Equilibrium between Dissolved Mn and O in Molten High-Manganese Steel

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ABSTRACT

This paper describes the equilibrium relation between dissolved manganese and oxygen in molten high-manganese steel equilibrated with solid MnO. The equilibrium constant of manganese deoxidation was obtained as follows,

$MnO(s) = \underline{Mn} + \underline{O}$
$\log K_{Mn} = -11\,900/T + 5.10 \quad (1823\text{ K} < T < 1923\text{ K})$

The interaction parameter between Mn and O in liquid iron was independent of temperature and is given by $e_{O}^{Mn} = -0.037$ (mass % Mn < 24, 1823 K< T <1923 K). The interaction parameter formalism with only the first order parameter can represent the variation of the activity coefficient up to 24 mass % Mn in this system, when appropriate correction for a_{MnO} is applied.

1. INTRODUCTION

Manganese is one of the very important alloying elements in steel for improving mechanical properties. It also functions as a deoxidizer of molten steel. Austenite stainless steel and non-magnetic steel, which contain more than 10 mass% manganese, have recently been produced. It is, therefore, important to investigate the equilibrium between dissolved Mn and O for assessing the yield of manganese in the production of high manganese steel. Many studies on the equilibrium between dissolved Mn and O have been reported. However, the manganese content was less than 3 mass% in most of these studies. The equilibrium relation has been extrapolated to the higher manganese content. Further, the reported data are not in complete accord.

In the present work, the equilibrium between dissolved Mn and O in melts containing up to 25 mass% Mn was investigated at MnO-saturation at steelmaking temperature. The results discussed in comparison with previous investigations, and useful thermodynamic values valid up to high manganese concentration have been established.

2. EQUILIBRIUM RELATION BETWEEN DISSOLVED Mn AND O IN LIQUID IRON

The equilibrium chemical reaction between dissolved Mn and O in liquid iron and the equilibrium constant are expressed by Eqs.(1) and (2), respectively.

$$MnO(s) = \underline{Mn} + \underline{O} \qquad (1)$$

$$K_{Mn} = a_{Mn} \cdot a_O / a_{MnO(s)} = f_{Mn}[\%Mn] \cdot f_O[\%O] / a_{MnO(s)} \quad (2)$$

The standard states for activities are infinite dilute solutions for dissolved Mn and O and pure solid for MnO(s), respectively. The deoxidation product of Mn and O defined by Eq. (3), obeyed with the formalism of Eq. (2) gives Eq. (4).

$$K'_{Mn} = [\%Mn][\%O] \quad (3)$$

$$\log K_{Mn} = \log K'_{Mn} + \log f_{Mn} + \log f_O - \log a_{MnO(s)} \quad (4)$$

The activity coefficients in Eq.(4) depend on composition as discussed by Eqs. (5) and (6), respectively.

$$\log f_{Mn} = e_{Mn}^{Mn}[\%Mn] + e_{Mn}^{O}[\%O] + e_{Mn}^{Si}[\%Si] \quad (5)$$

$$\log f_O = e_O^{Mn}[\%Mn] + e_O^{O}[\%O] + e_O^{Si}[\%Si] \quad (6)$$

A small amount of manganese silicate was used as binder to manufacture MnO crucibles used in this study. This resulted in the dissolution of up to 0.2 mass%Si in liquid iron. The effect of Si on each activity coefficient was, therefore, considered in Eqs. (5) and (6).

The relation between interaction parameters is

$$e_{Mn}^{O} = (M_{Mn}/M_O) e_O^{Mn} = 3.43 e_O^{Mn}. \quad (7)$$

Substitution of Eqs.(5) to (7) in Eq. (4) produces Eq. (8).

$$\log K_{Mn} = \log K'_{Mn} - \log a_{MnO(s)} + e_{Mn}^{Mn}[\%Mn] + e_O^{O}[\%O] + (e_{Mn}^{Si} + e_O^{Si})[\%Si] + e_O^{Mn}([\%Mn] + 3.43[\%O]) \quad (8)$$

The 19th committee on steelmaking of the Japan Society for the Promotion of Science /1/ recommends the following values for the equilibrium constant and interaction parameters.

