Standard Gibbs Free Energy of Formation of MnO-saturated MnO·Cr₂O₃ Solid Solution at 1873 K

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The standard Gibbs free energy of formation of MnO-saturated MnO·Cr₂O₃ solid solution (stoichiometric MnO·Cr₂O₃), which is one of important thermodynamic properties of the MnO–SiO₂–CrO_x inclusion system to clarify the equilibrium relation among molten stainless steel and the inclusions formed during the stainless steel Si-deoxidation process, was determined at 1873 K. By equilibrating molten iron or copper with MnO-saturated MnO·Cr₂O₃ crucible under controlled oxygen partial pressure, P_{O_2} , the standard Gibbs free energy changes of the following reactions at 1873 K were determined to be:

The values of ΔG° and $\Delta G_{f, \text{MnO} \cdot \text{Cr}_2\text{O}_3}^\circ$ are independent of the oxygen partial pressure within the P_{O_2} range in the present study.

KEY WORDS: deoxidation; stainless steel; non-metallic inclusion; intermediate compound; stoichiometry; standard Gibbs free energy; MnO·Cr₂O₃; MnO–SiO₂–CrO_x system.

1. Introduction

Deoxidizing of steel and controlling of non-metallic inclusion formation are necessary steps to produce clean steel. At the deoxidation stage in the steelmaking process, multiple deoxidizers are generally used, and the compositions of deoxidation products “non-metallic inclusions” greatly vary depending on deoxidizing elements and their contents. In case of the Si-deoxidation process of 18Cr–8Ni stainless steel, non-metallic inclusions of the MnO–SiO₂–CrO_x system are formed in molten steel and their compositions vary depending on the amount of silicon addition.¹⁾ In order to appropriately design this deoxidation process and to control non-metallic inclusion formation, it is essential to clarify the equilibrium relations among the MnO–SiO₂–CrO_x inclusions and molten stainless steel, because the types of inclusion present greatly affect the mechanical properties of the produced stainless steel. The thermodynamic properties of both inclusions and molten stainless

steel are required to estimate the equilibrium relations of this system. The thermodynamic properties of stainless steel have been well established.²⁾ On the other hand, the ones of the MnO–SiO₂–CrO_x system have been scarcely reported.

From this viewpoint, the authors have been conducting studies to determine the thermodynamic properties of the MnO–SiO₂–CrO_x system. In the previous study,³⁾ the phase equilibria of the MnO–Cr₂O₃ and the MnO–SiO₂–CrO_x systems at 1873 K were measured under controlled oxygen partial pressure, P_{O_2} , and the phase diagram of the MnO–SiO₂–CrO_x system for $P_{O_2} = 2 \times 10^{-6}$ Pa was determined. **Figure 1** shows the P_{O_2} -composition phase diagram of the MnO–Cr₂O₃ binary system at 1873 K.³⁾ The stable intermediate compound, Mn-chromite (MnO·Cr₂O₃), has a nonstoichiometry range, which greatly varies depending on the oxygen partial pressure. Thus, the thermodynamic properties of MnO·Cr₂O₃ solid solution have to be measured under the controlled oxygen partial pressure to fix its com-

Fig. 1. Experimental conditions in the present study plotted on the P_{O_2} -composition phase diagram of the MnO-Cr₂O₃ binary system at 1873 K (after the authors³⁾).

position. Although other investigators measured the standard Gibbs free energy of formation of MnO·Cr₂O₃ previously,^{4,5)} the dependence on the oxygen partial pressure has never been referred to in their paper.

