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

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ABSTRACT

According to the experimental data from literature sources, an empirical equation of carbon solubility in Fe-Cr-C melts has been regressed. Based on 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 , a calculating model of mass action concentrations for these melts has been formulated . According to this model , the standard free energies of formation for CrC and Cr_3C_2 have been obtained. Satisfactory agreement between 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 concentrations, saturated state

Fe-Cr-C melts are the key melts which the production of ferrochrome depends on. They also give direction to the manufacturing of stainless steel, bearing steel and steels containing chromium. This leads to wide attention of metallurgists to study them. Research on the phase diagram of Cr-C results in relatively consistent conclusion[1~4]. The solubility of carbon in Fe-Cr-C melts have been investigated by different scholars , though their results are inconsistent yet[5~7]. In regard to the activities of these melts, which also have been studied by several scholars[8~11], and useful empirical equations for calculation of activities have been obtained. However, theoretical models based on the mass action law haven't seen yet in literature. The aim of this paper is to formulate the empirical equation for carbon solubility and the calculating model of mass action concentrations for 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 in Fe-Cr-C melts

In literature[5] there are experimental data of carbon solubility in Fe-Cr-C melts at temperatures ranged from 1550 to 1800℃, chromium content ranged from 0 to 85.4% and carbon content ranged from 5.36 to 11.81%. In literature[12] there are also experimental data of carbon solubility in Fe-Cr-C melts at 1500℃. But in both cases there isn't any empirical equation of carbon solubility in these melts yet. So it is worthwhile to treat these experimental data by regression. In so doing, an empirical relationship of carbon solubility with temperature and chromium content has been obtained as follows:

$$[\%C]=12.62923-13133.9/T+0.063996[\%Cr]$$
$$(R=0.995936,\ F=2446.605)$$

Fig. 1 shows this relation. It is seen from the figure that carbon solubility increases with the increase of temperature and chromium content, as increasing in chromium content promotes the formation of greater amount of chromium carbides, which fix carbon in the melts and increasing temperature

facilitates the solution of chromium carbides in the melts. According to this empirical equation, the carbon solubility for Fe-Cr melts with different chromium content can be easily predicted.

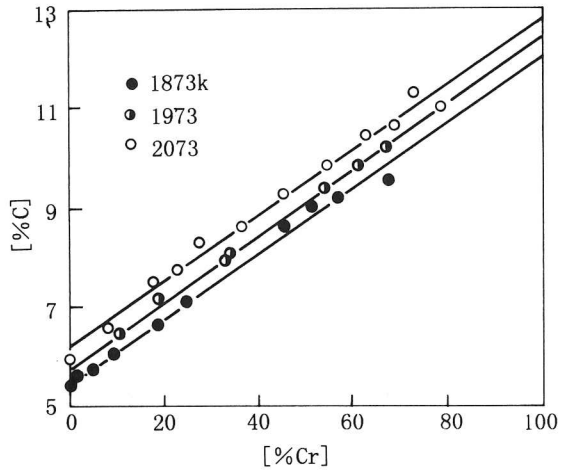

Fig. 1 Relationship between carbon solubility and temperature as well as[%Cr]

