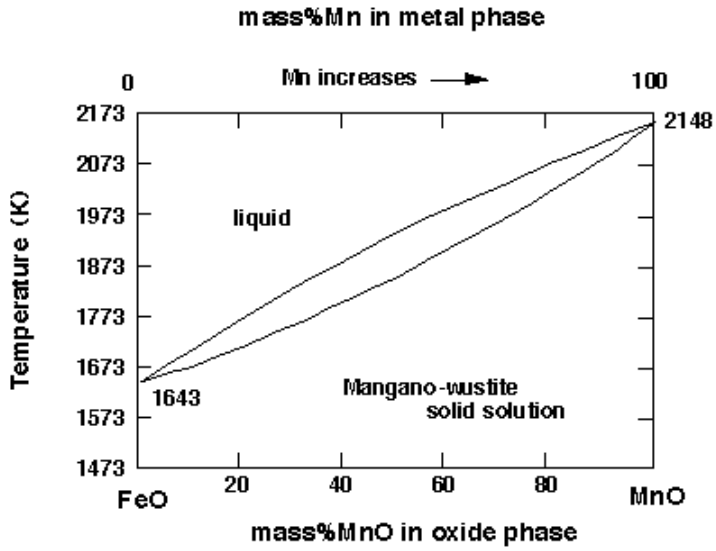

Fig.5 Phase diagram of Fe_tO-MnO system (after Fischer&Fleischer)

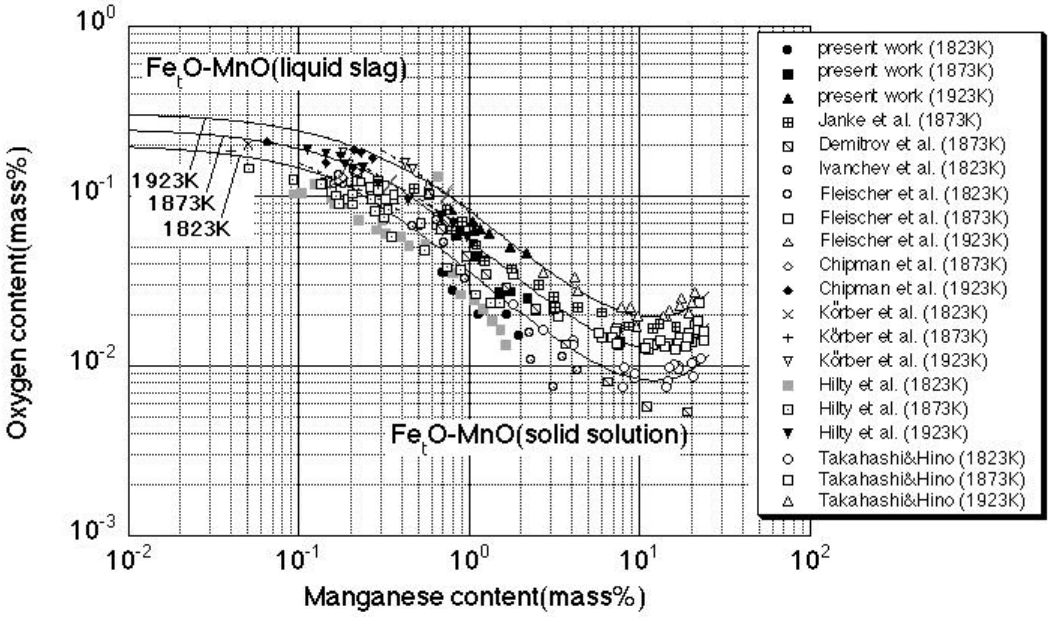

Fig.6 Equilibrium relation between [%Mn] and [%O] with Fe_tO-MnO slag.

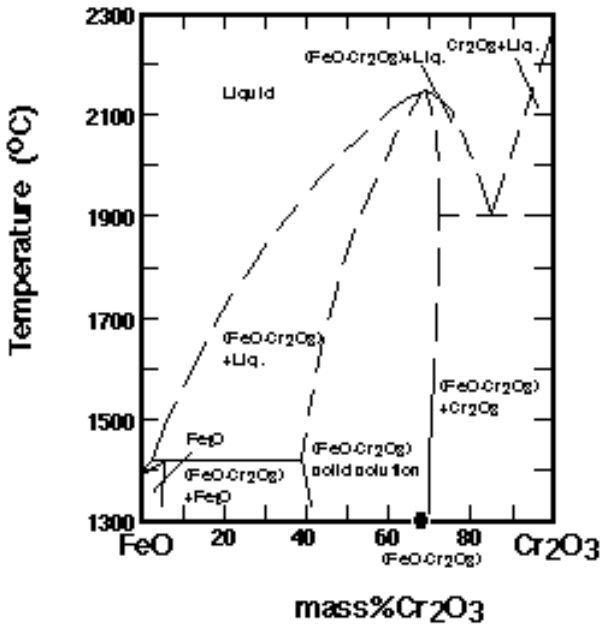

Fig.7 Phase diagram of FeO-Cr_2O_3 system after Riboud&Muan.

