Solubilities of Oxygen in Fe–Cr Melts in Equilibrium with $\text{MgO} \cdot \text{Cr}_2\text{O}_3$ and $\alpha\text{-CaCr}_2\text{O}_4$ *

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Synopsis

Experiments were made to study the relationship between chromium and oxygen in liquid iron in equilibrium with pure solid $\text{MgO} \cdot \text{Cr}_2\text{O}_3$ or $\alpha\text{-CaCr}_2\text{O}_4$ under an atmosphere of argon. The solubilities of oxygen in the melts were measured as a function of chromium concentrations (3 to 30%) over the temperature range from 1 600° to 1 800°C. Crucible used was lined with $\text{MgO} \cdot \text{Cr}_2\text{O}_3$ or $\alpha\text{-CaCr}_2\text{O}_4$ powder. By a least squares analysis of the data the following results were obtained as the equilibrium constants and the activity coefficient of oxygen dissolved in liquid alloys:

Equilibrium constants.

$$\log K_1 = -42\,470/T + 17.79$$

$$\log K_2 = -44\,270/T + 18.57$$

Activity coefficient of oxygen.

$$\log f_{\text{O}} = e_{\text{O}}^{\text{Cr}}[\% \text{Cr}] + q_{\text{O}}^{\text{Cr}}[\% \text{Cr}]^2$$

$$e_{\text{O}}^{\text{Cr}} = -380/T + 0.151$$

$$q_{\text{O}}^{\text{Cr}} = 10.2/T - 48.7 \times 10^{-4}$$

I. Introduction

The solubilities of oxygen in liquid Fe–Cr alloys in equilibrium with oxides containing chromium are of great importance to understand the chemical behavior of oxygen in various processes of chromium-steelmaking. The Fe–Cr–O ternary system has been, therefore, studied by a number of researchers.^{1–9)} It was reported that the equilibrium oxide phase was iron-chromite ($\text{FeO} \cdot \text{Cr}_2\text{O}_3$) at low concentrations of chromium in Fe–Cr alloys, distorted spinel at medium concentrations, and chromic oxide (Cr_2O_3) or Cr_3O_4 at high concentrations.^{2,10)} The reported values of oxygen solubility at 1 600°C show reasonable agreement among themselves. As a whole, the sufficient knowledge of Fe–Cr–O system has been available for controlling deoxidation of liquid iron with chromium.

On the other hand, little have been reported on solubilities of oxygen in liquid Fe–Cr alloys in equilibrium with chromium oxides containing MgO and CaO. Such oxides are of interest in connection with slag-metal and refractory-metal reactions. Picrochromite ($\text{MgO} \cdot \text{Cr}_2\text{O}_3$) and α -calcium chromite (CaCr_2O_4) are typical examples. $\text{MgO} \cdot \text{Cr}_2\text{O}_3$ and CaCr_2O_4 are known to be more stable than $\text{FeO} \cdot \text{Cr}_2\text{O}_3$ and Cr_2O_3 under reducing conditions.^{11,12)} These chromites are observed in molten slags as a dispersed solid phase. $\text{MgO} \cdot \text{Cr}_2\text{O}_3$ is also known to be the major

constituent of chromite refractories.¹⁰⁾ Therefore, $\text{MgO} \cdot \text{Cr}_2\text{O}_3$ and $\alpha\text{-CaCr}_2\text{O}_4$ are considered to give some effects on the chemical behavior of dissolved oxygen in liquid steels during redox periods of chromium-steelmaking.

Thus an investigation was undertaken to extend a fundamental knowledge in this field. The present experiments were made to obtain the values of the oxygen solubilities in Fe–Cr melt in equilibrium with pure $\text{MgO} \cdot \text{Cr}_2\text{O}_3$ and $\alpha\text{-CaCr}_2\text{O}_4$ as a function of chromium concentration. Liquid iron containing approximately 3 to 30%Cr was brought in equilibrium with $\text{MgO} \cdot \text{Cr}_2\text{O}_3$ or $\alpha\text{-CaCr}_2\text{O}_4$ over a wide range of temperature.

