Thermodynamics of Molten Fe–Cr–C_{satd.} Alloy

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The activity of chromium in molten Fe–Cr–C_{satd.} alloy has been measured at temperatures ranging from 1 548 to 1 773 K by a chemical equilibrium technique. There is little temperature dependence of the activity of chromium in the region of low chromium contents by weight, and the activity coefficient of chromium decreases as the chromium content increases.

The activity coefficient of chromium in silver, which was needed for the foregoing measurement, was predetermined.

By thermodynamic discussion in combination with the carbon solubility in molten iron–chromium alloys, the expression for the activity coefficient of chromium in Fe–Cr–C_{satd.} alloy has been obtained as a function of chromium content and temperature as follows.

$$\ln \gamma_{\text{Cr(s)}} = -2.52 + \frac{3880}{T} + \left(8.31 - \frac{23300}{T}\right) X_{\text{Cr}} + \left(-4.21 + \frac{14900}{T}\right) X_{\text{Cr}}^2 \quad (1623 \text{ to } 1773 \text{ K})$$

The standard Gibbs energy of mixing of Fe–Cr–C_{satd.} alloy was also estimated using the Gibbs–Duhem relationship, indicating that chromium and manganese behave similarly in terms of affinity for carbon and iron in molten carbon-saturated iron.

KEY WORDS: chromium-containing hot metal; chromium activity; carbon solubility; the Gibbs–Duhem relationship; the standard Gibbs energy of mixing.

1. Introduction

Recently, a smelting reduction technology of chromite ore has been developed as a new process of making stainless steels. For proper understanding of this process, the thermodynamic properties of chromium in molten Fe–Cr–C_{satd.} alloy is very important. For example, the activity data make possible to control smelting reduction operation and to give optimal refining conditions of chromium-containing hot metal.

There are many investigations^{1–3)} and estimations^{4,5)} about the activities of carbon and chromium in the Fe–Cr–C ternary system. The experimental measurement of the chromium activity for molten Fe–Cr–C_{satd.} alloy, however, has not been reported at temperatures lower than 1 773 K. In this study, the activity of chromium in molten Fe–Cr–C_{satd.} alloy has been measured by a chemical equilibration technique over a wide range of temperatures including those for hot metal pretreatment. In prior to the experiment, the activity coefficient of chromium in silver, which was necessary for determination of the activity of chromium, was measured.

An expression for the activity coefficient of chromium in molten Fe–Cr–C_{satd.} alloy was derived as a function of the chromium content and temperature by thermodynamically strict regression using the data for the carbon solubility and the Gibbs–Duhem relationship.

The standard Gibbs energy of mixing of Fe–Cr–C_{satd.} alloy was also calculated and compared with that of Fe–Mn–C_{satd.} alloy.

2. Principle

The principle of measuring the activity of chromium in molten Fe–Cr–C_{satd.} alloy is as follows. When molten Fe–Cr–C_{satd.} and Ag–Cr alloy are in equilibrium, both have the same activity of chromium as expressed by Eq. (1):

$$a_{\text{Cr in Fe–Cr–C}_{\text{satd.}}} = a_{\text{Cr in Ag}} \quad \dots\dots\dots(1)$$

The activity of chromium in Fe–Cr–C_{satd.} alloy can be derived according to Eq. (2) by measuring the chromium equilibrium content of Ag–Cr alloy and using the value for the activity coefficient of chromium in silver.

$$a_{\text{Cr in Ag}} = \gamma_{\text{Cr in Ag}} \cdot X_{\text{Cr in Ag}} \quad \dots\dots\dots(2)$$

where γ_{Cr} and X_{Cr} are the activity coefficient relative to pure solid chromium and the mole fraction of chromium in silver, respectively. Since the activity coefficient of chromium in silver has not been well known, we have measured it by equilibrating silver with solid Cr₂O₃ in a CO/CO₂ atmosphere on the basis of Eq. (3).

$$\Delta G^\circ = -267400 - 8.41T \quad (\text{J/mol})^{(6)} \quad \dots\dots(4)$$

$$\Delta G^\circ = RT[2 \ln(\gamma_{\text{Cr}} \cdot X_{\text{Cr}}) - 3 \ln(P_{\text{CO}}/P_{\text{CO}_2})] \quad \dots\dots(5)$$

According to Eqs. (4) and (5), the activity coefficient of chromium can be calculated from the chromium content of silver and the ratio of P_{CO} to P_{CO_2} .

