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Calculating Model of Mass Action Concentrations for Fe-Cr-P Melts and Optimization of Thermodynamic Parameters

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Abstract: According to the results of research on the thermodynamic properties of Fe-Cr, Fe-P and Cr-P melts, the measured activities of Fe-Cr-P melts from reference sources as well as the coexistence theory of metallic melts structure involving compound formation, a calculating model of the mass action concentrations for Fe-Cr-P melts has been formulated and some of its thermodynamic parameters have been optimized. The calculated mass action concentrations agree with the measured activities, which shows that this model can reflect the structural reality of Fe-Cr-P melts.

Key words: activity; dephosphorization of stainless steel; coexistence theory; mass action concentration

Ternary system Fe-Cr-P is the important melts for dephosphorization of stainless steel. However, the research work on these melts is very limited. A few papers in this field are confined to dilute solutions of chromium and phosphorus in iron [1~3], which are difficult to be used as practical basis for formulation of rigorous theoretical model according to the mass action law. Moreover, there isn't any information about the ternary phase diagram of Fe-Cr-P system. It is fortunately that in recent years, Russia scholars Zaitsev A.I., *et al.* have obtained pioneering investigation achievements in this field [4~7]. Choosing pure liquid components as standard states and using a Knudsen-cell mass spectrometer, they not only measured the activities of three components at different temperatures and compositions, but also successfully studied the structural units as well as the thermodynamic parameters of the melts. These achievements doubtless can be used as the practical basis for deducing rigorous theoretical model. The aim of this paper is just to work out a calculating model of the mass action concentrations for Fe-Cr-P melts on the basis of the above mentioned achievements, so as to provide the theoretical basis for dephosphorization of stainless steel.

1 Calculating Model

1.1 Structural units

The structural units of Fe-P melts have been determined in the preceding paper (in press) as Fe, P atoms as well as FeP, Fe_2P and Fe_3P molecules. According to references [5] and [6], in Cr-P melts there are CrP, Cr_2P, Cr_3P and Cr_3P_2 phosphides formed. By repeatedly verification it has been shown in reference [7] that there is a phosphide FeCrP formed in Fe-Cr-P melts. In reference [8], it has shown that there is FeCr formed in Fe-Cr melts, and the Gibbs standard free energy of FeCr formation has also been determined. Finally, the phase diagram Cr-P [9, 10] shows that there is CrP_2 formed in Cr-P melts. Hence, the structural units of Fe-Cr-P melts can be determined as Fe, Cr and P atoms as well as FeCr, FeP, Fe_2P, Fe_3P, CrP, Cr_2P, Cr_3P, Cr_3P_2, CrP_2 and FeCrP molecules.

1.2 Calculating model

Assuming the composition of the melts as $b_1=\sum x_{Fe}$, $b_2=\sum x_{Cr}$, $a=\sum x_P$; the equilibrium mole fraction of every structural unit expressed by the composition of the melts as $x_1=x_{Fe}$, $x_2=x_{Cr}$, $y=x_P$, $z_1=x_{FeCr}$, $z_2=x_{FeP}$, $z_3=x_{Fe_2P}$, $z_4=x_{Fe_3P}$, $z_5=x_{CrP}$, $z_6=x_{Cr_2P}$, $z_7=x_{Cr_3P}$, $z_8=x_{Cr_3P_2}$, $z_9=x_{CrP_2}$, $z_{10}=x_{FeCrP}$; the mass action concentration of every structural unit after normalization as $N_1=N_{Fe}$, $N_2=N_{Cr}$, $N_3=N_P$, $N_4=N_{FeCr}$, $N_5=N_{FeP}$, $N_6=N_{Fe_2P}$, $N_7=N_{Fe_3P}$, $N_8=N_{CrP}$, $N_9=N_{Cr_2P}$, $N_{10}=N_{Cr_3P}$, $N_{11}=N_{Cr_3P_2}$, $N_{12}=N_{CrP_2}$, $N_{13}=N_{FeCrP}$; $\sum x$ = the sum of all equilibrium mole fractions, then it gives

(1) Chemical equilibria.

$$Fe_{(l)} + Cr_{(l)} = FeCr_{(l)},$$

$$K_1 = \frac{N_4}{N_1N_2},\quad N_4 = K_1N_1N_2,\quad z_1 = K_1\frac{x_1x_2}{\sum x} \qquad (1)$$

$Fe_{(l)} + P_{(l)} = FeP_{(l)}$,

$$K = \frac{N_5}{N_1 N_3},\ N_5 = K_2 N_1 N_3,\ z_2 = K_2 \frac{x_1 y}{\sum x} \quad (2)$$

$\Delta G^{\ominus} = -81\,025 + 1.4\,T$ (J/ mol)[4].

$2Fe_{(l)} + P_{(l)} = Fe_2P_{(l)}$,

$$K_3 = \frac{N_6}{N_1^2 N_3},\ N_6 = K_2 N_1^2 N_3,\ z_3 = K_3 \frac{x_1^2 y}{(\sum x)^2} \quad (3)$$

$\Delta G^{\ominus} = -145\,990 + 15.6\,T$ (J/ mol)[4].

$3Fe_{(l)} + P_{(l)} = Fe_3P_{(l)}$,

$$K_4 = \frac{N_7}{N_1^3 N_3},\ N_7 = K_4 N_1^3 N_3,\ z_4 = K_4 \frac{x_1^3 y}{(\sum x)^3} \quad (4)$$

$\Delta G^{\ominus} = -207\,390 + 58.382\,T$ (J/ mol).