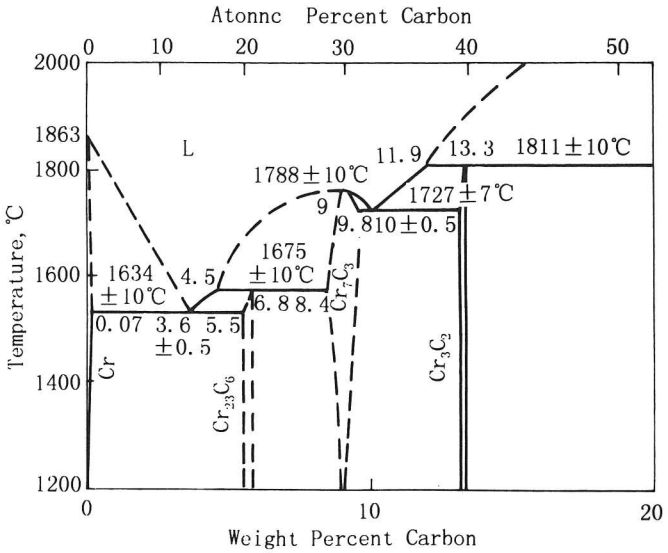

Fig. 2 Phase diagram for Cr-C system

2 Mass action concentrations

2. 1 Structural units

According to the literature[13], there are metastable carbides FeC, Fe_2C, Fe_3C and FeC_2 in Fe-C melts, where it also gives the relationships between the standard free energies of formation $\triangle G^0$and temperature for these carbides.

It can be seen from Fig. 2 [1]that there are chromium carbides Cr_3C_2, Cr_7C_3 and $Cr_{23}C_6$ in the Cr-C melts, from which Cr_7C_3 has congruent melting point, while Cr_3C_2 and $Cr_{23}C_6$ are peritectoids. In addition it is also shown that Cr_3C and probably CrC exists in Cr-C binary system.

Literature [2-4] not only shows the existence of FeCr, CrC, Cr_3C_2, Cr_7C_3, Cr_3C 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_3C_2, Fe_2C, Cr_7C_3, Fe_3C, Cr_3C, $Cr_{23}C_6$ and FeC_2.

2. 2 Calculating model

Assuming composition of the reactants $b_1=\Sigma x_{Fe}$, $b_2=(x_{Cr}, a=\Sigma x_C$; composition of products $x_1=x_{Fe}$, $x_2=x_{Cr}, y=x_C$, $z_1=x_{FeCr}$, $z_2=x_{FeC}$, $z_3=x_{CrC}$, $u=x_{Cr_3C_2}$, $w=x_{Fe_2C}, v=x_{Cr_7C_3}, g_1=x_{Fe_3C}$, $g_2=x_{Cr_3C}$, $r=x_{Cr_{23}C_6}, s=x_{FeC_2}$; mass action concentrations of the melts (mole fractions of the melts after nor-malization $Ni=xi/\Sigma x$) $N_1=N_{Fe}, N_2=N_{Cr}, N_3=N_C, N_4=N_{FeCr}, N_5=N_{FeC}, N_6=N_{CrC}, N_7=N_{Cr_3C_2}, N_8=N_{Fe_2C}$, $N_9=N_{Cr_7C_3}, N_{10}=N_{Fe_3C}, N_{11}=N_{Cr_3C}, N_{12}=N_{Cr_{23}C_6}$, $N_{13}=N_{FeC_2}$; $\Sigma x=$ sum of equilibrium mole fractions. Then it gives chemical equilibria:

$[Fe]+[Cr]=[FeCr]$ $K_1=N_4/N_1N_2$, $N_4=K_1N_1N_2$, $z_1=K_1x_1x_2/\Sigma x$ (1)

$\triangle G^0=-14550+6.65T$, J/mol[2]

$[Fe]+[C]=[FeC]$ $K_2=N_5/N_1N_3, N_5=K_2N_1N_3$, $z_2=K_2x_1y/\Sigma x$ (2)

$\triangle G^0=-97043+11.63T$, J/mol [13]

$[Cr]+[C]=[CrC]$ $K_3=N_6/N_2N_3$, $N_6=K_3N_2N_3$, $z_3=K_3x_2y/\Sigma x$ (3)

$\triangle G^0=-90526-25.9116T$, J/mol[2]