3. Experimental

The experimental apparatus consisted of a SiC electric resistance furnace which is connected to a proportional-integral-differential (PID) controller with a Pt/6%Rh-Pt/30%Rh thermocouple. The temperature was controlled within ± 1 K over a length of 50 mm in a mullite tube (50-mm o.d., 42-mm i.d., 1000-mm length) in the center of the furnace. The same apparatus was used in the two measurements described below.

3.1. Activity Coefficient of Chromium in Silver

A silver-chromium alloy with various chromium contents was prepared by mixing metallic chromium (99.2% purity) and silver (99.9% purity) in an alumina crucible placed in a graphite holder in a CO atmosphere at 1673 K for 24 hr. Thus, chromium content of the alloy was adjusted between 40 and 600 ppm. Seven grams of the silver-chromium alloy and 1 g of reagent grade Cr_2O_3 densely compressed to a pellet were equilibrated in an alumina crucible (15-mm o.d., 12-mm i.d., 50-mm length) in a CO/CO₂ atmosphere at temperatures ranging from 1573 to 1773 K. The equilibration time was determined to be 48 hr from the results of the preliminary experiments. The $P_{\text{CO}}/P_{\text{CO}_2}$ was selected between 44 and 100. After equilibration, the alumina crucible was rapidly withdrawn from the furnace and cooled in flushing argon. The chromium content of silver was analyzed by atomic absorption spectrometry.

3.2. The Activity of Chromium in Molten Fe-Cr-C_{satd.} Alloy

Carbon-saturated chromium iron alloy with various chromium contents was synthesized as follows. Preliminarily, carbon-unsaturated chromium iron alloy was prepared by mixing metallic chromium (99.2% purity), high purity electrolytic iron (99.99% purity) and graphite powder in an alumina crucible placed in a graphite holder in a CO atmosphere at 1673 K for 12 hr to avoid the formation of iron-chromium carbide. Subsequently, it was mixed with carbon saturated iron to be diluted to intended chromium content and subjected to the experiment. A silver-chromium alloy was prepared in the same fashion as described in Sec. 3.1. Three grams of Fe-Cr-C_{satd.} alloy and 7 g of silver-chromium alloy were equilibrated in an Ar atmosphere at temperatures ranging from 1548 to 1773 K. The holding time was determined to be 24 hr from the results of the preliminary experiments. After equilibration, the graphite crucible was quickly withdrawn and water-cooled by quenching in a water bath to avoid the precipitation of iron-chromium carbide. The chromium contents of Fe-Cr-C_{satd.} alloy and that of silver were analyzed by titration with potassium permanganate and atomic absorp-

tion spectrometry, respectively. The carbon content of Fe-Cr-C_{satd.} alloy was also determined by a LECO analyzer.

4. Results

4.1. Activity Coefficient of Chromium in Silver

The experimental results are listed in Table 1. Figure 1 shows the relationship between mole fraction of chromium in silver and the activity of chromium derived from the $P_{\text{CO}}/P_{\text{CO}_2}$ ratio and Eq. (4), at various temperatures. Confirming that Henry's law holds from linear correlation obtained at 1573, 1673, and 1773 K in Fig. 1, the activity coefficients of chromium in silver at infinite dilute solution, $\gamma_{\text{Cr(s)}}^\circ$, were determined as listed in Table 1.

The dependence of activity coefficient on temperature is shown in Fig. 2 by plotting logarithmic of activity coefficient against the reciprocal of temperature. The activity coefficient as a function of temperature ranging from 1573 to 1773 K is expressed as Eq. (6) by linear regression.

Table 1. The experimental results for the measurement of the activity coefficient of chromium in silver.