In the present study, by using chemical equilibration techniques, the standard Gibbs free energy of formation of stoichiometric MnO·Cr₂O₃ at 1873 K were determined in the oxygen partial pressure range from 2×10^{-6} to 1.5×10^{-4} Pa. This condition covers the operating condition of the stainless steel Si-deoxidation process.*¹

2. Experimental Principle

By measuring the composition of molten support metal, M, equilibrated with MnO-saturated MnO·Cr₂O₃ crucible under a CO-CO₂ atmosphere to control the oxygen partial pressure, the standard Gibbs free energy of the following reaction of MnO·Cr₂O₃ formation at 1873 K was determined for various oxygen partial pressures:

In the present study, the standard state of MnO·Cr₂O₃ was selected as being the MnO-saturated MnO·Cr₂O₃ solid solution. As shown in Fig. 1, in order to determine the standard free energy of stoichiometric MnO·Cr₂O₃, MnO-saturated MnO·Cr₂O₃ phase, which corresponds to the gray area, is necessary to be equilibrated with molten M.

Since the Reaction (1) is derived by combining the following three reactions:

the standard Gibbs free energy of formation of MnO-saturated MnO·Cr₂O₃ solid solution, $\Delta G_{f, \text{MnO} \cdot \text{Cr}_2\text{O}_3}^\circ$, can be written as:

$$\Delta G_{f, \text{MnO} \cdot \text{Cr}_2\text{O}_3}^\circ = \Delta G_2^\circ + \Delta G_3^\circ + 2\Delta G_4^\circ \quad (5)$$

where ΔG_2° , ΔG_3° and ΔG_4° are, respectively, the standard Gibbs free energy changes of the Reactions (2), (3) and (4). If the values of ΔG_3° and ΔG_4° (thermodynamic data of manganese and chromium in molten M) are available in literatures, the value of $\Delta G_{f, \text{MnO} \cdot \text{Cr}_2\text{O}_3}^\circ$ can be obtained by determining the value of ΔG_2° experimentally.

The equilibrium constant of the Reaction (2) is written as:

$$K_2 = \frac{a_{\text{MnO} \cdot \text{Cr}_2\text{O}_3}}{h_{\text{Mn}} \cdot h_{\text{Cr}}^2 \cdot p_{\text{O}_2}^2} \quad (6)$$

where p_{O_2} is the normalized oxygen partial pressure,*² $a_{\text{MnO} \cdot \text{Cr}_2\text{O}_3}$ is the Raoultian activity of MnO·Cr₂O₃ with respect to MnO-saturated MnO·Cr₂O₃ solid solution as the standard state and h_i is the Henrian activity of component, i , with respect to 1 mass% in molten M as the standard state. As $a_{\text{MnO} \cdot \text{Cr}_2\text{O}_3}$ is unity in the present study, the standard Gibbs free energy change of the Reaction (2) is written as:

$$\Delta G_2^\circ = -RT \ln \left(\frac{1}{(f_{\text{Mn}} \cdot [\%\text{Mn}]) \cdot (f_{\text{Cr}} \cdot [\%\text{Cr}])^2 \cdot p_{\text{O}_2}^2} \right) \quad (7)$$

The f_i is the Henrian activity coefficient of component, i , and expressed in terms of the Wagner's first-order interaction parameters by:

$$\log f_i = \sum_j e_i^j [\%j] \quad (8)$$

If the interaction parameters in molten M have been well established, the value of ΔG_2° can be determined by measuring the concentrations of solutes in molten M equilibrated with MnO-saturated MnO·Cr₂O₃ under controlled oxygen partial pressure.

In the present study, iron was used as a support metal, M, because the thermodynamic properties of the Fe-Mn-O and the Fe-Cr-O systems are relatively well established.²⁾ When the experiments were conducted at a oxygen partial pressure higher than 3×10^{-5} Pa, not only iron but also copper was used as M. The reason for selecting copper as M is to be described in the latter Chap. 4.

A MnO-saturated MnO·Cr₂O₃ crucible of the authors' own making was used in the experiments. If the crucible made of other refractory material such as alumina and magnesia is used, there is some possibility that sample in the crucible is contaminated or reacts with the refractory material. This is a bottle neck in the research field of the high temperature physical chemistry. In order to overcome this bottle neck, by positively making use of the reaction of a support metal with a crucible made of MnO-saturated

*¹ In the previous paper,³⁾ the oxygen partial pressure in the atmosphere of the current Si-deoxidation process at 1873 K has been roughly estimated to be of the order of 10^{-6} Pa from the following equilibrium relation among non-metallic inclusions containing SiO₂ and molten steel: $\text{Si}(\text{mass\%, in molten steel}) + \text{O}_2(\text{g}) = \text{SiO}_2(\text{s})$.