$3[Cr]+2[C]=[Cr_3C_2]$ $K_4=\frac{N_7}{N_2^3N_3^2}$, $N_7=K_4N_2^3N_3^2$,

thermodynamic data reasonable and in conformity with practice, Eqs (11), (15) and (16) have been transformed to the following form:

$$K_{41}=\frac{(1-N_1-N_2-N_3-N_4-N_5-N_6-N_7-N_8-N_9-N_{10}-N_{11}-N_{12}-N_{13})}{N_2^3N_3^2} \quad (11)'$$

$$K_{42}=\frac{(a(N_2+N_4)+(a-b_1)N_5-b_1(N_3+N_6+3N_9+N_{11}+6N_{12})+(2a-b_1)N_8+(3a-b_1)N_{10}+(a-2b_1)N_{13})}{2b_1N_2^3N_3^2} \quad (15)'$$

$$K_{43}=\frac{(-a(N_2+N_4)+b_2(N_3+N_5+N_8+N_{10}+2N_{13})-(a-b_2)N_6-(7a-2b_2)N_9-(3a-b_2)N_{11}-(23a-6b_2)N_{12})}{(3a-2b_2)N_3^2N_3^2} \quad (16)'$$

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

Equations (11)', (15)' and (16)' are different expressions of $K_4(=(K_{Cr_3C_2})$. Having Eqs. (11)' ~ (16)' and (21), K_4 in conformity with practice can be evaluated in condition of known $N_{Cr}=a_{Cr}$.
where a_{Cr} is calculated by Dresler's equation as follows:

$$a_{Cr}=\mathrm{Exp}[\ln(x_{Cr})-571/T+786x_{Cr}/T-215x_{Cr}^2/T+(10.267-27675/T)x_C+9.164-33610/T)x_C^2+(-2.808+15543/T)x_Cx_{Cr}] \quad (22)$$

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

2.3 Calculated results and discussions

In the course of calculating the mass action concentrations with the aforementioned model, it was found that $K_3(=K_{CrC})$ was still too big to make agreement between N_{Cr} and a_{Cr}. In order to solve this problem, try and error method was used, putting

$$K_3(=K_{CrC})=\mathrm{Exp}((90526+25.9116T)/4.575/4.1868/T)/c \quad (23)$$

changing c from 1 to 8.6, it was found that when c = 4, it made $R_{Cr}=a_{Cr}/N_{Cr}=0.94253$ for these carbon saturated melts and gave

$$\triangle G^{\circ}_{CrC(1823\sim2073K)}=-RT\ln K_3=-90526-14.3794T, J/mol \quad (24)$$

substituting this value into Eqs. (11)', (15)', (16)' and (21), it gave

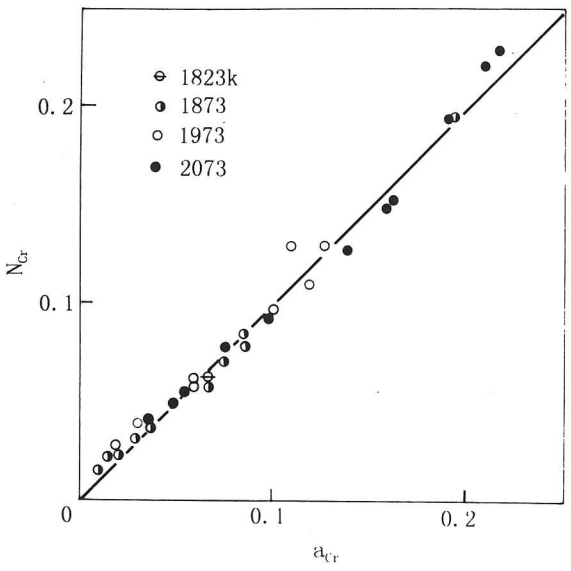

Fig. 3 Comparison of calculated Ncr with measured a_{Cr} for carbon saturated Fe-Cr-C melts