Temperature (K)	$P_{\text{CO}}/P_{\text{CO}_2}$	Cr (mass ppm)	$X_{\text{Cr}} \times 10^6$	$\gamma_{\text{Cr(s)}}^\circ$
1573	50	18.2	37.7	204
	80	36.0	74.7	
	100	55.0	114	
	50	18.4	38.1	
	80	36.3	75.3	
1623	100	55.9	116	184
	44	22.7	47.1	
	44	22.7	47.1	
1673	62	61.7	128	156
	44	35.3	73.2	
1723	44	53.0	110	140
1773	60	126	262	124
	44	77.1	160

Fig. 1. Relationship between X_{Cr} and a_{Cr} in Ag.

Fig. 2. The activity coefficient of Cr in Ag as a function of temperature.

$$\log \gamma_{\text{Cr(s)}}^{\circ} = \frac{3080}{T} + 0.356 \quad (1573 \text{ to } 1773 \text{ K}) \quad \dots (6)$$

Equation (6) was used in the following measurements.

4.2. The Activity of Chromium in Molten Fe–Cr–C_{satd.} Alloy

The experimental results are listed in Table 2. The measurement is limited up to a certain chromium content due to the formation of (Cr, Fe)₇C₃ according to the Fe–Cr–C ternary phase diagram.⁷⁾ The activities of chromium are plotted in Fig. 3 together with those of other investigators.^{5,8,9)} In the region of low chromium content by weight, little temperature dependence of the activity of chromium is observed. The activity coefficient of chromium decreases as the chromium content increases at each temperature. Although this trend agrees with the results of Ohtani, the present results show higher activities than those by Ohtani at the content above approximately 8 mass%.

In order to confirm the carbon saturation, the carbon content of several samples at the temperatures over 1623 K was also measured. The results are listed in Table 2 and the relationships between the mole fraction of chromium and the carbon solubility are plotted in Fig. 4, together with those by Matoba *et al.*¹⁰⁾ The carbon saturation was confirmed by good agreement between both results.

5. Discussion

As shown in Fig. 3, several investigations^{5,8,9)} have been reported for this system. These are divided roughly into the following two trends in terms of the activity coefficient of chromium. The results of Ohtani⁹⁾ and present work show the decrease in the activity coefficient with increasing chromium content, whereas others show relative constancy. The former is experimentally obtained and the latter is extrapolation from the measurement

Table 2. The experimental results for the measurement of the activity of chromium in Fe–Cr–C_{satd.} alloy.

Temperature (K)	Cr in alloy (mass%)	C in alloy (mass%)	Cr in Ag (mass ppm)	$a_{\text{Cr(s)}}$
1548	2.23	—	28.2	0.0130
	3.83	—	54.7	0.0251
	5.75	—	85.2	0.0392
	8.56	—	111	0.0510
	10.7	—	114	0.0524
	8.50	—	108	0.0497
1573	2.91	—	45.8	0.0196
	11.5	—	143	0.0609
	7.57	—	106	0.0453
	12.6	—	137	0.0586
	7.80	—	109	0.0464
	14.1	—	145	0.0620
1598	2.64	—	39.0	0.0155
	5.65	—	89.0	0.0354
	7.40	—	110	0.0438
	12.8	—	141	0.0562
	10.1	—	137	0.0546
1623	3.54	5.00	59.0	0.0220
	6.77	5.30	101	0.0376
	9.79	5.48	146	0.0543
	11.5	5.68	147	0.0547
	14.2	—	139	0.0517
	15.5	5.78	145	0.0539
1673	11.4	—	160	0.0522
	11.0	—	157	0.0513
	4.31	—	74.1	0.0242
	18.4	—	180	0.0588
	3.45	—	66.1	0.0216
	12.7	5.88	164	0.0535
	16.5	6.20	185	0.0604
	19.3	6.33	176	0.0575
	6.25	5.40	98.2	0.0320
	8.22	5.53	—	—
1773	6.14	—	111	0.0285
	10.6	6.06	186	0.0479
	17.1	6.49	227	0.0582
	19.9	6.57	245	0.0631
	23.3	7.01	231	0.0594
	21.3	6.85	239	0.0614

performed in low carbon contents⁸⁾ or estimation based on “sub-lattice model”.⁵⁾

The relationship between the mole fraction and the activity coefficient of chromium in Fig. 5 shows that the activity coefficient of chromium decreases with increasing chromium content at each temperature.