$$\log K_{Mn} = -15\,050/T + 6.75 \;\; (Mn < 1 \text{ mass }\%) \quad (9)$$

$$e_o^{Mn} = (\partial \log f_o / \partial[\text{mass}\%\text{Mn}])_{\text{mass}\%\text{Mn}\to 0.\text{mass}\%\text{O}\to 0} = -0.021 \;(Mn < 1 \text{ mass }\%) \quad (10)$$

$$e_{Mn}^{Mn} = (\partial \log f_{Mn} / \partial[\text{mass}\%\text{Mn}])_{\text{mass}\%\text{Mn}\to 0.} = 0.0 \;(Mn < 1 \text{ mass }\%) \quad (11)$$

$$e_o^{o} = (\partial \log f_o / \partial[\text{mass}\%\text{O}])_{\text{mass}\%\text{O}\to 0} = -1.750/T + 0.76 \quad (12)$$

$$e_o^{Si} = (\partial \log f_o / \partial[\text{mass}\%\text{Si}])_{\text{mass}\%\text{Si}\to 0..\text{mass}\%\text{O}\to 0} = -0.066 \;(Si < 3 \text{ mass }\%) \quad (13)$$

$$e_{Mn}^{Si} = (\partial \log f_o / \partial[\text{mass}\%\text{Si}])_{\text{mass}\%\text{Mn}\to 0..\text{mass}\%\text{Si}\to 0} = 0.0 \;(Si < 1 \text{ mass }\%) \quad (14)$$

However, the recommended values of $\log K_{Mn}$ and e_O^{Mn} are not available at higher manganese content, and therefore these values have to be assessed for high manganese steel production.

3. EXPERIMENTAL

In the present work, a high frequency furnace was used for heating and melting samples, and MnO crucibles were manufactured in the laboratory. The experimental temperatures were 1823 K, 1873 K and 1923 K. The temperature was controlled by power supplier manually. Temperature measurement was conducted by an optical pyrometer, which was calibrated against the melting temperatures of iron and nickel under hydrogen atmosphere. The accuracy of temperature measurement was ± 10 K.

The schematic diagram of experimental apparatus is shown in Fig. 1. The experimental procedure was as follows. After a MnO crucible containing premelted Fe-Mn 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 times and at constant temperatures.

The equilibrium measurement of dissolved Mn and O in liquid iron was conducted by suction sampling with a SiO_2 tube. The melt was also quenched in the reaction tube by switching off the power and directing a

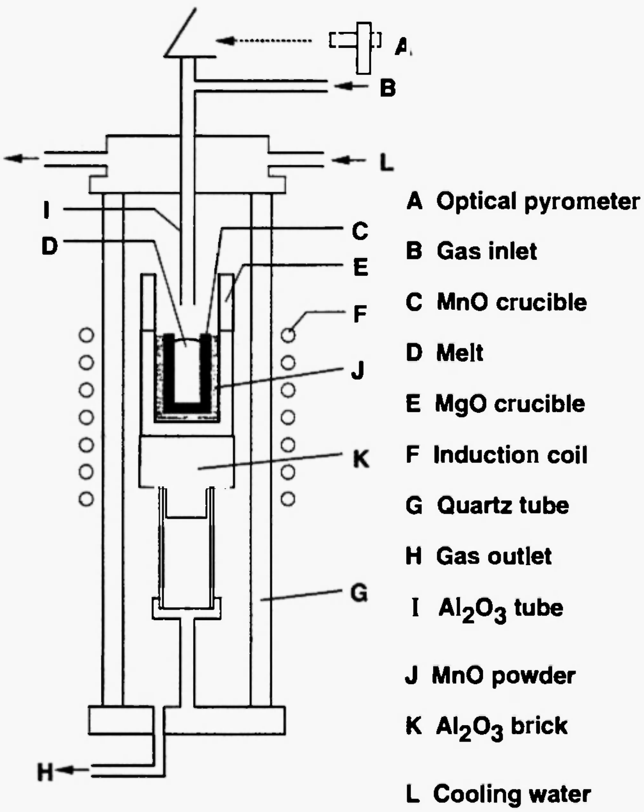

Fig 1: Furnace cross section.

jet of Ar on to the surface of the sample.

It was confirmed in preliminary experiments that the Mn content became a constant after 15 min when 90g of a given high concentration of manganese containing steel was melted in a MnO crucible and the experimental temperature was kept constant. The approach to equilibrium is shown in Fig. 2. In the case of the quenching method, 20g of the manganese containing steel were melted in the crucible at a given temperature.