II. Experimental

1. Apparatus

The equipment used to measure the solubility of oxygen in Fe–Cr melt consists of a seven turn induction coil, an electrical supply, a rotary pump, a flow meter, and a reaction tube. Figure 1 schematically shows the reaction tube which was essentially of the same design as that reported previously.⁸⁾ Crucibles were made of magnesia, 17 mm in inner diameter and 150 mm length. The inner surface of the crucibles was lined with $\text{MgO} \cdot \text{Cr}_2\text{O}_3$ or CaCr_2O_4 powder. The high frequency power for heating was provided by a 30 kVA–40 kHz generator. In-put of about 7 kW was enough to keep the melt at 1 800°C. Cylinder argon of extra-high purity was used as an atmosphere

Fig. 1. Schematic cross-section of reaction furnace

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inside the reaction tube without further purification. The temperature of the melt was measured by an optical pyrometer. The pyrometer was calibrated against a thermocouple under the same experimental conditions. The thermocouple of Pt/6%Rh-Pt/30%Rh protected with an alumina tube was inserted into the bulk of melt from the bottom of the crucible. The alloys containing 4.1, 9.6, 18.4, and 27.1%Cr were used for the calibration of the pyrometer. The emissivity of liquid alloys was practically independent of the concentration of chromium in the temperature range from 1 550° to 1 850°C. The temperature of the melt was controlled by frequent optical observation and manual adjustment. Considering possible factors, the maximum total uncertainty of the temperature measurement was less than 10°C. The temperature change of graphite block (Fig. 1) was continuously measured with a thermocouple during the experiment. This auxiliary measurement was

Table 1. Compositions of starting materials

Element		Cr	O	C	Si
Mother alloy	AK	5.2%	0.0021%	0.041%	<0.05%
	AL	20.9	0.0054	0.008	<0.05
	BK	5.04	0.0081	0.002	<0.03
	BL	20.3	0.0114	0.002	<0.03
Electrolytic Cr		99.8	0.25	—	—
Electrolytic Fe		0.001	0.07	0.005	0.001

useful to monitor indirectly the tendency of the temperature change of the melt.

2. Metals and Master Alloys

Electrolytic iron of 99.9% purity and electrolytic chromium of 99.8% purity were used. Four master alloys were prepared from these pure metals by vacuum melting. The compositions of the master alloys and the metals are shown in Table 1. The charge of about 70 g for each run consisted of a few pieces of master alloys and of the pure metals.

3. Preparation of Crucible

1. MgO·Cr₂O₃ Crucible

MgO·Cr₂O₃ was prepared from a mechanical mixture of MgO and Cr₂O₃ (1:1 molar ratio). The mixture was heated at 1 300°C in air for 2 hr. It was ascertained by an X-ray diffraction analysis that the powder thus made was MgO·Cr₂O₃ (spinel) as shown in Table 2. Any diffraction patterns corresponding to MgO or Cr₂O₃ could not be detected. The MgO·Cr₂O₃ powder was ground and mixed mechanically with a small amount of MgO powder (total MgO: 22 wt%, total Cr₂O₃: 78 wt%).

The mixture of MgO·Cr₂O₃ and MgO was suspended in ethyl alcohol and charged into magnesia crucible wrapped with a sheet of gauze. The crucible was set on the slant and rotated manually. While ethyl alcohol evaporated gradually through the porous wall of the crucible, the mixture was uniformly adhered to the inner surface. The crucible was dried in air and heated at 1 300°C for 2 hr without cracking.