*² The p_{O_2} is defined as $p_{\text{O}_2} = (P_{\text{O}_2}/\text{Pa}) / (P^\circ/\text{Pa})$, where P_{O_2} is the oxygen partial pressure in Pa unit and $P^\circ = 101325$ Pa.

MnO·Cr₂O₃ solid solution, the M(l)–MnO·Cr₂O₃ (MnO-satd.)–Gas equilibrium was achieved in the experimental system.*³

3. Experimental Procedure

3.1. Production of MnO-saturated MnO·Cr₂O₃ Crucible

A MnO-saturated MnO·Cr₂O₃ crucible was produced under the condition represented by the open circle in Fig. 1. MnO and Cr₂O₃ powders were mixed in the mole ratio of 2:1, and the mixture was compressed into a shape of a crucible (9 mm i.d., 15 mm o.d., 18 mm h.) by a hydraulic rubber press at a pressure of around 0.2 GPa. Then, it was sintered at 1873 K for 86.4 ks (24 h) in CO–1%CO₂ atmosphere ($P_{O_2}=2\times 10^{-6}$ Pa⁸).

3.2. Equilibrium Experiment

The prepared crucible was charged with 3 g of electrolytic iron (99.999 mass% pure) or 3.5 g of high purity copper (99.99 mass% pure). It was placed in an isothermal zone of an electric resistance furnace and heated at 1873 K under a CO–CO₂ atmosphere for a time period longer than 18 ks (5 h). After the equilibrium was reached, the crucible was pulled out of the furnace and quenched rapidly by jetting helium gas.

The equilibrium experiments of the Fe(l)–MnO·Cr₂O₃(MnO-satd.)–Gas system, where iron was used as a support metal, were conducted for $P_{O_2}=2\times 10^{-6}$ – 6×10^{-5} Pa, and the ones of the Cu(l)–MnO·Cr₂O₃(MnO-satd.)–Gas system, where copper was used as a support metal, were conducted for $P_{O_2}=3\times 10^{-5}$ – 1.5×10^{-4} Pa.

The quenched metallic samples were subjected to the following three kinds of analyses for the determination of iron or copper equilibrium composition. Manganese and chromium concentrations were analyzed by ICP-AES, oxygen by inert gas fusion-infrared absorptiometry and carbon by coulometric titration method. The samples of the crucible were subjected to electron probe microanalysis (EPMA) for the identification of equilibrium phase and the determination of equilibrium composition.

4. Results and Discussion

4.1. Fe(l)–MnO·Cr₂O₃(MnO-satd.)–Gas System

4.1.1. Attainment of Equilibrium

Figure 2, giving an example of the experimental results of this system, shows the time dependences of (a) the concentrations of manganese, chromium, carbon and (b) the oxygen partial pressure in molten iron phase reacted with the MnO-saturated MnO·Cr₂O₃ crucible under the CO–2.4%CO₂ atmosphere at 1873 K. The values of the oxygen partial pressure in molten iron phase, plotted in Fig. 2(b), were calculated from iron composition in the following way. The dissolution reaction of oxygen into molten iron and its equilibrium constant can be expressed as:

Fig. 2. Time dependences of (a) concentrations of manganese, chromium, carbon and (b) oxygen partial pressure in molten iron phase reacted with MnO-saturated MnO·Cr₂O₃ crucible under CO–2.4%CO₂ atmosphere at 1873 K.