An inert gas impulse melt - infrared spectroscopic analysis was used for quantitative analysis of oxygen in the quenched sample. In this case, a Sn bath was used to suppress the gettering effect by manganese vapor. A high-frequency inductively coupled plasma atomic emission spectroscopy was used for quantitative analysis of Mn and Si in the quenched sample.

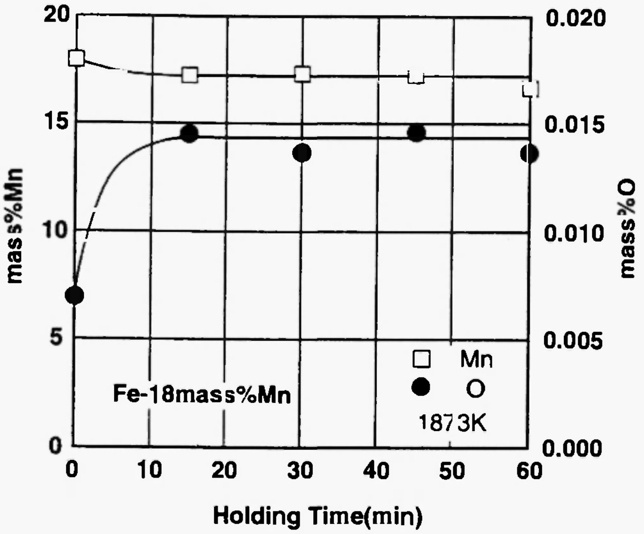

Fig. 2: Approach to equilibrium between Mn and O.

4. EXPERIMENTAL RESULTS

Figure 3 shows the relation between dissolved Mn and O concentrations at different temperatures obtained in the present work. The extrapolated relation up to 25 mass% Mn based on values recommended by JSPS /1/ is also shown in Fig. 3 for comparison. A considerable discrepancy is recognized between the present result and the extrapolated values especially at higher

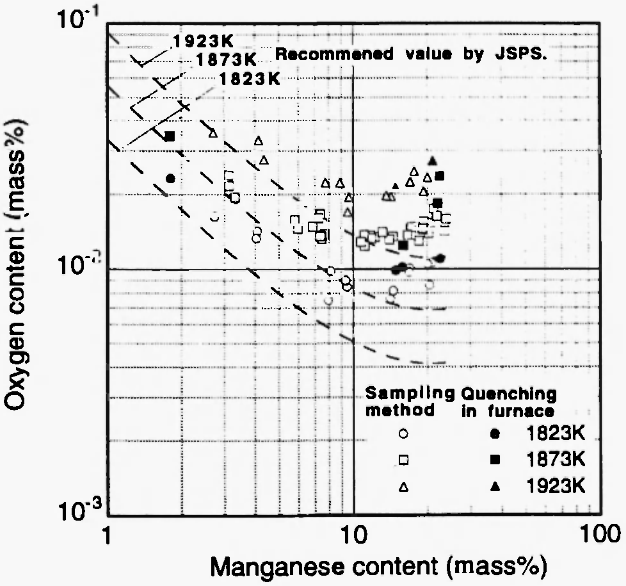

Fig. 3: Relation between [%Mn] and [%O] in liquid iron.

manganese concentration. It is concluded from Fig. 3 that the values recommended by JSPS for equilibrium constant and e_O^{Mn} cannot be utilized in high manganese steel production.

As it is very easy for MnO as a material of crucible to form solid solution with Fe_tO, the activity of MnO would be less than unity. Therefore, the extent of Fe_tO solid solubility in MnO crucible at 1873 K and 1.8 mass% Mn, the lowest content in the present work, was measured by EPMA. The result is illustrated in Fig. 4, and the concentration of Fe_tO decreases 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.

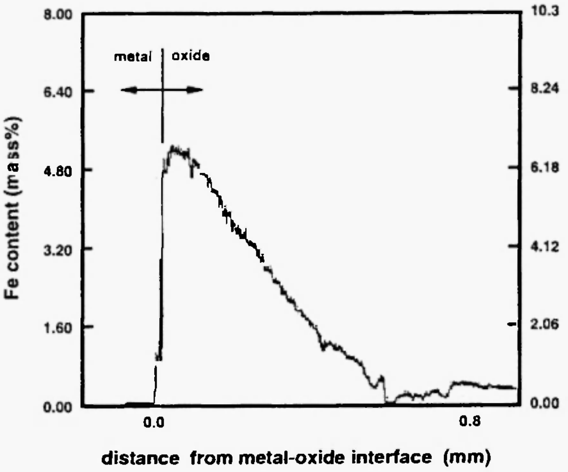

Fig. 4: Concentration profile of Fe in MnO crucible by EPMA.

