Metallurgy

Carbon Solubility and Mass Action Concentrations of Fe-Cr-C Melts

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Abstract: An empirical equation of carbon solubility in Fe-Cr-C melts is regressed based on the experimental data from references. A calculating model of mass action concentrations for these melts is formulated on the basis of the coexistence theory of metallic melts involving compound formation, the phase diagram of Cr-C system as well as thermodynamic data of Fe-Cr-C melts. According to the model, the standard Gibbs free energies of formation of CrC and Cr_3C_2 are obtained. Satisfactory agreement between the calculated and measured values shows that the model can reflect the structural characteristics of Fe-Cr-C melts.

Key words: activity; coexistence theory; mass action concentration; saturated state

Fe-Cr-C melts are the key melts that the production of ferrochrome depends on. They also give direction to the manufacturing of stainless steel, bearing steel and steels containing chromium. This is the reason why many metallurgists pay much attention to studying them. Up to now, the research on the phase diagram of Cr-C results in relatively consistent conclusions [1-4], and the solubility of carbon in Fe-Cr-C melts have been investigated by different scholars, though their results are inconsistent yet [5-7]. In addition, the activities of these melts have been studied [8-11], and useful empirical equations have been obtained for calculation of the activities. However, theoretical models based on the mass action law haven't seen yet in references. The aim of this paper is to formulate an empirical equation of carbon solubility and the calculating model of mass action concentrations in Fe-Cr-C melts on the basis of aforementioned experimental results as well as the coexistence theory of metallic melts structure involving compound formation.

1 Empirical Equation of Carbon Solubility

There are experimental data of carbon solubility in Fe-Cr-C melts, in which, the temperatures range from 1 550 to 1 800°C, the mass fraction of chromium from 0 to 85.4%, and the mass fraction of carbon from 5.36% to 11.81% [5]. The experimental data of carbon solubility in Fe-Cr-C melts at 1 500°C also exist in reference [12]. But in both cases there isn't any empirical equation of carbon solubility in these melts yet. Therefore, it is worthwhile to treat these experimental data by regression and an empirical relationship of carbon solubility with temperature and mass fraction of chromium is obtained as

$$[\%C] = 12.629\,23 - 13\,133.9/T + 0.063\,996\,[\%Cr]$$

$$(R = 0.995\,936,\ F = 2\,446.605).$$

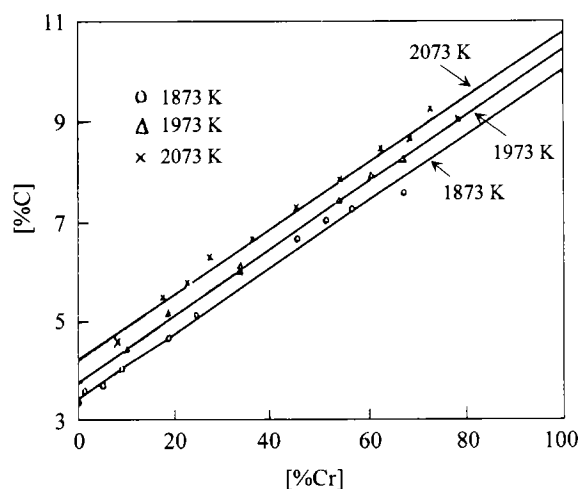**Figure 1** shows this relationship. From the figure, it

Figure 1 Relationship between carbon solubility and temperature as well as [%Cr].

is seen that carbon solubility increases with the increases of temperature and chromium mass fraction, for the increase of chromium mass fraction promotes the formation of greater amount of chromium carbides, which fix carbon in the melts, and the increase of temperature facilitates the solution of chromium carbides in the melts. According to this empirical equation, the carbon solubility of Fe-Cr melts with different chromium mass fraction can be easily predicted.

2 Mass Action Concentrations

2.1 Structural units

According to reference [13], there are metastable carbides FeC, Fe$_2$C, Fe$_3$C and FeC$_2$ in Fe-C melts, where it also gives the relationships between the standard Gibbs free energies of formation $\Delta G^\ominus$ and the temperature for these carbides.