At carbon saturation, the carbon solubility and the activity coefficient of chromium and iron thermodynamically are interrelated as described below.

$$\ln \gamma_{\text{Cr(s)}} = A + BX_{\text{Cr}} + CX_{\text{Cr}}^2 \quad \dots (7)$$

$$\ln \gamma_{\text{Fe(s)}} = D + EX_{\text{Cr}} + FX_{\text{Cr}}^2 \quad \dots (8)$$

$$X_{\text{C}} = \alpha + \beta X_{\text{Cr}} \quad \dots (9)$$

$$X_{\text{C}} d \ln \gamma_{\text{C(s)}} + X_{\text{Cr}} d \ln \gamma_{\text{Cr(s)}} + X_{\text{Fe}} d \ln \gamma_{\text{Fe(s)}} = 0 \quad \dots (10)$$

Suppose the activity coefficients of chromium and iron can be expressed approximately by the quadratic form

Fig. 3. Relationship between chromium content by weight and a_{Cr} in Fe-Cr- $C_{satd.}$ alloy.

Fig. 4. Solubility of carbon in iron-chromium alloy.

as Eqs. (7) and (8) and the carbon saturation content by a linear function of chromium content as Eq. (9), the coefficients of these equations are restrained by the following relationships derived from the Gibbs-Duhem equation described as Eq. (10), where the activity coefficient of carbon is the reciprocal of the mole fraction of carbon since the activity of carbon is unity.

$$C = F(1 + \beta) \quad \text{.....(11)}$$

$$B + 2F(1 - \alpha) = E(1 + \beta) \quad \text{.....(12)}$$

$$E(1 - \alpha) = \beta \quad \text{.....(13)}$$

Considering good agreement between the results of the present work and those by other investigators¹⁰⁾ regarding the carbon saturation contents shown in Fig. 4, B and C of the Eq. (7) can be related as Eqs. (14)–(16) at each temperature by fixing the values for α and β which can be determined by a linear regression of the

Fig. 5. Relationship between the mole fraction and the activity coefficient of chromium in Fe-Cr- $C_{satd.}$ alloy.

carbon solubility data in iron-chromium alloy shown in Fig. 4 and that of iron¹¹⁾ as are described as Eqs. (17)–(19).

$$B = 0.385 - 1.30C \text{ at } 1623 \text{ K} \quad \text{.....(14)}$$

$$B = 0.423 - 1.27C \text{ at } 1673 \text{ K} \quad \text{.....(15)}$$

$$B = 0.430 - 1.26C \text{ at } 1773 \text{ K} \quad \text{.....(16)}$$

$$X_C = 0.189 + 0.250X_{Cr} \text{ at } 1623 \text{ K} \quad \text{.....(17)}$$

$$X_C = 0.193 + 0.269X_{Cr} \text{ at } 1673 \text{ K} \quad \text{.....(18)}$$

$$X_C = 0.202 + 0.271X_{Cr} \text{ at } 1773 \text{ K} \quad \text{.....(19)}$$

Using these relationships, the values for A , B , C , E , and F were determined as Eqs. (20)–(22) at each temperature by the second order regression of the experimental data shown in Fig. 5, leading to Eq. (23) as a function of temperature.

$$\ln \gamma_{Cr(s)} = -0.113 - 6.21X_{Cr} + 5.08X_{Cr}^2 \quad 1623 \text{ K} \quad \text{... (20)}$$

$$\ln \gamma_{Cr(s)} = -0.218 - 5.41X_{Cr} + 4.59X_{Cr}^2 \quad 1673 \text{ K} \quad \text{... (21)}$$

$$\ln \gamma_{Cr(s)} = -0.321 - 4.93X_{Cr} + 4.26X_{Cr}^2 \quad 1773 \text{ K} \quad \text{... (22)}$$

$$\ln \gamma_{Cr(s)} = -2.52 + \frac{3880}{T} + \left(8.31 - \frac{23300}{T} \right) X_{Cr} + \left(-4.21 + \frac{14900}{T} \right) X_{Cr}^2 \quad (1623 \text{ to } 1773 \text{ K}) \quad \text{.....(23)}$$

The relationships based on Eq. (23) are drawn in Fig. 5 as the curves for three temperature levels.