5. DISCUSSION

5.1. Discussion on the Activity of MnO(s) as Deoxidation Product

Since Fe_tO dissolved in solid MnO used as a crucible when Mn content of the melt was low, the activity of MnO in the deoxidation product was estimated for each experiment.

The equilibrium chemical reaction between MnO and Fe_tO is represented by Eq. (15).

$$Fe_tO(s) + Mn(l) = MnO(s) + tFe(l) \qquad (15)$$

$$K_{15} = \{a_{MnO(s)} \cdot a^{t}_{Fe(l)}\}/\{a_{FetO(s)} \cdot a_{Mn(l)}\} \qquad (16)$$

Since both the Fe_tO-MnO solid solution and molten Fe-Mn alloy are almost ideal solutions, the equilibrium constant can be expressed in terms of mole fraction of MnO at the crucible interface and Mn in the melt.

$$K_{15} = \{N_{MnO(s)} \cdot N^{t}_{Fe(l)}\}/\{N_{Fe_tO(s)} \cdot N_{Mn(l)}\}$$
$$= \{N_{MnO(s)}(1 - N_{Mn(l)})^{t}_{Fe(l)}\}/\{(1 - N_{MnO(s)}) \cdot N_{Mn(l)}\} \qquad (17)$$

As *t* is nearly unity, the activity of MnO can be expressed as a function of manganese content in liquid iron and be shown by Eq.(18).

$$a_{MnO(s)} = N_{MnO(s)} = K_{15} \cdot N_{Mn(l)}/\{1 - N_{Mn(l)} + K_{15} \cdot N_{Mn(l)}\} \qquad (18)$$

The value of standard free energy change for Eq. (15) can be obtained from many sources. The data recommended by Turkdogan /2/ shown by Eq. (19) is utilized in the present paper.

$$\Delta G^0_{15} = -113\,600 + 11.59T \text{ (J)} \qquad (19)$$

The relation between activity of MnO and mole fraction of dissolved Mn in liquid iron is drawn as in Fig. 5 from Eqs. (18) and (19). It is clear from Fig. 5 that the activity of MnO becomes less than unity with decreasing dissolved Mn content. In addition to this,

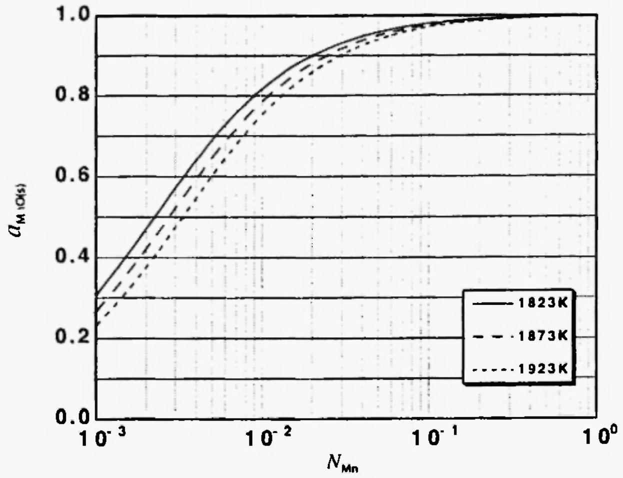

Fig. 5: Activity of MnO(*s*) vs. N_{Mn}.

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 %.

5.2. Estimation of the Equilibrium Constant of Manganese Deoxidation and the Interaction Parameter

Based on the above-mentioned consideration of the activity of MnO(s) as a deoxidation product, at first the experimental results obtained beyond 4 mass% Mn, where the activity of MnO was close to unity, was utilized for determination of the equilibrium constant and interaction parameter.

The present experimental results according to Eq. (20) obtained from rearranging Eq. (8) are plotted in Fig. 6 with the concentration product of Mn and O as abscissa and the left hand side of Eq. (20) as ordinate.