$$K_9 = \frac{f_O \cdot [\%O]}{P_{O_2}^{1/2}} \quad \dots\dots\dots (10)$$

From Eq. (8), the f_O is related to the interaction parameters and the concentrations of oxygen, manganese, chromium and carbon in molten iron by:

$$\log f_O = e_O^O[\%O] + e_O^{Mn}[\%Mn] + e_O^{Cr}[\%Cr] + e_O^C[\%C] \dots\dots\dots (11)$$

Using the values of the standard Gibbs free energy change of the Reaction (9), $\Delta G_9^\circ (= -RT \ln K_9)$,^{2,8)} and the interaction parameters, e_i^j ,²⁾ summarized in Table 1(a), the values of P_{O_2} in molten iron phase were determined from Eqs. (10) and (11).

As shown in Figs. 2(a) and 2(b), the concentrations of all elements and P_{O_2} in molten iron phase had already reached constant values after 18 ks (5 h). In addition, the values of P_{O_2} in molten iron phase are in good agreement with the one in the gas phase ($P_{O_2}=1.1\times 10^{-5}$ Pa⁸) fixed by the CO–CO₂ equilibrium, represented by the broken line in Fig. 2(b). From these facts, the equilibrium among molten iron, MnO-saturated MnO·Cr₂O₃ and gas phases is attained in 18 ks (5 h). Therefore, the period of 18 ks was taken in the following experiments of the Fe(l)–MnO·Cr₂O₃(MnO-satd.)–Gas system. In this system, the P_{O_2} in molten iron phase was regarded as the one in the experimental system.

4.1.2. Standard Gibbs Free Energy of Formation of MnO-saturated MnO·Cr₂O₃ Solid Solution

Based on the results obtained, the standard Gibbs free energy change of the Reaction (2) in case of M=Fe, $\Delta G_{2,M=Fe}^\circ$, was determined as follows. From Eq. (8), the values of f_{Mn} and f_{Cr} in molten iron required for the determination of the value of $\Delta G_{2,M=Fe}^\circ$ were obtained using the first-order interaction parameters in molten iron²⁾ summarized in Table 1(a) and the equilibrium concentrations of manganese, chromium, oxygen and carbon in iron phase.

*³ In the previous study, the authors used a CaS crucible of their own making in the equilibrium experiments between molten iron and the CaS-saturated CaO–Al₂O₃–CaS slag at 1873 K⁶⁾ and between molten copper and the CaS-saturated CaO–SiO₂–CaS slag at 1773 K.⁷⁾

Table 1. Thermodynamic properties related to molten iron (a) and copper (b) used for determination of standard Gibbs free energy of formation of MnO-saturated MnO·Cr₂O₃ solid solution in the present study.^{2,8-15)}

(a) Iron

Standard Gibbs Free Energy Change									
Reaction				ΔG° / J		Temp. Range / K		Ref.	
1/2 O ₂ (g) = <u>O</u> (mass%, in molten Fe)				−113700 − 5.83 (<i>T</i> / K)		1823 − 1973		2, 8)	
Mn(l) = <u>Mn</u> (mass%, in molten Fe)				−6000 − 35.10 (<i>T</i> / K)		1823 − 1973			
Cr(s) = <u>Cr</u> (mass%, in molten Fe)				5400 − 38.8 (<i>T</i> / K)		1850 − 1923			
Interaction Parameter									
<i>i</i>	<i>j</i>	e_i^j	Temp. Range / K	Ref.	<i>i</i>	<i>j</i>	e_i^j	Temp. Range / K	Ref.
Mn	Mn	0.00	1823 − 1973	2)	Cr	Mn	0.0038 [†] (0.0039 at 1843 K)	1873	2)
	Cr	0.0038 [†] (0.0039 at 1843 K)	1873			Cr	0.00 ([% Cr] < 3)	1823 − 1923	
	O	−0.083	1823 − 1973			O	−0.189 ([% Cr] < 3)	1823 − 1923	
	C	−1370 (<i>T</i> / K) ^{−1} + 0.690	1823 − 1873			C	−0.114	1873	
O	Mn	−0.021	1823 − 1973		O	O	−1750 (<i>T</i> / K) ^{−1} + 0.76	1823 − 1923	
	Cr	−0.055	1823 − 1923			C	−0.421	1733 − 2033	