Table 2. Results of X-ray analysis

MgO·Cr ₂ O ₃				β-CaCr ₂ O ₄				α-CaCr ₂ O ₄					
Obs.		ASTM 10-351		Obs.		ASTM 9-146		Obs.		ASTM 9-151		ASTM 14-444	
d (Å)	I/I _o	d (Å)	I/I _o	d (Å)	I/I _o	d (Å)	I/I _o	d (Å)	I/I _o	d (Å)	I/I _o	d (Å)	I/I _o
4.84	S	4.813	65	4.53	W	4.52	40	5.53	S	5.51	100	5.56	60
				3.45	W	3.43	40						
2.95	W	2.945	13					2.76	M	2.76	80	2.77	20
				2.65	M	2.65	80						
				2.62	S	2.62	100						
2.52	S	2.512	100					2.54	W	2.52	60	2.52	40
2.41	W	2.406	13	2.48	M	2.48	60						
								2.31	M	2.29	80	2.31	80
				2.21	W	2.21	60						
2.09	M	2.085	55	2.08	M	2.08	60	2.09	M	2.09	80	2.085	60
1.91	VW	1.912	5	1.93	W	1.925	40	1.87	M	1.866	80	1.865	100
				1.81	M	1.811	60						
1.70	VW	1.701	3	1.77	W	1.774	40						
1.60	M	1.603	40	1.64	M	1.644	80						
				1.53	M	1.526	80						
				1.51	M	1.510	80						
				1.50	M	1.497	80	1.49	M	1.490	80	1.490	60
				1.49	W	1.490	60						
				1.48	W	1.483	60	1.47	W	1.460	80	1.459	60
								1.38	M	1.382	80	1.383	20
								1.21	M	1.213	80	1.215	40

The thickness of lining was about 2 mm. The bottom of the crucible was stamped with the $\text{MgO}\cdot\text{MgO}\cdot\text{Cr}_2\text{O}_3$ mixture of about 2 g before the experiment.

2. $\alpha\text{-CaCr}_2\text{O}_4$ Crucible

The preparation of $\alpha\text{-CaCr}_2\text{O}_4$ crucible is similar to that of $\text{MgO}\cdot\text{Cr}_2\text{O}_3$ crucible. The mechanical mixture of CaO and Cr_2O_3 was heated at $1\,300^\circ\text{C}$ for 3 hr under an atmosphere of argon to convert to the powder of $\beta\text{-CaCr}_2\text{O}_4$. The patterns of X-ray diffraction are shown in Table 2. The inner surface of the crucible was lined with the powder thus made. Then the crucible was heated at $1\,700^\circ\text{C}$ for 3 hr under an atmosphere of argon. By this heat treatment $\beta\text{-CaCr}_2\text{O}_4$ was changed into $\alpha\text{-CaCr}_2\text{O}_4$ which is more stable at higher temperatures than $1\,570^\circ\text{C}$.¹³⁾ The observed diffraction patterns of $\alpha\text{-CaCr}_2\text{O}_4$ are shown in Table 2.

4. Experimental Procedure

The purpose of the present experiments was to measure the effects of pure solid phases of $\text{MgO}\cdot\text{Cr}_2\text{O}_3$ or $\alpha\text{-CaCr}_2\text{O}_4$ on the solubilities of oxygen in Fe–Cr alloys. It is, therefore, desirable to exclude any contamination of lining materials with iron oxide or iron chromite, which might be formed by oxidation of the alloys used. For this reason each experiment started from a melt containing less oxygen than an anticipated equilibrium value. Under such experimental conditions lining materials would be continuously decomposed into the melt and kept freshly. As another caution against contamination, over-heating of the melt was carefully avoided.

The charge was heated in the mixture gas of hydrogen and argon. After the charge was melted down, the atmosphere was replaced by argon. The temperature of the melt was gradually raised and held at a specified value ($1\,606^\circ$, $1\,715^\circ$, and $1\,823^\circ\text{C}$ in the case of $\text{MgO}\cdot\text{Cr}_2\text{O}_3$, and $1\,600^\circ$, $1\,700^\circ$, and $1\,800^\circ\text{C}$ in the case of CaCr_2O_4). The holding time was 90 min, which was enough to attain equilibrium, as shown in Fig. 2. A sample of chemical analysis of chromium and oxygen was taken from the melt with a silica tube. Then the temperature of the melt was raised further and the similar procedure was repeated.