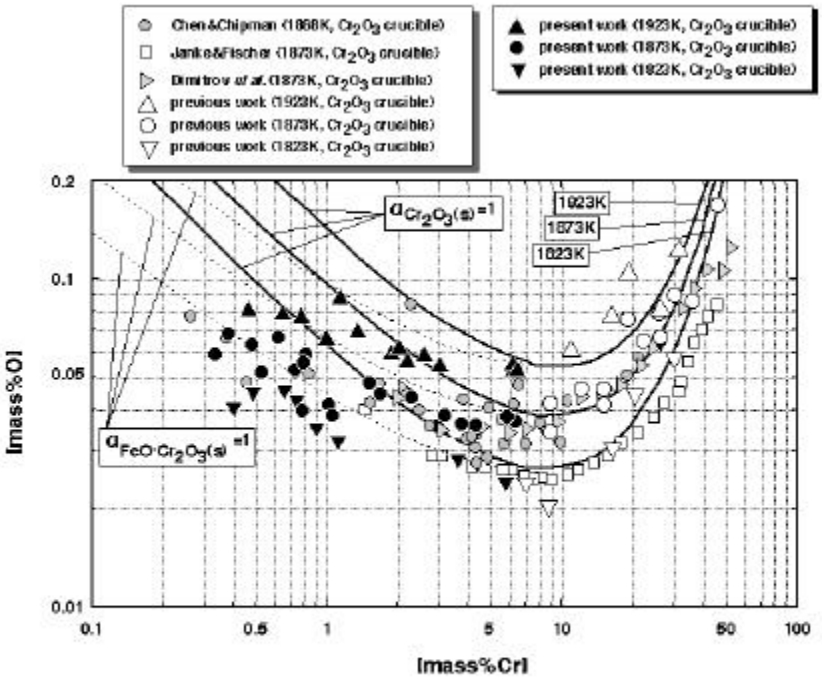

Fig.8 Equilibrium relation between Cr and O contents in liquid iron.

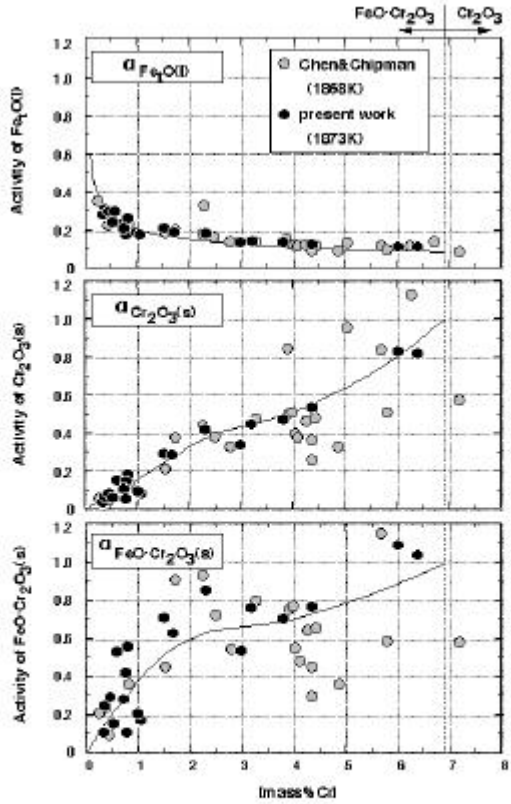

Fig.9 Activities of FeO(l), Cr_2O_3(s) and FeO·Cr_2O_3(s) in oxide phase which is in equilibrium with liquid Fe-Cr-O alloy at 1873K.

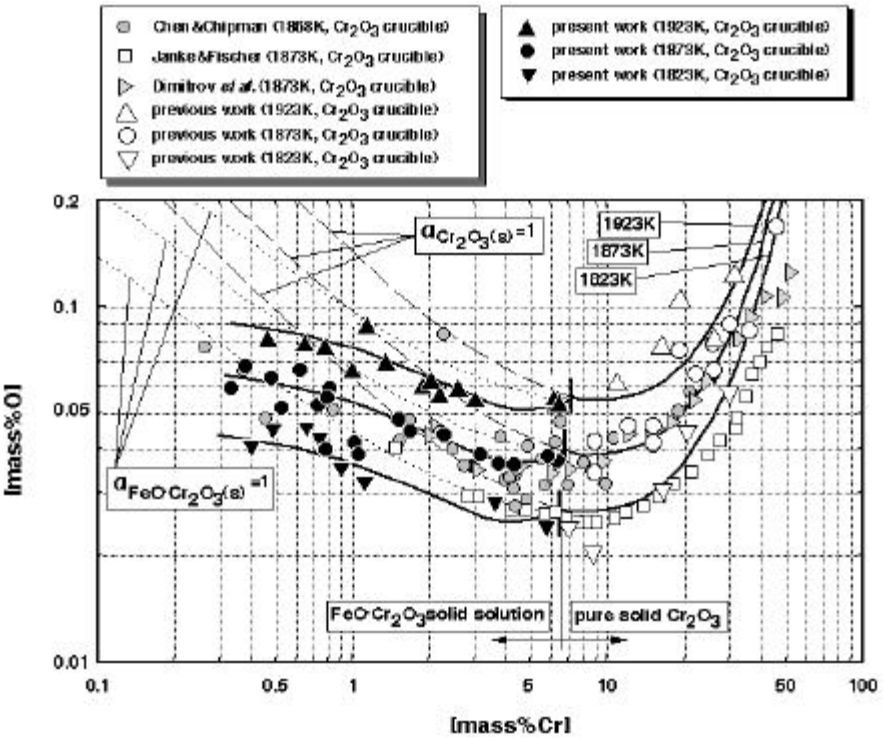

Fig.10 Equilibrium relation between Cr and O contents in liquid iron saturated with pure solid Cr_2O_3 and $FeO{\cdot}Cr_2O_3$ solid solution.