(b) Copper

Standard Gibbs Free Energy Change									
Reaction					ΔG° / J			Temp. Range / K	Ref.
Mn(l) = <u>Mn</u> (mass%, in molten Cu)					-79800 ^{††}			1873	9)
Cr(s) = <u>Cr</u> (mass%, in molten Cu)					-34000 ^{††}			1873	10-13)
Interaction Parameter									
<i>i</i>	<i>j</i>	e_i^j	Temp. Range / K	Ref.	<i>i</i>	<i>j</i>	e_i^j	Temp. Range / K	Ref.
Cr	Cr	0 [†] (0 at 1423-1573 K)	1873	14)	Mn	Mn	0.024 [†] (0.03 at 1517 K)	1873	15)

[†] The values of e_i^j at 1873 K were estimated from the value at T K, using $e_i^j [at 1873 \text{ K}] = (T / 1873) \cdot e_i^j [at T \text{ K}]$.

^{††} The values of $\Delta G^\circ / \text{J}$ at 1873 K were determined from the Raoultian activity coefficient of manganese and chromium in molten copper, γ_{Mn}° and γ_{Cr}° , at infinite dilution. The value of γ_{Mn}° at 1873 K was estimated from the reported values of γ_{Mn}° at 1517 K,⁹⁾ by approximating the Cu-Mn system as the regular solution. The value of γ_{Cr}° at 1873 K was estimated using its regression equation of temperature dependence: $\log \gamma_{\text{Cr}}^\circ = 5760 (T / \text{K})^{-1} - 2.11$ ($T = 1523 - 1873 \text{ K}$), which was obtained from the previously reported values.¹⁰⁻¹³⁾

Fig. 3. Effect of oxygen partial pressure on determined values of $\Delta G_{2,\text{M}=\text{Fe}}^\circ$ and $\Delta G_{\text{f},\text{MnO} \cdot \text{Cr}_2\text{O}_3}^\circ$ at 1873 K.

By substituting the equilibrium concentrations of manganese and chromium, the values of f_{Mn} , f_{Cr} and p_{O_2} in molten iron phase into Eq. (7), the values of $\Delta G_{2,\text{M}=\text{Fe}}^\circ$ were determined.

The relation between the values of $\Delta G_{2,\text{M}=\text{Fe}}^\circ$ at 1873 K and P_{O_2} in molten iron phase are plotted in Fig. 3 by the open circles. The values of $\Delta G_{2,\text{M}=\text{Fe}}^\circ$ are independent of the oxygen partial pressure within the P_{O_2} range from 2×10^{-6} to 6×10^{-5} Pa. The standard Gibbs free energy changes of the following reaction at 1873 K were determined to be:

By combining the value of $\Delta G_{2,\text{M}=\text{Fe}}^\circ$ with the reported values of ΔG_3° and ΔG_4° related to molten iron^{2,8)} summarized in Table 1(a), the values of the standard Gibbs free energy of formation of MnO-saturated MnO·Cr₂O₃ solid solution, $\Delta G_{\text{f},\text{MnO} \cdot \text{Cr}_2\text{O}_3}^\circ$, at 1873 K were determined from Eq. (5). In Fig. 3, these results are also represented by the closed circles. As shown in the figure, the value of $\Delta G_{\text{f},\text{MnO} \cdot \text{Cr}_2\text{O}_3}^\circ$ at 1873 K was determined to be $-961 \pm 4 \text{ kJ} \cdot \text{mol}^{-1}$, independent of P_{O_2} .