The concentration of chromium in the quenched samples taken with silica tubes was determined by the volumetric method by ammonium-per-sulfate oxidation. Oxygen in the samples was determined with the combustion-coulometric method that is essentially the same as the conductivity method combined with inert gas carrier method.¹⁴⁾ Oxide inclusions in the samples were extracted with an iodine-alcohol solution. The presence of MgO and CaO in the oxide inclusions was not evidenced by an emission spectroscopy. Therefore the uncertainty of oxygen determination caused by lining material suspending in liquid alloy would be negligible.

The thin layer of oxide phases adhered to the side wall of alloys solidified in crucible after the equilibrium experiment were examined by an emission spectroscopy, X-ray diffraction method, and chemical analysis. It was found that the oxide phase contains

less iron than 0.5% in the case of $\text{MgO}\cdot\text{Cr}_2\text{O}_3$ crucible, and less iron than 1% and less magnesium than 1% in the case of $\alpha\text{-CaCr}_2\text{O}_4$. Contamination with magnesium is supposed to be originated from the magnesia crucible used as a supporter of lining.

At the preliminary experiments, an initial oxygen content in liquid alloys started from higher value than an equilibrium one, that is, the melt was held at a reaction temperature after having kept for 15 min at 50° to 100°C higher than the reaction temperature.

As shown in Fig. 2, oxygen content decreased with holding time and approached closely to that observed in the experiment previously mentioned. It is indicated that oxygen concentration in the melts attains to a constant value (equilibrium one) regardless of the direction of approach. However, the lining materials adhered to the surface of the alloys solidified in crucible after the experiments contained iron of about 5 to 10%. These results show that small amount of contaminant in the lining materials would not affect seriously equilibrium oxygen content in the present experiments.

III. Result and Discussion

1. Oxygen Content in Equilibrium

The observed values of the oxygen and chromium concentrations at each reaction temperature are shown in Figs. 3 and 4. The oxygen–chromium isothermals have minima between 5 and 10% of chromium concentration. At higher chromium concentrations, the oxygen content of the melts increases with increasing chromium one. Such behaviour of oxygen in liquid Fe–Cr alloys in equilibrium with the spinels is similar to that in equilibrium with the deoxidation products.^{3,10)} The logarithms of solubility products $([\%\text{Cr}]^2 \cdot [\%\text{O}]^3)$ calculated from the observed values

○ ● ▲: experimental points at a specified temperature
⊗ ⊙ △: experimental points after liquid alloys have kept for 15 min at a temperature of 50°C higher or lower than a specified one.

Fig. 2. Holding time to attain equilibrium

Fig. 3. Oxygen solubility in the melt in equilibrium with $\text{MgO} \cdot \text{Cr}_2\text{O}_3$

Fig. 4. Oxygen solubility in the melt in equilibrium with $\alpha\text{-CaCr}_2\text{O}_4$

Fig. 5. Relation between the values of $[\% \text{Cr}]^2 \cdot [\% \text{O}]^3$ and $[\% \text{Cr}]$ in the case where $\text{MgO} \cdot \text{Cr}_2\text{O}_3$ crucible was used

Fig. 6. Relation between the values of $[\% \text{Cr}]^2 \cdot [\% \text{O}]^3$ and $[\% \text{Cr}]$ in the case where $\alpha\text{-CaCr}_2\text{O}_4$ crucible was used

Fig. 7. Relation between activity coefficient of oxygen and chromium concentration in liquid Fe-Cr alloy

are plotted as a function of chromium concentration in Figs. 5 and 6. The solubility products seem to be apparently linear to chromium concentration up to approximately 20%. It is, however, noted that the observed data at higher chromium concentrations deviate from this linearity.