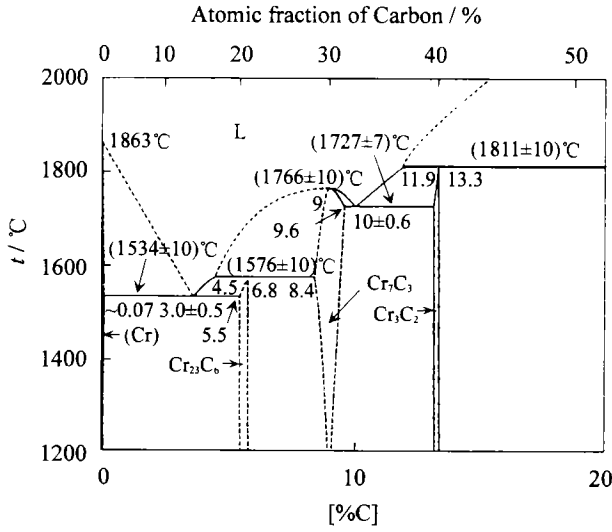It can be seen from **figure 2** [1], that there are chro-

Atomic fraction of Carbon / %

Figure 2 Phase diagram for Cr-C system.

mium carbides Cr$_3$C$_2$, Cr$_7$C$_3$ and Cr$_{23}$C$_6$ in the Cr-C melts, from which Cr$_7$C$_3$ has congruent melting point, while Cr$_3$C$_2$ and Cr$_{23}$C$_6$ are peritectoids. In addition, it is also shown that Cr$_3$C and probably CrC exists in Cr-C binary system.

References [2–4] not only shows the existence of FeCr, CrC, Cr$_3$C$_2$, Cr$_7$C$_3$, Cr$_3$C and Cr$_{23}$C$_6$ in Fe-Cr-C melts, but also give us their pertinent thermodynamic parameters.

From the above mentioned, the structural units can be determined as FeCr, FeC, CrC, Cr$_3$C$_2$, Fe$_2$C, Cr$_7$C$_3$, Fe$_3$C, Cr$_3$C, Cr$_{23}$C$_6$ and FeC$_2$.

2.2 Calculating model

Assuming the composition of reactants $b_1=\Sigma x_{Fe}$, $b_2=\Sigma x_{Cr}$, $a=\Sigma x_C$; the composition of products $x_1=x_{Fe}$, $x_2=x_{Cr}$, $y=x_C$, $z_1=x_{FeCr}$, $z_2=x_{FeC}$, $z_3=x_{CrC}$, $u=x_{Cr_3C_2}$, $w=x_{Fe_2C}$, $v=x_{Cr_7C_3}$, $g_1=x_{Fe_3C}$, $g_2=x_{Cr_3C}$, $r=x_{Cr_{23}C_6}$, $s=x_{FeC_2}$; the mass action concentrations of the melts (mole fractions of the melts after normalization $N_i=x_i/\Sigma x$) $N_1=N_{Fe}$, $N_2=N_{Cr}$, $N_3=N_C$, $N_4=N_{FeCr}$, $N_5=N_{FeC}$, $N_6=N_{CrC}$, $N_7=N_{Cr_3C_2}$, $N_8=N_{Fe_2C}$, $N_9=N_{Cr_7C_3}$, $N_{10}=N_{Fe_3C}$, $N_{11}=N_{Cr_3C}$, $N_{12}=N_{Cr_{23}C_6}$, $N_{13}=N_{FeC_2}$; Σx = the sum of equilibrium mole fractions. Then the chemical equilibria are given as
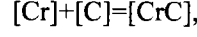
[Fe]+[Cr]=[FeCr],
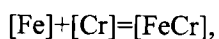
$$K_1=\frac{N_4}{N_1N_2}, \quad N_4=K_1N_1N_2, \quad z_1=\frac{K_1x_1x_2}{\Sigma x}, \tag{1}$$

$\Delta G^\ominus=-14\,550+14.196\,T$ (J/mol) [2,14].

[Fe]+[C]=[FeC],
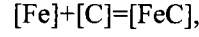
$$K_2=\frac{N_5}{N_1N_3}, \quad N_5=K_2N_1N_3, \quad z_2=\frac{K_2x_1y}{\Sigma x}, \tag{2}$$

$\Delta G^\ominus=-97\,043+11.63\,T$ (J/mol) [13].