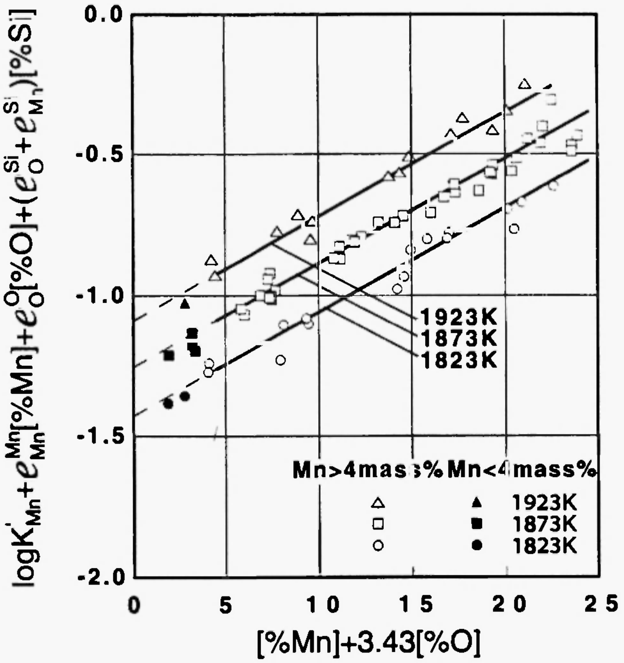

Fig. 6: Plot of [%Mn] + 3.43 [%O] vs. $\log K'_{Mn} + e_{Mn}^{Mn}[\%Mn] + e_O^O[\%O] + \left(e_O^{Si} + e_{Mn}^{Si}\right)[\%Si]$.

$$\log K'_{Mn} + e_{Mn}^{Mn}[\%Mn] + e_O^O[\%O] + (e_O^{Si} + e_{Mn}^{Si})[\%Si]$$
$$= \log K_{Mn} - e_O^{Mn}([\%Mn] + 3.43[\%O]) \qquad (20)$$

The results were analyzed by the method of linear least squares at each temperature. The equilibrium constant is obtained as the intercept on the ordinate, and the interaction parameter e_O^{Mn} is obtained from the slope of each straight line in Fig. 6, assuming the values of the other quantities taken from the literature are correct.

The temperature dependence of equilibrium constant was shown by Eq. (21) in the present work. It is compared with previous studies /3-24/ in Fig. 7.

$$\log K_{Mn} = - 11\,900/T + 5.10$$
$$(18823\ \mathrm{K} < T < 1923\ \mathrm{K}) \qquad (21)$$

The present value is in fairly good agreement with the results of Chipman *et al.* /3/, but the temperature dependency is different.

On the other hand, the interaction parameter between dissolved Mn and O in liquid iron was independent of temperature in the present experimental temperature region and was shown by Eq. (22).

$$E_o^{Mn} = - 0.037\ (4 < \text{mass}\ \%\ \text{Mn} < 24,$$
$$1823\ \mathrm{K} < T < 1923\ \mathrm{K}) \qquad (22)$$

It is compared with previous studies /3-24/ in Fig. 8. It is almost twice as much as the value recommended by Sigworth and Elliott /26/ and JSPS. Therefore, it is recognized that the discrepancy in equilibrium relation of dissolved Mn and O in high Mn concentration range is caused by the difference in the interaction parameter e_O^{Mn}.

5.3 Equilibrium Relation between Dissolved Mn and O 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 mentioned in 5.1. This has, therefore, to be considered exactly when the equilibrium relation between dissolved Mn and O in deoxidation of liquid iron is discussed.