Although Eq. (23) has been derived from the data at temperatures over 1623 K at which the carbon solubilities were experimentally obtained, the extrapolation to lower temperatures may be reasonable because the range of temperature for its determination was as wide as 150 K.

A further thermodynamic discussion on the Fe-Cr- $C_{satd.}$ alloy can be made regarding the standard Gibbs

Fig. 6. The standard Gibbs energy of mixing in the Fe-Cr-C_{satd.} and Fe-Mn-C_{satd.} systems at 1673 K.

energy of mixing. At carbon saturation, the activity coefficient of iron for this system can be derived as Eq. (24) by the method described in the preceding paragraph combining the activity coefficient of chromium in molten Fe-Cr-C_{satd.} alloy, the carbon solubility of iron,¹¹⁾ and the activity coefficient of iron in the molten carbon-saturated iron¹²⁾ which corresponds to D .

$$\ln \gamma_{\text{Fe(s)}} = -0.320 + 0.323X_{\text{Cr}} + 3.74X_{\text{Cr}}^2 \quad \text{at } 1673 \text{ K} \quad (24)$$

Combining the iron and chromium activities derived from Eqs. (23) and (24), respectively, the standard Gibbs energy of mixing can be calculated as Eq. (25), where the last term in the parenthesis on the right side can be discarded at carbon saturation.

$$\Delta G^M = RT(X_{\text{Cr}} \ln a_{\text{Cr}} + X_{\text{Fe}} \ln a_{\text{Fe}} + X_{\text{C}} \ln a_{\text{C}}) \quad \dots\dots(25)$$

The calculated ΔG^M as a function of the mole fraction of chromium in Fe-Cr-C_{satd.} alloy at 1673 K is drawn in Fig. 6, together with that of Fe-Mn-C_{satd.} alloy using the data for the manganese activity.¹³⁾ The curves for both alloys drawn in Fig. 6 are very close, indicating that chromium and manganese behave similarly in molten carbon-saturated iron because of their similarity of the nature in terms of the affinity for carbon and iron.

6. Conclusions

The activity of chromium in molten Fe-Cr-C_{satd.} alloy and the activity coefficient of chromium in silver have been measured by a chemical equilibrium technique. The

results can be summarized as follows:

(1) The temperature dependence of the activity coefficient of chromium in silver is expressed as follows:

$$\log \gamma_{\text{Cr(s)}}^\circ = \frac{3080}{T} + 0.356 \quad (1573 \text{ to } 1773 \text{ K})$$

(2) The activities of chromium in molten Fe-Cr-C_{satd.} alloy have been measured at temperatures ranging from 1548 to 1773 K. Temperature dependence of activity is found to be small in the region of low chromium content by weight. The activity coefficient of chromium decreases with increasing chromium content.

(3) Combining the data for the carbon solubility in iron-chromium alloys, a thermodynamically strict approximation can be performed regarding the activity coefficient of chromium using the Gibbs-Duhem equation, and the following expression for the activity coefficient of chromium was obtained as a function of chromium content and temperature:

$$\ln \gamma_{\text{Cr(s)}} = -2.52 + \frac{3880}{T} + \left(8.31 - \frac{23300}{T}\right)X_{\text{Cr}} + \left(-4.21 + \frac{14900}{T}\right)X_{\text{Cr}}^2 \quad (1623 \text{ to } 1773 \text{ K})$$

(4) The standard Gibbs energy of mixing of Fe-Cr-C_{satd.} is estimated to be close to that of Fe-Mn-C_{satd.}

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