[Cr]+[C]=[CrC],

$$K_3=\frac{N_6}{N_2N_3}, \quad N_6=K_3N_2N_3, \quad z_3=\frac{K_3x_2y}{\Sigma x}, \tag{3}$$

$\Delta G^\ominus=-90\,526-25.911\,6\,T$ (J/mol) [2].

3[Cr]+2[C]=[Cr$_3$C$_2$],

$$K_4=\frac{N_7}{N_2^3N_3^2}, \quad N_7=K_4N_2^3N_3^2, \quad u=\frac{K_4x_2^3y^2}{(\Sigma x)^4}, \tag{4}$$

$\Delta G^\ominus=-89\,999-17.2\,T$ (J/mol) [14],

$\Delta G^\ominus=-79\,177.765-16.939\,T$ (J/mol) [15],

$\Delta G^\ominus=-347\,273.963-199.709\,435\,T+39.654\,6\,T\ln T -$

$0.034\,857\,25\,T^2+4.431\,63\times10^{-6}\,T^3+$

$7.128\,45\times10^{-21}\,T^7-5\,542\,950/T+5.286\times10^8/T^2-$
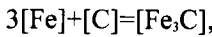
$2.4\times10^{10}/T^3$ (J/mol) [2].

2[Fe]+[C]=[Fe$_2$C],
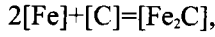
$$K_5=\frac{N_8}{N_1^2N_3}, \quad N_8=K_5N_1^2N_3, \quad w=\frac{K_5x_1^2y}{(\Sigma x)^2}, \tag{5}$$

$\Delta G^\ominus=-155\,707+45.4\,T$ (J/mol) [13].

7[Cr]+3[C]=[Cr$_7$C$_3$],

$$K_6=\frac{N_9}{N_2^7N_3^3}, \quad N_9=K_6N_2^7N_3^3, \quad v=\frac{K_6x_2^7y^3}{(\Sigma x)^9}, \tag{6}$$

$\Delta G^\ominus=-188\,790-18.54\,T$ (J/mol) [14].

3[Fe]+[C]=[Fe$_3$C],

$$K_7=\frac{N_{10}}{N_1^3N_3}, \quad N_{10}=K_7N_1^3N_3, \quad q_1=\frac{K_7x_1^3y}{(\Sigma x)^3}, \tag{7}$$

$\Delta G^\ominus=-159\,302+29.23\,T$ (J/mol) [13].

3[Cr]+[C]=[Cr$_3$C],
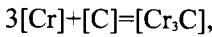
$$K_8=\frac{N_{11}}{N_2^3N_3}, \quad N_{11}=K_8N_2^3N_3, \quad q_2=\frac{K_8x_2^3y}{(\Sigma x)^3}, \tag{8}$$

$\Delta G^\ominus=-219\,768.79+100.54\,T-9.32\,T\ln T+$

$2.628\,2\times10^{-3}\,T^2-7.128\,45\times10^{-21}\,T^7$ (J/mol).

23[Cr]+6[C]=[Cr$_{23}$C$_6$],

$$K_9=\frac{N_{12}}{N_2^{23}N_3^6}, \quad N_{12}=K_9N_2^{23}N_3^6, \quad r=\frac{K_9x_2^{23}y^6}{(\Sigma x)^{28}}, \tag{9}$$

$\Delta G^\ominus=-411\,480-38.55\,T$ (J/mol) [14].

[Fe]+2[C]=[FeC$_2$],
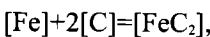
$$K_{10}=\frac{N_{13}}{N_1 N_3^2}, \quad N_{13}=K_{10}N_1 N_3^2, \quad s=\frac{K_{10}x_1 y^2}{(\Sigma x)^2}, \quad (10)$$

$$\Delta G^{\ominus}=-40\,681+172.93\,T\,(\text{J/mol})\,[13].$$

The mass balance:

$$N_1+N_2+N_3+N_4+N_5+N_6+N_7+N_8+N_9+N_{10}+N_{11}+$$

$$N_{12}+N_{13}-1=0 \quad (11)$$

$$b_1=x_1+z_1+z_2+2w+3q_1+s=\Sigma x\,(N_1+N_4+N_5+2N_8+3N_{10}+N_{13})$$

$$\quad (12)$$

$$b_2=x_2+z_1+z_3+3u+7v+3q_2+23r=$$

$$\Sigma x\,(N_2+N_4+N_6+3N_7+7N_9+3N_{11}+23N_{12}) \quad (13)$$

$$a=y+z_2+z_3+2u+w+3v+q_1+q_2+6r+2s=$$

$$\Sigma x\,(N_3+N_5+N_6+2N_7+N_8+3N_9+N_{10}+N_{11}+6N_{12}+2N_{13})$$

$$\quad (14)$$

From equations (12) and (14),

$$a(N_1+N_4)+(a-b_1)N_5-b_1(N_3+N_6+2N_7+3N_9+N_{11}+6N_{12})+$$

$$(2a-b_1)N_8+(3a-b_1)N_{10}+(a-2b_1)N_{13}=0 \quad (15)$$

From equations (13) and (14),

$$a(N_2+N_4)-b_2(N_3+N_5+N_8+N_{10}+2N_{13})+(a-b_2)N_6+$$

$$(3a-2b_2)N_7+(7a-3b_2)N_9+(3a-b_2)N_{11}+$$

$$(23a-6b_2)N_{12}=0 \quad (16)$$

The preceding equations are the calculating model of mass action concentrations of Fe-Cr-C melts. In order to use this model to calculate, one of the following schemes is recommended:

(1) Combining equations (1)–(14) as a coupled equation and solving it;

(2) Combining equations (1)–(11), (15) and (16) as a coupled equation and solving it;

(3) Solving the coupled equations (11), (15) and (16).

After the solution by scheme (1), it is necessary to use the following equations for transforming the results into the mass action concentrations.

$$N_{Fe}=N_1=x_1/\Sigma x, \quad N_{Cr}=N_2=x_2/\Sigma x, \quad N_C=N_3=y/\Sigma x \quad (17)$$

As there is limitation of carbon solubility in these melts, if the carbon solubility reaches this limit, then it will become saturated ($a_C=1$). So the calculated N_C can only be called the mass action concentration of carbon during chemical reaction, while the mass action concentration of carbon after saturation and phase separation N_C' should be calculated by considering the transforming coefficient from pure carbon to its saturated standard state L_C.

$$N'_C=L_C N_C=N_C/N_{C,sat}, \quad L_C=1/N_{C,sat} \quad (18)$$

where $N_{C,sat}$ is the mass action concentration of carbon in case of carbon saturation.

L_C has intimate relation with the temperature and the mole fractions of carbon and chromium of the melts. After multivariable regression, the following relationships are obtained:

For carbon saturated Fe-Cr-C melts,

$$L_C=\exp\,[-16.959\,9-10.932\,1\,\ln a+(25\,808.78-$$

$$198\,208\,a+631\,587.6\,a^2+91\,372.52\,b_2+$$

$$61\,263.55\,b_2^2-404\,431\,ab_2)/T],$$

$$(R=0.993\,443,\,F=476.193\,9) \quad (19)$$

For carbon saturated and unsaturated Fe-Cr-C melts,

$$L_C=\exp\,[-1.659\,393\times10^{-4}-0.364\,120\,5\,\ln a+$$

$$9\,413.717/T+(-7.977\,966+19\,341.56/T)b_1 b_2+$$

$$(-252.019\,1+279\,634.3/T)ab_1+(315.465\,1-$$

$$292\,925.2/T)ab_1^2+(-192.430\,4+264\,999.8/T)ab+$$

$$(336.291\,5-500\,651.8/T)a^2b_1+(60.142\,66-$$

$$2\,645.986/T)ab_2+(864.871\,9-2\,791\,523/T)a^2b_2^3+$$

$$(-44\,675.88+9.723\,217\times10^7/T)a^3b_2^7+(-313.281+$$

$$681\,187.2/T)ab_2^3+(3.316\,329\times10^9-6.927\,093\times$$

$$10^{12}/T)a^6b_2^{23}],\,(R=0.999\,729\,196,\,F=4\,781.785) \quad (20)$$

On account of great difference between the K_4 values (from equation (4)) calculated by thermodynamic data from three references [2,15,16], equations (11), (15) and (16) are transformed to the following form so as to get the thermodynamic data reasonable and conformable with practice:

$$K_{41}=(1-N_1-N_2-N_3-N_4-N_5-N_6-N_8-N_9-N_{10}-$$

$$N_{11}-N_{12}-N_{13})/N_2^3 N_3^2 \quad (11')$$

$$K_{42}=[a(N_1+N_4)+(a-b_1)N_5-b_1(N_3+N_6+3N_9+N_{11}+6N_{12})+$$

$$(2a-b_1)N_8+(3a-b_1)N_{10}+(a-2b_1)N_{13}]/2b_1 N_2^3 N_3^2$$

$$\quad (15')$$

$$K_{43}=[-a(N_2+N_4)+b_2(N_3+N_5+N_8+N_{10}+2N_{13})-$$

$$(a-b_2)N_6-(7a-3b_2)N_9-(3a-b_2)N_{11}-$$

$$(23a-6b_2)N_{12}]/(3a-2b_2)N_2^3 N_3^2 \quad (16')$$

$$u=K_{41}-K_{42}, \quad v=K_{41}-K_{43} \quad (21)$$

Equations (11'), (15') and (16') are different expressions of K_4 (i.e. $K_{Cr_7C_3}$). By using (11'), (15') and (16') and (21), K_4 in conformity with practice can be evaluated in the condition that the value $N_{Cr}=a_{Cr}$ is

known. Here a_{Cr} is calculated by Dresler's equation as

$$a_{Cr}=\exp[\ln b_2 - 571/T + 786\, b_2/T - 215\, b_2^2/T + (10.267 - $$
$$27\,675/T)\,a + (9.164 - 33\,610/T)\,a^2 + (-2.808 + $$
$$15\,543/T)\,ab_2] \qquad (22)$$

Using the calculated results of equation (21), the correctness of the aforementioned model can also be judged to a certain extent.

2.3 Calculated results and discussion

During calculation of the mass action concentrations with the aforementioned model, it was found that K_3 (*i.e.* K_{CrC}) was still too big to make agreement between N_{Cr} and a_{Cr}. In order to solve this problem, the try and error method was used. Let

$$K_3 = \frac{e^{\frac{90\,526 + 25\,911.6\,T}{4.575 \times 4.186\,8\,T}}}{c} \qquad (23)$$

Changing c from 1 to 8.6, it was found that when $c=4$,

Figure 3 Comparison of calculated N_{Cr} with measured a_{Cr} for carbon saturated Fe-Cr-C melts.

comparison of N_{Cr} with measured a_{Cr} for carbon saturated and unsaturated Fe-Cr-C melts. From the figure, it is shown that the agreement between N_{Cr} and a_{Cr} is also satisfactory. For the calculating model was formulated based on the mass action law, it is feasible to evaluate N_{Cr} of carbon unsaturated Fe-Cr-C melts by the calculating model of mass action concentrations deduced in condition of carbon saturated Fe-Cr-C melts, and the results should be independent of the composition of the melts (carbon saturated or unsaturated).

The comparison of N'_C with measured a_C at different temperatures and chromium mass fraction is shown in **figure 5**, from which it is seen that N'_C calculated at different temperatures have good agreement with a_C. As the calculated N'_C can meet carbon saturated and unsa-

$R_{Cr}=a_{Cr}/N_{Cr}=1.096\,895$ for these carbon saturated melts and

$$\Delta G^{\ominus}_{CrC(1\,823-2\,073\,K)}=-RT\ln K_3=-90\,526-14.379\,4\,T$$
(J/mol) $\qquad (24)$

Substituting this value into equations (11'), (15'), (16') and (21),

$$\Delta G^{\ominus}_{Cr,C,(1\,823-2\,073\,K)}=-RT\ln K_4=-855\,969.5+273.44\,T$$
(J/mol) $\qquad (25)$

Substitution of equations (24) and (25) into the model of mass action concentrations not only makes $R_{Cr}=0.972\,991\,2$, but also $R_C=1.061\,44$, hence it satisfies the agreement of both N_{Cr} and N'_C with practice.