4.1.3. Composition Change of MnO·Cr₂O₃ Phase during Experiments

By the EPMA analysis of the crucible after the experiments of the Fe(l)–MnO·Cr₂O₃(MnO-satd.)–Gas system, the decrease of the manganese concentration and the presence of iron in the MnO·Cr₂O₃ phase were identified in the crucible inner wall facing to the iron phase. As the FeO_n–MnO binary system is well known as one of the typical complete solid solution systems,¹⁶⁾ it was assumed that the MnO·Cr₂O₃ solid solution changes its composition to “(Mn_{1-x}Fe_x)O·Cr₂O₃” during the experiments, and the value of x was determined from the quantitative analysis of EPMA. The determined values of x are plotted in Fig. 4 against the oxygen partial pressure in molten iron phase. The iron concentration in the MnO·Cr₂O₃ phase facing to the iron phase increases with increasing oxygen partial pressure.

The effect of the substitution of iron for manganese in the MnO·Cr₂O₃ phase on the $\Delta G_{2,\text{M}=\text{Fe}}^\circ$ values obtained is roughly evaluated assuming that MnO·Cr₂O₃ in the equilibrium intermediate compound phase obeys Raoult's law ($a_{\text{MnO} \cdot \text{Cr}_2\text{O}_3} = X_{\text{MnO} \cdot \text{Cr}_2\text{O}_3}$, X_i : mole fraction of component, i). Even in case of $P_{\text{O}_2} = 5 \times 10^{-5}$ Pa, when the composition

Fig. 4. Effect of oxygen partial pressure on composition of “(Mn_{1-x}Fe_x)O·Cr₂O₃” phase facing to molten iron phase in experiments of the Fe(l)–MnO·Cr₂O₃(MnO-satd.)–Gas system for 18 ks at 1 873 K.

change of MnO·Cr₂O₃ phase was identified to be the most remarkable in the present study, the $\Delta G_{2,M=Fe}^\circ$ value was calculated to increase by only 1.6 kJ. The increment of the $\Delta G_{2,M=Fe}^\circ$ value due to the composition change of MnO·Cr₂O₃ phase is within the limits of the scatter of the results, as shown in Fig. 3 and Eq. (2').

However, in case that P_{O_2} is higher than 5×10^{-5} Pa, when the substitution of iron for manganese in the MnO·Cr₂O₃ phase is expected to be more remarkable during the experiments of the Fe(l)–MnO·Cr₂O₃(MnO-satd.)–Gas system, the composition change of MnO·Cr₂O₃ phase may lead to an error in the results of $\Delta G_{2,M=Fe}^\circ$ and $\Delta G_{f,MnO·Cr_2O_3}^\circ$. Consequently, by conducting the Cu(l)–MnO·Cr₂O₃(MnO-satd.)–Gas system, where copper was used as a support metal, the standard Gibbs free energy change of the Reaction (2) in case of M=Cu, $\Delta G_{2,M=Cu}^\circ$, and $\Delta G_{f,MnO·Cr_2O_3}^\circ$ were determined in relatively high P_{O_2} range from 3×10^{-5} to 1.5×10^{-4} Pa.

4.2. Cu(l)–MnO·Cr₂O₃(MnO-satd.)–Gas System

4.2.1. Attainment of Equilibrium

Figure 5, giving an example of the experimental results of this system, shows the time dependences of the (a) manganese and (b) chromium concentrations in molten copper phase reacted with the MnO-saturated MnO·Cr₂O₃ crucible under the CO–6.1%CO₂ atmosphere at 1 873 K. Similarly to the Fe(l)–MnO·Cr₂O₃(MnO-satd.)–Gas system, the concentrations of manganese and chromium in molten copper had already reached constant values after 18 ks (5 h). In this system, dissolutions of carbon and oxygen into molten copper phase under the present experimental condition are expected to be negligible. Thus, their concentrations were ignored in the determination of the standard Gibbs free energy of formation of MnO-saturated MnO·Cr₂O₃ solid solution, and the values of the oxygen partial pressure in molten copper phase were not calculated from the oxygen concentration. As shown in Fig. 5, the equilibrium in this system is attained in 18 ks (5 h).