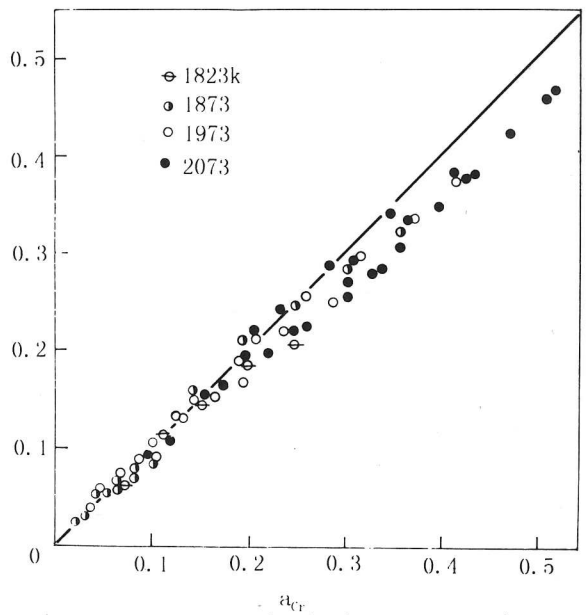

Fig. 4 Comparison of calculated Ncr with measured a_{Cr} for both carbon saturated and unsaturated Fe-Cr-C melts

$$\Delta G^{0}_{Cr_3C_2(1823\sim2073K)} = -RT\ln K_4 = -749672.11 + 231.3989T, J/mol \quad (25)$$

Substitution of Eqs. (24) and (25) into the model of mass action concentrations not only made $R_{Cr} = 1.014583$, but also $R_C = 1.002952$, hence it satisfied the agreement of both N_{Cr} and N'C with practice.

Fig. 3 shows the comparison of N_{Cr} with measured a_{Cr} for carbon saturated Fe-Cr-C melts at different temperatures. It is seen in the figure that the agreement between N_{Cr} and a_{Cr} is well.

Fig. 4 shows the comparison of N_{Cr} with measured a_{Cr} for carbon saturated and unsaturated Fe-Cr-C melts. Though N_{Cr} is a little less than a_{Cr}, but the difference between them is so little, as to interfere with the preliminary evaluation of the mass action concentration of chromium N_{Cr} for carbon unsaturated Fe-Cr \ | C melts by using of the calculating model of mass action concentrations deduced in condition of carbon saturated Fe-Cr-C melts, because the calculating model was for mulated according to the mass action law, and its results should be independent of the composi tion of the melts (carbon saturated or unsaturated).

Fig. 5 shows the comparison of the calculated mass action concentration of carbon N'C with