The decomposition of $\text{MgO} \cdot \text{Cr}_2\text{O}_3$ and $\alpha\text{-CaCr}_2\text{O}_4$ can be expressed by the reaction schemes,

where the underscored chemical symbols represent the elements dissolved in liquid iron and (s) indicates pure solid phase. The equilibrium constants for these reactions may, therefore, be written as

$$\log K_1 \text{ or } \log K_2 = \log a_{\text{Cr}}^2 \cdot a_{\text{O}}^3 = \log f_{\text{Cr}}^2 f_{\text{O}}^3 + \log [\% \text{Cr}]^2 \cdot [\% \text{O}]^3 \dots\dots\dots(3)$$

where K_1, K_2 : equilibrium constant for the reaction (1) and (2)

$a_{\text{Cr}}, a_{\text{O}}$: activities of chromium and oxygen

$f_{\text{Cr}}, f_{\text{O}}$: activity coefficients of chromium and oxygen

$[\% \text{Cr}], [\% \text{O}]$: wt% of chromium and oxygen in alloys.

The reference states for oxygen and chromium are the infinitely dilute solution in liquid pure iron with the compositions in weight percent.

The value of f_{Cr} can be presumed from the work of R. B. Reese, R. A. Rapp, and G. R. St. Pierre¹⁵⁾ to be unity in the whole range of chromium concentration of the present study. Because of the low concentration of oxygen in chromium-iron alloys and/or high temperature, the effect of oxygen on the value of $\log f_{\text{O}}$ is assumed to be neglected compared with the effect of chromium. On these assumptions, Eq. (3) can be expressed as follows.

$$\log K_1 \text{ or } \log K_2 = \log [\% \text{Cr}]^2 \cdot [\% \text{O}]^3 + 3 \log f_{\text{O}} \dots\dots\dots(4)$$

$$\log f_{\text{O}} = e_{\text{O}}^{\text{Cr}} [\% \text{Cr}] + q_{\text{O}}^{\text{Cr}} [\% \text{Cr}]^2 \dots\dots\dots(5)$$

The quadratic term of $[\% \text{Cr}]$ is included in Eq. (5) in order to account for the observed non-linearity between the solubility product and the content of chromium shown in Figs. 5 and 6. Terms of higher order of $[\% \text{Cr}]$ were omitted. According to Eqs. (4) and (5), the values of equilibrium constant, e_{O}^{Cr} , and q_{O}^{Cr} for both cases of $\text{MgO} \cdot \text{Cr}_2\text{O}_3$ and $\alpha\text{-CaCr}_2\text{O}_4$ and of their standard deviations at each reaction temperature are calculated with a method of least squares. The

obtained results are summarized in Table 3 and represented as full-line curves in Figs. 3 to 6.

2. Activity Coefficient

The values of the activity coefficient of oxygen, f_o , can be calculated by using the obtained values of e_o^{Cr} and q_o^{Cr} . Figure 7 shows the relations between the calculated values of f_o and chromium concentration in the alloys in equilibrium with $MgO \cdot Cr_2O_3$ at 1 606°C and $\alpha\text{-}CaCr_2O_4$ at 1 600°C. The value of the activity coefficient should be dependent only on the compositions of alloys, but not of oxide phase coexisted. The curves of f_o shown in Fig. 7, however, tend to deviate slightly from each other at high chromium concentrations. The deviation may be attributed to uncertainties in the calculated values of e_o^{Cr} and q_o^{Cr} , and to the difference of the reaction temperatures.