The comparison of N_{Cr} with measured a_{Cr} for carbon saturated Fe-Cr-C melts at different temperatures is shown as **figure 3**, in which it is seen that the agreement between N_{Cr} and a_{Cr} is well. **Figure 4** shows the
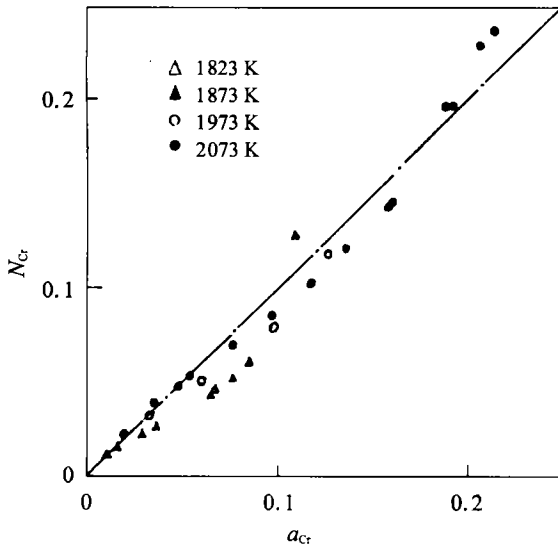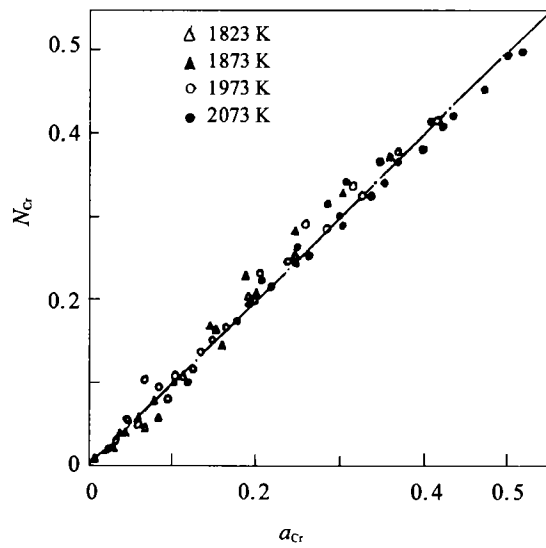

Figure 4 Comparison of calculated N_{Cr} with measured a_{Cr} for both carbon saturated and unsaturated Fe-Cr-C melts.

turated conditions, the agreement of N'_C with a_C as well as that of N_{Cr} with a_{Cr} confirms the aforementioned calculating model is applicable to different conditions (temperature, chromium and carbon mass fractions), and it can reflect the structural reality of Fe-Cr-C melts.

In order to clarify why L_C varies with temperature, chromium and carbon mass fractions, a multivariable regression of L_C with temperature and the mass action concentrations of carbides is carried out, and the result shows as

$$L_C=-4.258\,52+27\,538.18/T+11.529\,3\,N_{FeCr}-$$
$$37.144\,N_{FeC}+0.733\,181\,N_{CrC}+2.582\,699\,N_{Cr_3C}+$$
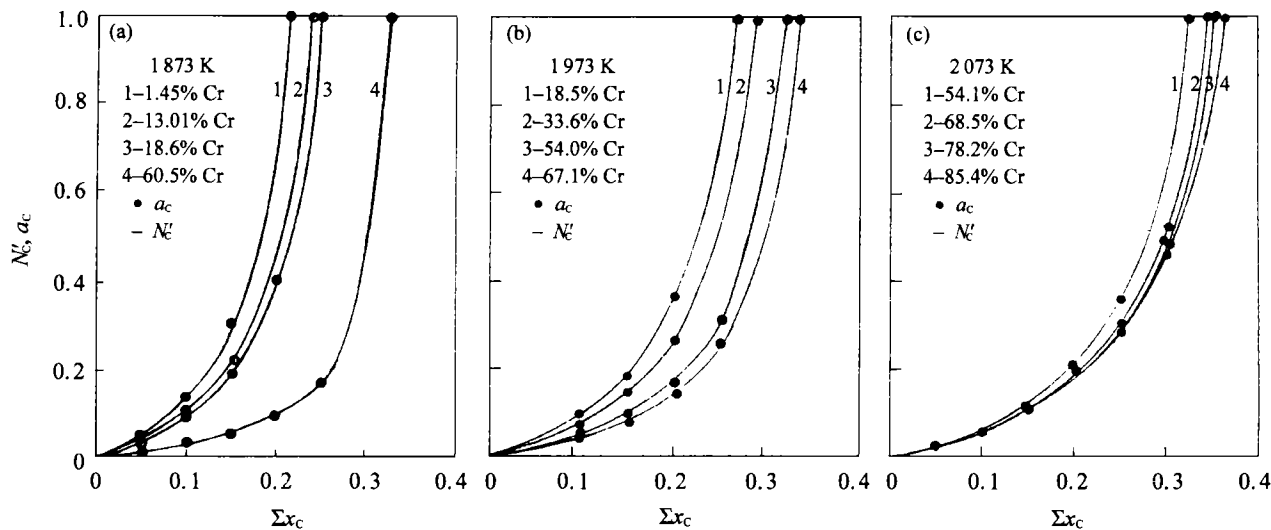$$2.968\,671\,N_{Fe_3C}-1.5 \times 10^7\,N_{Cr_7C_3}-0.056\,1\,N_{Fe_3C}+$$