The activity of MnO(*s*) was assessed exactly as

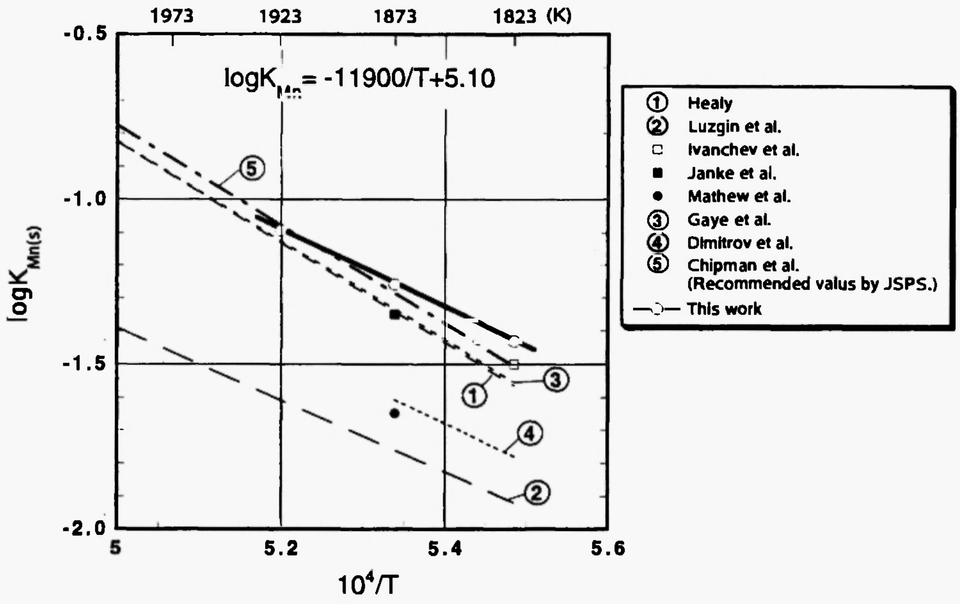

Fig. 7: Temperature dependence of $\log K_{Mn(s)}$.

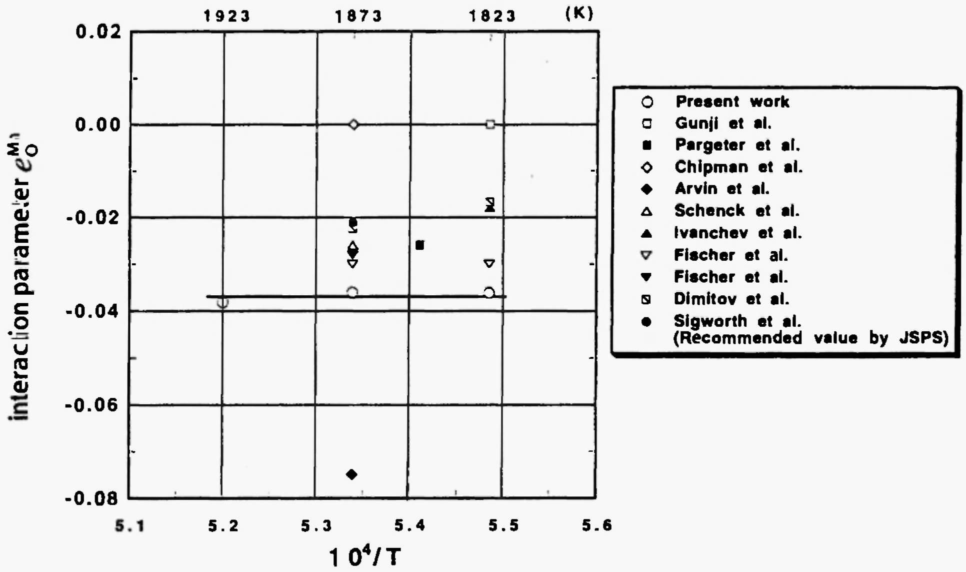

Fig. 8: Temperature dependence of interaction parameter e_O^{Mn}.

follows using our equilibrium constant and interaction parameter in the present study.

Taylor and Chipman /27/ reported the following value for oxygen distribution between molten iron oxide and liquid iron.

$$Fe_tO(l) = tFe(l) + \underline{O} \qquad (23)$$

$$\Delta G^0_{23} = 117\,700 - 49.83\,T \text{ (J)} \qquad (24)$$

Combination of Eqs. (1), (21), (23), (24) and (25), (26), which is the free energy change of fusion of Fe_tO reported by Schenck *et al.* /28/, gives us Eq. (28) as the equilibrium constant of Eq. (27).

$$Fe_tO(s) = Fe_tO(l) \qquad (25)$$

$$\Delta G^0_{25} = 33\,470 - 20.30\,T \text{ (J)} \tag{26}$$

$$Fe_tO(s) + \underline{Mn} = t\,Fe(l) + MnO(s) \tag{27}$$

$$\log K_{27} = 4\,005/T - 1.44 \tag{28}$$

$a_{MnO(s)}$ is expressed by Eq. (29) derived from Eq. (28) with the same derivation as mentioned in 5.1.

$$a_{MnO(s)} = N_{MnO(s)} = 1 - 1/\{1 + K_{27}\,f_{Mn}[\%Mn]\} \tag{29}$$

f_{Mn} in Eq. (29) is represented by Eq. (30) from the present results.

$$\log f_{Mn} = 3.43 e_O^{Mn}[\%O] = -0.121[\%O] \tag{30}$$

The equilibrium relation between dissolved Mn and O both using the correct activity of MnO(*s*), and unit activity of MnO(*s*) are shown in Fig. 9. Both agree with the present experimental results for Mn concentration greater than 4 mass%. However, the relation based on unit of MnO(*s*) deviates from the experimental points with decreasing Mn content.