The values of e_o^{Cr} and q_o^{Cr} have been statistically adjusted to conform to the experimental results by a method of least squares. Therefore, the validity of f_o given by such statistical method should be checked by the values of f_o investigated with direct measurements. The values of $\log f_o$ at 1 600°C given by T. E. Turkdogan,⁴⁾ J. Chipman,⁷⁾ H. Sakao and K. Sano,³⁾ R. J. Fruehan,⁵⁾ and W. A. Fischer and M. Hassmann¹⁶⁾ are also shown in Fig. 7 for comparison. Their results were obtained from the equilibrium experiment of $H_2\text{-}H_2O/Fe\text{-}Cr$ melt and the direct measurement of oxygen activity with a solid electrolyte. As seen in Fig. 7, the present result is in excellent agreement with these of H. Sakao, J. Chipman, and R. J. Fruehan over the range of chromium concentration examined. This agreement shows that the obtained value of $\log f_o$ appears to be reliable in spite of the indirect measurement of the activity coefficient.

Differential of Eq. (5) with [%Cr] gives the following:

$$\frac{\partial \log f_o}{\partial [\%Cr]} = e_o^{Cr} + 2q_o^{Cr}[\%Cr] \dots\dots\dots(6)$$

The left hand side of Eq. (6) is a definition of interaction coefficient and is evidently equal to e_o^{Cr} at the infinite dilution of chromium. The value of e_o^{Cr} determined from the present experiments is approximately -0.051 ± 0.005 , as shown in Table 3. The reported values of the interaction coefficient at 1 600°C were

-0.048 by H. Sakao and K. Sano,³⁾ -0.053 by K. Sanbongi and K. Ōmori,¹⁷⁾ and -0.051 by J. K. Pargeter.¹⁸⁾ These values are in good agreement with the present result. However, other reported values,^{1,5,9,16,19)} except the data of T. E. Turkdogan,⁴⁾ are in the range from -0.041 to -0.031 . The discrepancy would be caused by the assumption that $\log f_o$ is proportional to chromium wt% up to relatively high concentration of chromium. This problem is related to the contribution of the quadratic term of $q_o^{Cr}[\%Cr]^2$ to $\log f_o$ in the present analysis, as shown in Eq. (5). However, the value and meaning of q_o^{Cr} have not been elucidated in earlier works. Thus further study on detailed measurement of f_o and theoretical and quantitative treatment of data will be necessary.

The present results at higher temperatures than 1 600°C could not be compared with those reported already, because little have been studied on $\log f_o$ at such high temperatures. Table 3 shows that the absolute values of $\log f_o$ decrease with increasing reaction temperature. Furthermore, it may be stated that the values of e_o^{Cr} and q_o^{Cr} obtained from the $MgO \cdot Cr_2O_3$ experiment at each reaction temperature are very close to those from the $\alpha\text{-}CaCr_2O_4$ experiment within the values of the standard deviation. Therefore, all the values of e_o^{Cr} and q_o^{Cr} obtained from both experiments can be summarized as follows.

$$e_o^{Cr} = -380/T + 0.151,$$
$$q_o^{Cr} = 10.2/T - 48.7 \times 10^{-4}$$

3. Equilibrium Constant

The obtained values of $\log K_1$ and K_2 vary linearly with the reciprocal value of the absolute temperature over the entire range studied, as shown in Fig. 8. The temperature dependencies are expressed as follows.

$$\log K_1 = -42\,470/T + 17.79 \dots\dots\dots(7)$$

$$\log K_2 = -44\,270/T + 18.57 \dots\dots\dots(8)$$

The corresponding free energy changes are, therefore, given by following equations:

$$\Delta G_1^\circ = 194\,300 - 81.4T \dots\dots\dots(9)$$

and
$$\Delta G_2^\circ = 202\,500 - 84.9T \dots\dots\dots(10)$$

Fig. 8. Temperature dependence of equilibrium constants

Table 3. Values of e_o^{Cr} , q_o^{Cr} , and equilibrium constants				
	Tempera- ture (°C)	1 606	1 715	1 823
$MgO \cdot Cr_2O_3$	$e_o^{Cr} \times 10^2$	-5.1 ± 0.5	-4.3 ± 0.6	-3.2 ± 0.1
	$q_o^{Cr} \times 10^4$	$+4.9 \pm 1.5$	$+2.7 \pm 1.6$	—
	$\log K_1$	-4.77 ± 0.12	-3.62 ± 0.17	-2.45 ± 0.07
	Tempera- ture (°C)	1 600	1 700	1 800
$\alpha\text{-}CaCr_2O_4$	$e_o^{Cr} \times 10^2$	-5.2 ± 0.6	-4.0 ± 0.4	-3.1 ± 0.1
	$q_o^{Cr} \times 10^4$	$+6.2 \pm 2.3$	$+2.4 \pm 1.3$	—
	$\log K_2$	-5.06 ± 0.1	-3.89 ± 0.1	-2.78 ± 0.1

The solid straight lines shown in Fig. 8 represent Eqs. (7) and (8), respectively. The dotted line represents the theoretical value of $\log K_1$ derived by the following procedure. J. D. Tretjakow and H. Schmelzried²⁰⁾ investigated the free energy change for the following reaction in the temperature range from 1 000° to 1 500°K.

$$\Delta G_3^\circ = -10\,270 + 1.7T \dots\dots\dots(11')$$

The free energy at steelmaking temperatures can be computed by combining Eq. (11') with the selected values of entropy and enthalpy for MgO, Cr₂O₃, and MgO·Cr₂O₃ compiled by K. K. Kelley.²¹⁾ The result is as follows.

$$\Delta G_3^\circ = -9\,400 + 1.2T \quad (\pm 500 \text{ cal/mol}) \dots\dots(12)$$

The numerical value of ΔG_3° in the temperature range studied is approximately constant to be -7 kcal/mol .

On the other hand, the equilibrium of the dissolution of Cr₂O₃ into liquid iron over the temperature range 1 600° to 1 800°C has been obtained by the present authors as follows.⁸⁾

$$\begin{aligned} \log K_4 &= \log [\% \text{Cr}]^2 \cdot [\% \text{O}]^3 + 3 \log f_{\text{O}} \\ &= -44\,040/T + 19.42 \end{aligned}$$

$$\Delta G_4^\circ = 201\,500 - 88.87T \dots\dots\dots(14)$$

Since the subtraction of Eq. (11) from Eq. (13) gives Eq. (1), the equilibrium constant, K_1 , can be calculated from Eqs. (12) and (14). The obtained result is represented as the dotted line in Fig. 7. The observed value of $\log K_1$, as shown in Fig. 7, is in good agreement with the calculated within experimental errors.

Unfortunately very little has been reported concerning thermodynamic data of $\alpha\text{-CaCr}_2\text{O}_4$. The crystal structure of $\alpha\text{-CaCr}_2\text{O}_4$ is tetragonal by the study of W. F. Ford and W. J. Rees,²²⁾ and hexagonal by F. P. Glasser and L. S. Glasser,²³⁾ while MgO·Cr₂O₃ is spinel type. The discrepancy would be due to the difference between the radii of magnesium and calcium ions. However, the difference of the free energy changes between Eqs. (9) and (10) is only about 1 kcal/mol. In other words, the free energy change for the following exchange reaction is very small.

4. Comparison with the Solubility of Oxygen in Iron in Equilibrium with Cr₂O₃

The equilibrium relation between oxygen and chromium concentrations in liquid Fe–Cr alloys in equilibrium with Cr₂O₃ is given by Eq. (14). Thus, the ratio of oxygen solubilities in Fe–Cr alloys in equilibrium with Cr₂O₃ and MgO·Cr₂O₃ can be calculated from Eqs. (14) and (7) at a given chromium concentration.

$$[\% \text{O}]_1 / [\% \text{O}]_4 = (K_1 / K_4)^{1/3}$$

Here, $[\% \text{O}]_1$ and $[\% \text{O}]_4$ are the equilibrium oxygen content in the melt coexisting with MgO·Cr₂O₃ and Cr₂O₃, respectively. The value of $(K_1 / K_4)^{1/3}$ is about 0.53 in the temperature range studied. By the similar procedure the ratio of the oxygen solubilities in equilibrium with $\alpha\text{-CaCr}_2\text{O}_4$ and Cr₂O₃ is represented by $(K_2 / K_4)^{1/3}$, and its value is about 0.48. As a whole, the solubility limits of oxygen in the melts in equilibrium with MgO·Cr₂O₃ or $\alpha\text{-CaCr}_2\text{O}_4$ may be approximately a half of that in equilibrium with Cr₂O₃.