Unlike the Fe(l)–MnO·Cr₂O₃(MnO-satd.)–Gas system, copper was not detected in the MnO·Cr₂O₃ crucible inner wall facing to the copper phase even at a higher oxygen

Fig. 5. Time dependences of (a) manganese and (b) chromium concentrations in molten copper phase reacted with MnO-saturated MnO·Cr₂O₃ crucible under CO–6.1%CO₂ atmosphere at 1 873 K.

partial pressure.

4.2.2. Standard Gibbs Free Energy of Formation of MnO-saturated MnO·Cr₂O₃ Solid Solution

Similarly to the Fe(l)–MnO·Cr₂O₃(MnO-satd.)–Gas system, using the thermodynamic properties of manganese and chromium in molten copper^{9–15)} summarized in Table 1(b), the standard Gibbs free energy change of the Reaction (2) in case of M=Cu, $\Delta G_{2,M=Cu}^\circ$, and $\Delta G_{f,MnO·Cr_2O_3}^\circ$ were determined from the experimental results for this system. In case of this system, the dissolved chromium, oxygen and carbon in copper phase are so dilute that the terms of their interaction can be neglected. Especially, the parameter of e_{Cr}^{Mn} is reported to be zero even at much lower temperature than 1 873 K.¹⁴⁾ According to Eq. (8), in order to evaluate the values of f_{Mn} and f_{Cr} , the parameters of e_{Mn}^{Mn} and e_{Cr}^{Mn} in molten copper at 1 873 K are required. Since the parameter of e_{Mn}^{Mn} at 1 873 K can be estimated from the reported one at 1 517 K,¹⁵⁾ the values of f_{Mn} were determined using the estimated self-interaction parameter of manganese. On the other hand, since the parameter of e_{Cr}^{Mn} in molten copper is not reported, the value of f_{Cr} is estimated as follows. Considering that the parameter of e_{Cr}^{Mn} in molten iron is small value,²⁾ as shown in Table 1, its parameter in molten copper is expected to be negligibly small value. Thus, the chromium in molten copper was regarded to obey Henry's law ($f_{Cr}=1$). The oxygen partial pressure in the gas phase was regarded as the one in this experimental system.

The determined values of $\Delta G_{2,M=Cu}^\circ$ and $\Delta G_{f,MnO·Cr_2O_3}^\circ$ at 1 873 K are plotted in **Fig. 6** against the oxygen partial pressure. The open and the closed circles, respectively, represent the results of $\Delta G_{2,M=Cu}^\circ$ and $\Delta G_{f,MnO·Cr_2O_3}^\circ$. The double circles represent the values of $\Delta G_{f,MnO·Cr_2O_3}^\circ$ obtained from the experiments of the Fe(l)–MnO·Cr₂O₃(MnO-satd.)–Gas system. Similarly to case of M=Fe (Fig. 3), the values of $\Delta G_{2,M=Cu}^\circ$ and $\Delta G_{f,MnO·Cr_2O_3}^\circ$ are also independent of the oxygen partial pressure within the P_{O_2} range from 3×10^{-5} to 1.5×10^{-4} Pa. The standard Gibbs free energy changes of the following reaction at 1 873 K were determined to be:

Fig. 6. Effect of oxygen partial pressure on determined values of $\Delta G_{2,M=Cu}^\circ$ and $\Delta G_{f,MnO \cdot Cr_2O_3}^\circ$ at 1873 K.

As shown in the figure, the results of $\Delta G_{f,MnO \cdot Cr_2O_3}^\circ$ obtained from the experiments of the two different systems are in good agreement and almost constant independent of the oxygen partial pressure within the limits of experimental error. Thus, the errors due to the substitution of iron oxide for some of MnO in $MnO \cdot Cr_2O_3$ solid solution during the experiments of the Fe(l)– $MnO \cdot Cr_2O_3$ (MnO-satd.)–Gas system, which is mentioned in the Sec. 4.1, can be neglected in the determination of $\Delta G_{f,MnO \cdot Cr_2O_3}^\circ$. Based on both the results for the Fe(l)– $MnO \cdot Cr_2O_3$ (MnO-satd.)–Gas and the Cu(l)– $MnO \cdot Cr_2O_3$ (MnO-satd.)–Gas systems, the standard Gibbs free energy of formation of MnO-saturated $MnO \cdot Cr_2O_3$ solid solution at 1873 K was determined to be:

in the P_{O_2} range from 2×10^{-6} to 1.5×10^{-4} Pa.