The reasonable agreement of the equilibrium relation assessed in this study and shown solid lines with experimental results reported in the literature for Mn concentrations less than 1 mass%, confirms that the activity of MnO(*s*) is not unity at equilibrium, even if a MnO crucible is used, at low Mn concentration.

5.4 Equilibrium Relation between Dissolved Mn and O in Liquid Iron Coexisting with Fe$_t$O-MnO Slag

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

The equilibrium between dissolved Mn and O equilibrium with MnO(*l*) is expressed by Eq. (31). The equilibrium constant is estimated as Eq. (34) by combining Eq. (21) representing solid deoxidation product obtained in the present work with Eq. (33) for the free energy of fusion of MnO(*s*) reported by Schenck *et al.* /28/.

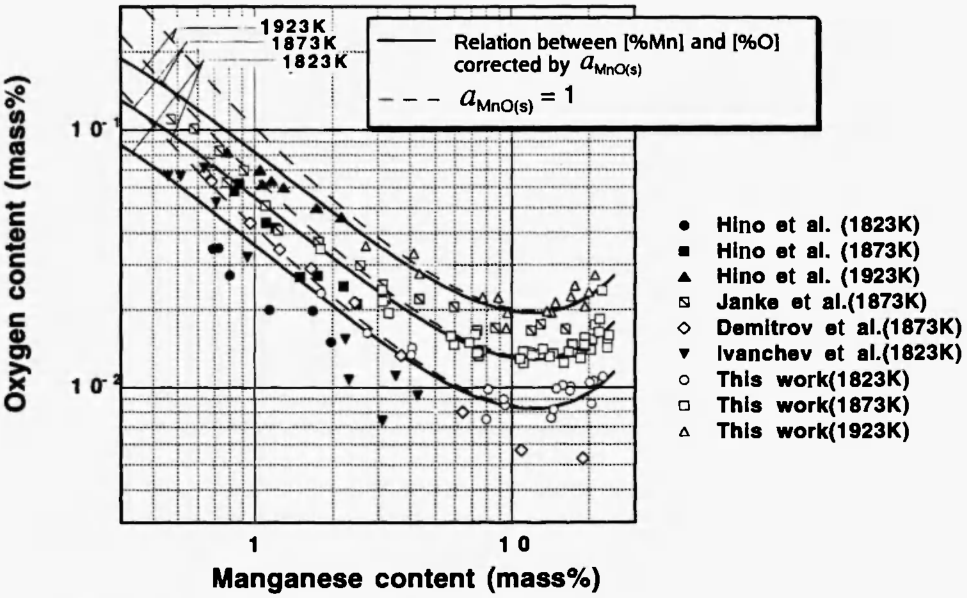

Fig. 9: Relation between [%Mn] and [%O] compared with previous works.

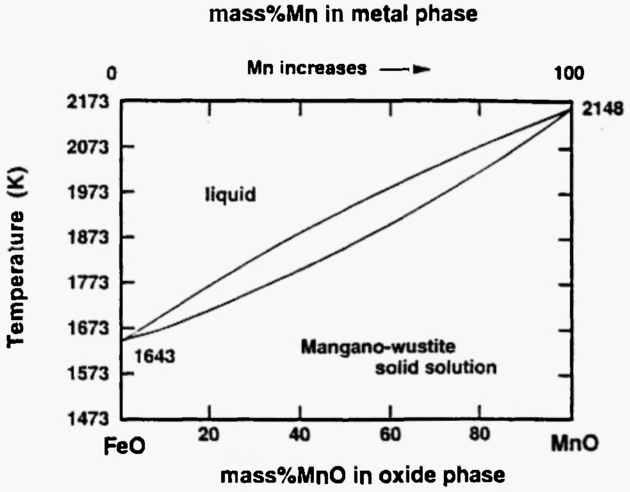

Fig. 10: Phase diagram of Fe_tO-MnO system. (after Fischer and Fleischer /10/)

$$MnO(l) = \underline{Mn} + \underline{O} \tag{31}$$

$$MnO(s) = MnO(l) \tag{32}$$

$$\Delta G^0_{32} = 43\,920 - 21.64\,T \ \text{(J)} \tag{33}$$

$$\log K_{31} = -\,9\,610/T + 3.97 \tag{34}$$

Since the activity of MnO(l) will also deviate from unity, it is estimated by Eq. (37), in the same manner as in 5.3.

$$Fe_tO(l) + \underline{Mn} = MnO(l) + tFe(l) \tag{35}$$

$$\log K_{35} = 3\,290/T - 1.23 \tag{36}$$

$$a_{MnO(l)} = N_{MnO(l)} = 1 - 1/\{1 + K_{35} f_{Mn} [\%Mn]\} \tag{37}$$

Where Eq. (36) representing the equilibrium constant of Eq. (35) is derived from a combination of Eqs. (24) and (34) obtained in the present work.