The present result may give an explanation concerning slag–metal reactions occurred in operating furnace for stainless-steelmaking. Slag is expected to be saturated with magnesium and calcium chromites as well as solid Cr₂O₃ at the end of oxygen-gas blowing. Under such oxidizing condition, oxygen content in liquid steel approaches the equilibrium one for the Fe–Cr–O system in contact with pure solid Cr₂O₃. In the succeeding period, called “reducing period,” Cr₂O₃ is gradually reduced by silicon. Under such weakly reducing condition, magnesium and calcium chromites in slag would control oxygen content in liquid steel according to the equilibrium relations of Eqs. (7) and (8).

The following reaction scheme is available for understanding of various slag–metal reactions:

The equilibrium constant for the reaction is given by

$$K = a_{\text{Cr}}^2 \cdot a_{\text{O}}^3 / a_{\text{Cr}_2\text{O}_3} (= K_4)$$

where $a_{\text{Cr}_2\text{O}_3}$ is the activity of Cr₂O₃ and defined as unity for pure solid state. Furthermore, it is noted that the values of (K_1 / K_4) and (K_2 / K_4) described already are just equivalent to that of the activity of Cr₂O₃ component in MgO·Cr₂O₃ and $\alpha\text{-CaCr}_2\text{O}_4$, respectively.

IV. Conclusion

The solubilities of oxygen in liquid Fe–Cr alloys in equilibrium with solid MgO·Cr₂O₃ and $\alpha\text{-CaCr}_2\text{O}_4$ were studied as a function of chromium concentrations in the range from about 3 to 30% of chromium and at the temperatures from 1 600° to 1 823°C. The conclusions are as follows.

(1) The solubilities of oxygen at a given concentration of chromium are approximately a half of that in the Fe–Cr–O system in contact with pure solid Cr₂O₃.

(2) The free energy changes for the decomposition of MgO·Cr₂O₃ and $\alpha\text{-CaCr}_2\text{O}_4$ are expressed as follows.

* As a result, the value of the free energy change for the reduction of $\alpha\text{-CaCr}_2\text{O}_4$ with a reducing element dissolved in liquid iron (*e.g.*, C, Al, Si, etc.) is expected to be almost the same as that of MgO·Cr₂O₃.

$$\Delta G^\circ = 202\,500 - 84.9T$$

(3) The corresponding equilibrium constants are, respectively:

$$\begin{aligned}\log K &= \log [\% \text{Cr}]^2 \cdot (f_{\text{O}}[\% \text{O}])^3 \\ &= -42\,470/T + 17.79\end{aligned}$$

and

$$\begin{aligned}\log K &= \log [\% \text{Cr}]^2 \cdot (f_{\text{O}}[\% \text{O}])^3 \\ &= -44\,270/T + 18.57\end{aligned}$$

(4) The activity coefficient of oxygen dissolved in liquid Fe-Cr alloys is represented by the following quadratic equation of chromium concentration.

$$\log f_{\text{O}} = e_{\text{O}}^{\text{Cr}}[\% \text{Cr}] + q_{\text{O}}^{\text{Cr}}[\% \text{Cr}]^2$$

The obtained values of e_{O}^{Cr} and q_{O}^{Cr} are shown in Table 3. The temperature dependencies are as follows.

$$e_{\text{O}}^{\text{Cr}} = -380/T + 0.151$$

$$q_{\text{O}}^{\text{Cr}} = 10.2/T - 48.7 \times 10^{-4}$$

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