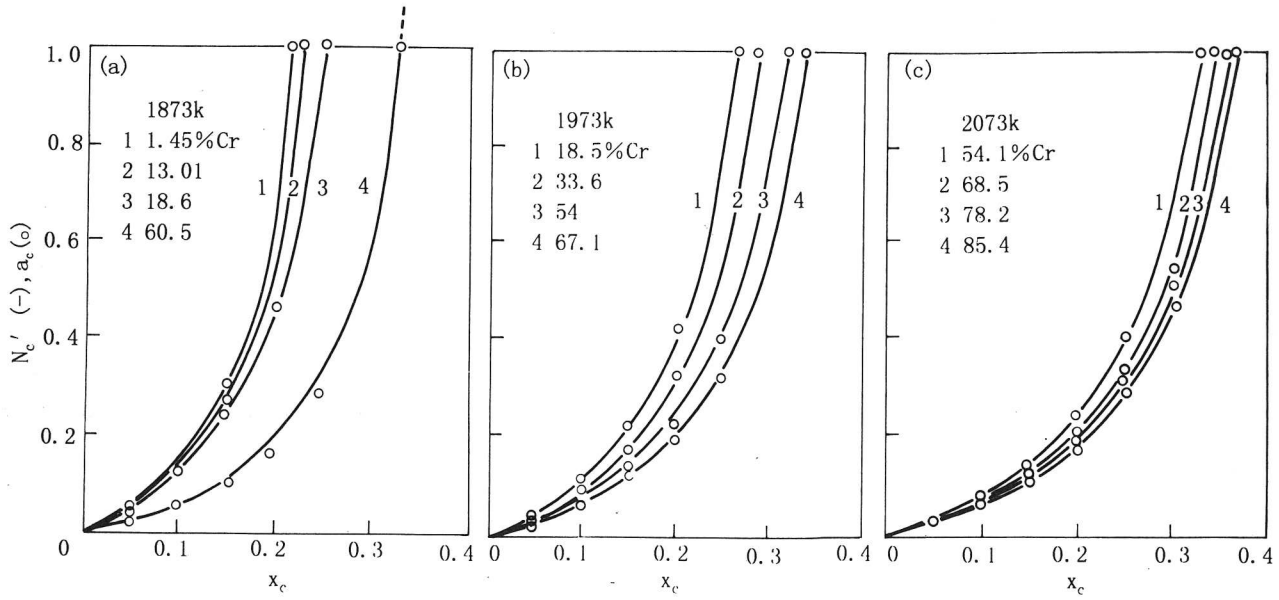

Fig. 5 Comparison of calculated N'C with measured a_C at different temperatures

measured a_C at different temperatures and chromium content, except the 4th curve at 1873 K, where it gives some difference between N'C and a_C, the rest of N'C have good agreement with a_C. As the calculated N'C can meet carbon saturated and unsaturated conditions, so the agreement between N'C and a_C as well as between N_{Cr} and a_{Cr} confirms that the aforementioned calculating model is applicable to different conditions (temperature, chromium and carbon content), and it can reflect the structural reality of Fe-Cr-C melts.

Why L_C varies with temperature, chromium and carbon content (In order to clarify this problem, a multivariable regression of L_C with temperature and the mass action concentrations of carbides has been carried out, and it gives

$$L_C = -8153.38 + 16477928/T + 2706.363N_{FeCr} - 3064.54N_{FeC} + 515.4522N_{CrC} + 1058.687N_{Cr_3C_2} + 23722.16 N_{Fe_2C} - 1.1\times10^{9}N_{Cr_7C_3} - 3548.38N_{Fe_3C} + 4187.141N_{Cr_3C} - 9.1\times10^{13} N_{Cr_{23}C_6} + 4.58\times10^{13}N_{FeC_2} \quad (R = 0.91260,\ F = 27.17629) \quad (26)$$

From this equation, it can be seen that temperature and various carbides have different effect on the carbon solubility of the melts, raising temperature has the effect of increasing the carbon solubility in the melts, so it makes L_C decrease; FeCr, CrC, Cr_3C_2, Fe_2C and Cr_3C have the effect of decreasing

the carbon solubility, so they make L_C increase; FeC, Fe_3C, FeC_2, Cr_7C_3 and $Cr_{23}C_6$ have the effect of increasing the carbon solubility in the melts, so they make L_C decrease.

Fig. 6 shows the variation of NFe with car-bon and chromium content at 1873 K, It is seenfrom the figure, that N_{Fe} decreases with the increase of carbon content, however, with the increase of

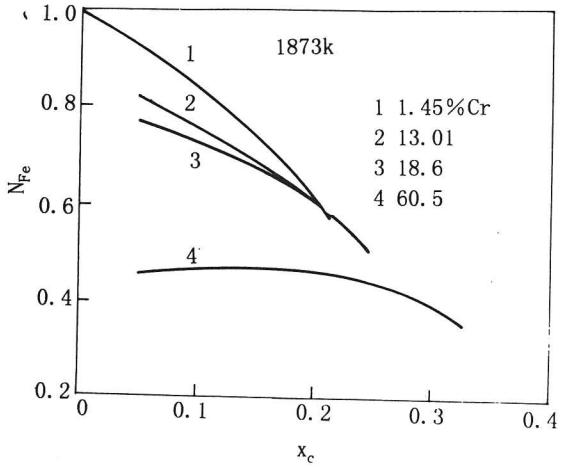

Fig. 6 Effect of carbon and chromium . content on N_{Fe}

chromium content, the tendency of N_{Fe} decreasing slows down. The slowing down of the tendency of N_{Fe} decreasing with the inc-rease of carbon arises from the consumptionof iron with the formation of iron carbides; while the slowing down of the tendency of N_{Fe} decreasing with increasing of chromium contentis caused by reduction of the absolute amount of iron. The situation of N_{Fe} variation at other temperatures is similar as in Fig. 6

3 Conclusions

(1) An empirical equation of carbon solubility in Fe-Cr-C melts based on the experimental data from literature sources has been formulated, which shows that the carbon solubility increaseswith the increase of temperature and chromium content.