Figure 5   Comparison of calculated N_c' with measured a_C at different temperatures.

$$13.662\,35\,N_{Cr_7C}+9.1\times10^8 N_{Cr_3C}+9.56\times10^8\,N_{FeC_3},$$

$$(R=0.954\,616, F=56.034\,06) \tag{26}$$

From this equation, it can be seen that temperature and various carbides have different effect on the carbon solubility of the melts. Raising temperature results in the increase of carbon solubility of the melts, and makes L_C decrease. FeCr, CrC, Cr_3C_2, Fe_2C, Cr_3C, $Cr_{23}C_6$ and FeC_2 cause the carbon solubility to decrease, and make L_C increase. FeC, Fe_3C and Cr_7C_3 lend to the increase of carbon solubility of the melts, and make L_C decrease.

The variation of N_{Fe} with carbon and chromium mass fractions at 1 873 K is shown as **figure 6**, from which it is seen that N_{Fe} decreases with the increase of carbon
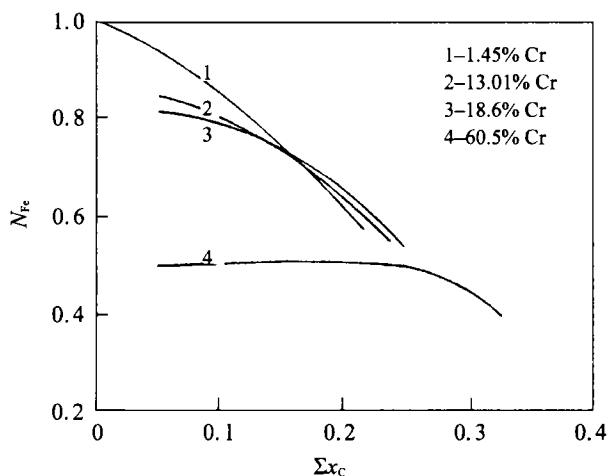

Figure 6   Effect of carbon and chromium contents on N_{Fe}.

mass fraction. However, with the increase of chromium mass fraction, the tendency of N_{Fe} decreasing slows down. Moreover, the slowing down of the tendency of N_{Fe} decreasing with the increase of carbon arises from consumption of iron with formation of iron carbides.

While the slowing down of the tendency of N_{Fe} decreasing with increase of chromium mass fraction is caused by reduction of the absolute amount of iron. The situation of N_{Fe} variation at other temperatures is similar as that in figure 6.

3 Conclusions

(1) An empirical equation of carbon solubility in Fe-Cr-C melts based on the experimental data from references is formulated, which shows that carbon solubility increases with the increase of temperature and chromium mass fraction.

(2) A calculating model of mass action concentrations for Fe-Cr-C melts is deduced. Based on this model the standard free energies of formation for CrC and Cr_3C_2 in conformity with practice are determined as

$$\Delta G^{\ominus}_{CrC(1\,823-2\,073\,K)}=-RT\ln K_3=-90\,526-14.379\,4\,T,$$

$$\Delta G^{\ominus}_{Cr_3C_2(1\,823-2\,073\,K)}=-RT\ln K_4=-855\,969.5+273.44\,T.$$

(3) Conformability of the calculated data with practice shows that the model deduced can reflect the structural reality of Fe-Cr-C melts.

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