4.3. Standard Gibbs Free Energy of Formation of MnO-saturated $MnO \cdot Cr_2O_3$ Solid Solution from Its Constituent Oxides MnO and Cr_2O_3

By combining Eq. (1') with the following standard Gibbs free energies of formation of MnO and Cr_2O_3 :

the standard Gibbs free energy of formation of the intermediate compound, $MnO \cdot Cr_2O_3$ saturated with MnO, from its constituent oxides MnO and Cr_2O_3 at 1873 K was obtained as follows:

Fig. 7. Standard Gibbs free energy change of formation of MnO-saturated $MnO \cdot Cr_2O_3$ solid solution from its constituent oxides as a function of temperature.

The value of ΔG_{14}° obtained in the present study was plotted in Fig. 7 against temperature, together with the previously reported results by other investigators.^{4,5} The standard entropy change of the reaction among solid phases, such as the Reaction (14), which corresponds to the temperature dependence of ΔG_{14}° , is generally expected to be much smaller than that of a reaction involving liquid and/or gas phases. As expected, the present result is in agreement with not only the result measured at 1873 K by Tsai and Muan⁵ but also the results measured at different temperatures^{4,5} within the limits of experimental error, and the value of ΔG_{14}° is almost constant within the temperature range from 1523 to 1873 K.

5. Conclusions

The standard Gibbs free energy of formation of MnO-saturated $MnO \cdot Cr_2O_3$ solid solution at 1873 K were determined by equilibrating molten iron or copper with MnO-saturated $MnO \cdot Cr_2O_3$ crucible in the P_{O_2} range from 2×10^{-6} to 1.5×10^{-4} Pa. The results obtained under the present experimental conditions are summarized as follows:

(1) From the experimental results of the Fe(l)– $MnO \cdot Cr_2O_3$ (MnO-satd.)–Gas and the Cu(l)– $MnO \cdot Cr_2O_3$ (MnO-satd.)–Gas systems, the standard Gibbs free energy changes of the following reactions were, respectively, determined to be:

(2) The standard Gibbs free energy of formation of

MnO-saturated MnO·Cr₂O₃ solid solution (stoichiometric MnO·Cr₂O₃) at 1873 K was determined to be:

$$\Delta G_{\text{f, MnO} \cdot \text{Cr}_2\text{O}_3}^\circ / \text{kJ} \cdot \text{mol}^{-1} = -958 \pm 8$$

$$(P_{\text{O}_2} = 2 \times 10^{-6} - 1.5 \times 10^{-4} \text{ Pa})$$

independent of the oxygen partial pressure. The values of $\Delta G_{\text{f, MnO} \cdot \text{Cr}_2\text{O}_3}^\circ$ obtained in both the Fe(l)–MnO·Cr₂O₃(MnO-satd.)–Gas and the Cu(l)–MnO·Cr₂O₃(MnO satd.)–Gas systems agree well with each other.

(3) During the experiments of the Fe(l)–MnO·Cr₂O₃(MnO-satd.)–Gas system, MnO·Cr₂O₃ solid solution equilibrated with molten iron is identified to change its composition to “(Mn_{1-x}Fe_x)O·Cr₂O₃” by substituting iron oxide for some sites of MnO in the solid solution. This behavior tends to be more remarkable with increasing oxygen partial pressure. However, the obtained value of $\Delta G_{\text{f, MnO} \cdot \text{Cr}_2\text{O}_3}^\circ$ was not affected by the composition change of MnO·Cr₂O₃ phase.

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