The relation between dissolved Mn and O in liquid iron equilibrated with solid and liquid Fe_tO-MnO slag is estimated by Eqs. (21) and (34) and is shown in Fig. 11. It is understood from Fig. 11 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. 11 for comparison. Hino *et al.* /19/, Ivanchev *et al.* /22/, Janke *et al.* /23/ and Dimitrov *et al.* /25/ measured the equilibrium using solid MnO, and the other investigators /3,4,5,10,11,15,16/ did the same using liquid slag. These experimental results, except those of Hilty *et al.* /5/ and Dimitrov *et al.* /25/, are in good harmony with the present estimated relation between dissolved Mn and O. As a result, it is concluded that the equilibrium constant and interaction parameter obtained in the present work are very useful over a very wide concentration range of dissolved manganese in liquid iron.

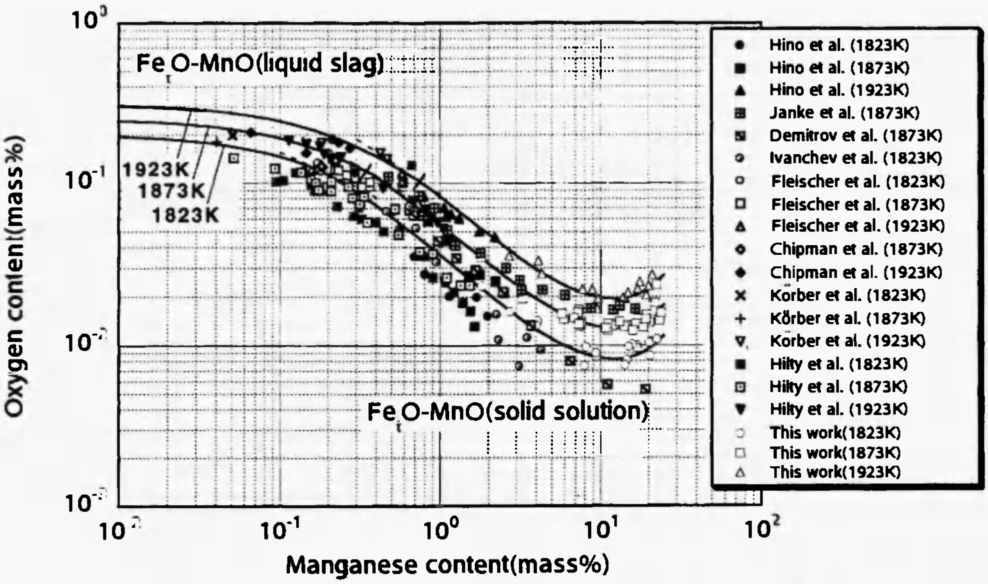

Fig. 11: Equilibrium relation between [%Mn] and [%O] with Fe_tO-MnO slag.

6. CONCLUSIONS

The equilibrium relation between dissolved Mn and O in liquid iron saturated with solid MnO was measured in the temperature range 1823 – 1923 K using a MnO crucible. The following results were obtained:

(1) The equilibrium constant for the reaction between dissolved Mn and O in liquid iron to form MnO(s), obtained from measurements on high manganese steel is given by:

$$\text{MnO}(s) = \underline{\text{Mn}} + \underline{\text{O}}$$
$$\log K_{\text{Mn}} = -11\,900/T + 5.10 \quad (1823\text{ K} < T < 1923\text{ K})$$

(2) The interaction parameter between dissolved Mn and O in liquid iron is independent of temperature in the experimental range and is given by:

$$e_{\text{O}}^{\text{Mn}} = -0.037.$$
$$(\text{mass\% Mn} < 24,\ 1823\text{ K} < T < 1923\text{ K})$$

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

(4) The values for equilibrium constant and interaction parameter obtained in this study are found to be in good agreement with the previous experimental reports, when appropriate correction for a_{MnO} is applied.

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