(2) A calculating model of mass action concentrations for Fe-Cr-C melts has been deduced. Based on this model the standard free energies of formation for CrC and Cr_3C_2 in conformity with practice have been determined as: $\Sigma G^0_{CrC(1823\sim2073K)} = -RT\ln K_3 = -90526\text{-}14.3794T$, J/mol; $\Sigma G^0_{Cr3C2(1823\sim2073K)} = -RT\ln K_4 = -749672.11+231.3989T$, J/mol。

(3) The calculated results agree well with practice, this in turn shows that the model deduced can reflect the structural reality of Fe-Cr-C melts.

References

1 H. Baker et al., ASM Handbook Vol. 3, Alloy Phase Diagrams (Ohio, The Materials Information Socety, 1992), 2.109

2 J. O. Andersson," Thermodynamic Evaluation of the Fe-Cr-C System," Met. Trans. ,19A(3)(1988), 627-636

3 M. Hillert and Caian Qiu," A Thermodynamic Assessment of the Fe-Cr-Ni-C System," Met. Trans., 22A(10)(1991),2187-2198

4 B. J. Lee, " On the Stability of Cr Carbides," CALPHAD,16(2) (1992),121-149

5 N. R. Griffing et al. ,"C-Cr-Fe Liquidus Surface," Trans. Met. Society AIME,. 224(1962),148-159

6 G. Hadrys, M. G. Frohberg and J. F. Elliot," Activities in the Liquid Fe-Cr-C(sat),Fe-P-C(sat) and Fe-Cr-P Systems at 1600(C," Met. Trans., 1 (1970),1867-1874

7 Гельд П. В Баум Б. А Петушевский М。С. Распла- вы Ферросплавного производства, (Москва, Металлургия, 1975),280

8 Dresler W. " The Effect 0f Nickel and Nickel Oxide on the Reduction of Chromites," (Electric Furnace Conference Proceedings, Vol. 47, Orlando, 1989),49-55

9 Y. Kobayashi, K. Morita and N. Sano, " Thermodynamics of Molten Fe-Cr-C Satd Alloy," ISIJ International,36(8) (1996),1009-1013

10 G. W. Healy, "The Thermodynamics of Chromite Ore Smelting," Trans. ISS., 9(1988), 153-161

11 Jiang Guochang ,Zhang Xiaobing, Xu Kuangdi. " Activities of C-Fe-X (X = Mn、Si、Cr、Ni)" (Proceedings for congratulation of 80th birthday of Professor Zhu Jiao, Press of Me- tallurgical Industry, Beijing ,1994), 87-93

12 Yang Yindong, " Dissertation on Dephosphorization of Crude Stainless Steel Melts under Oxidizing Conditions," (The Royal Institute of Technology, Stockholm,1991), 1:9

13 E. Sch (rmann and R. Schmid," Ein Nahordnungsmodell zur Berechnung thermodynamischer Mischungsgrößen und seine

Awendung auf das System Eisen-Kohlenstoff," Archiv. Eisen- huttenwes 50(3) (1979),101-106
14 Гасик М И, Лякишев Н П, Емлин Ь И. Теория и Технология Производства Ферросплавов, (под ред. Полторацкая идр. Металлургия, Москва,1988),308
15 I. Barin, O. Knacke and O. Kubaschewski, Thermochemical Properties of Inorganic Substances Ⅰ, Ⅱ, (Springer -Verlag, Verlag Stahleisen, 1991),264,503,530-532