$Cr_{(l)} + P_{(l)} = CrP_{(l)}$

$$K_5 = \frac{N_8}{N_2 N_3},\ N_8 = K_5 N_2 N_3,\ z_5 = K_5 \frac{x_2 y}{\sum x} \quad (5)$$

$\Delta G^{\ominus} = -103\,560 + 1.2\,T$ (J/ mol)[6].

$2Cr_{(l)} + P_{(l)} = Cr_2P_{(l)}$

$$K_6 = \frac{N_9}{N_2^2 N_3},\ N_9 = K_6 N_2^2 N_3,\ z_6 = K_6 \quad (6)$$

$\Delta G^{\ominus} = -150\,607 + 34.2\,T$ (J/ mol)[6].

$3Cr_{(l)} + P_{(l)} = Cr_3P_{(l)}$

$$K_7 = \frac{N_{10}}{N_2^3 N_3},\ N_{10} = K_7 N_2^3 N_3,\ z_7 = K_7 \frac{x_2^3 y}{(\sum x)^3} \quad (7)$$

$\Delta G^{\ominus} = -229\,587 + 53.6\,T$ (J/ mol)[6].

$3Cr_{(l)} + 2P_{(l)} = Cr_3P_{2(l)}$

$$K_8 = \frac{N_{11}}{N_2^3 N_3^2},\ N_{11} = K_8 N_2^3 N_3^2,\ z_8 = K_8 \frac{x_2^3 y^2}{(\sum x)^4} \quad (8)$$

$\Delta G^{\ominus} = -261\,070 + 0.4\,T$ (J/ mol)[6].

$Cr_{(l)} + 2P_{(l)} = CrP_{2(l)}$

$$K_9 = \frac{N_{12}}{N_2 N_3^2},\ N_{12} = K_9 N_2 N_3^2,\ z_9 = K_9 \frac{x_2 y^2}{(\sum x)^2} \quad (9)$$

$\Delta G^{\ominus} = -479\,274.51 + 165.778\,T$ (J/ mol).

$Fe_{(l)} + Cr_{(l)} + P_{(l)} = FeCrP_{(l)}$

$$K_{10} = \frac{N_{13}}{N_1 N_2 N_3},\ N_{13} = K_{10} N_1 N_2 N_3,\ z_{10} = K_{10} \quad (10)$$

$\Delta G^{\ominus} = -150\,060 + 25.1\,T$ (J/ mol)[7].

(2) Mass balance.

$$N_1 + N_2 + N_3 + N_4 + N_5 + N_6 + N_7 + N_8 + N_9 + N_{10} + N_{11} + N_{12} + N_{13} - 1 = 0 \quad (11)$$

$$b_1 = \sum x(N_1 + N_4 + N_5 + 2N_6 + 3N_7 + N_{13}) = x_1 + z_1 + z_2 + 2z_3 + 3z_4 + z_{10} \quad (12)$$

$$b_2 = \sum x\,(N_2 + N_4 + N_8 + 2N_9 + 3N_{10} + 3N_{11} + N_{12} + N_{13}) = x_2 + z_1 + z_5 + 2z_6 + 3z_7 + 3z_8 + z_9 + z_{10} \quad (13)$$

$$a = \sum x\,(N_3 + N_5 + N_6 + N_7 + N_8 + N_9 + N_{10} + 2N_{11} + 2N_{12} + N_{13}) = y + z_2 + z_3 + z_4 + z_5 + z_6 + z_7 + 2z_8 + 2z_9 + z_{10} \quad (14)$$

From equations(12) and (14),

$$a(N_1+N_4) - b_1 N_3 + (a-b_1) N_5 + (2a-b_1) N_6 + (3a-b_1) N_7 - b_1(N_8+N_9+N_{10}+2N_{11}+2N_{12}) + (a-b_1) N_{13} = 0 \quad (15)$$

From equations (13) and (14),

$$a(N_2+N_4) - b_2(N_3+N_5+N_6+N_7) + (a-b_2)(N_8+N_{13}) + (2a-b_2) N_9 + (3a-b_2) N_{10} + (3a-2b_2) N_{11} + (a-2b_2) N_{12} = 0 \quad (16)$$

Equations (11) + (15) + (16):

$$1 - (a+1)(N_1+N_2) - aN_3 = K_1(2a+1) N_1 N_2 + 2K_2 a N_1 N_3 + 3K_3 a N_1^2 N_3 + 4K_4 a N_1^3 N_3 + 2K_5 a N_2 N_3 + 3K_6 a N_2^2 N_3 + 4K_7 a N_2^3 N_3 + K_8(5a-1) N_2^3 N_3^2 + K_9(3a-1) N_2 N_3^2 + 3K_{10} a N_1 N_2 N_3 \quad (17)$$

The aforementioned equations (1) ~ (17) are the calculating model of the mass action concentrations for Fe-Cr-P melts, in which equations (1) ~ (16) are used for the calculation of mass action concentrations for the melts, while equations (11) and (17) are applied for the determination of equilibrium constants. The calculation of the mass action concentrations can be done in three ways:

(1) Combining equations (1) ~ (10), (12) ~ (14) as a coupled equation, then solve it and use the following equations for transforming the results into the mass action concentrations.

$$N_{Fe} = \frac{x_{Fe}}{\sum x},\ N_{Cr} = \frac{x_{Cr}}{\sum x},\ N_P = \frac{x_P}{\sum x};\ N_i = \frac{z_i}{\sum x}$$
$$(i = 1\sim10) \quad (18)$$

(2) Combining equations (1) ~ (10) as well as (11), (15) and (16) as a coupled equation, then solve it.

(3) Solve the coupled equation (11), (15) and (16).

2 Calculated Results and Discussions

The thermodynamic parameters of equations (1) ~ (8) of the above mentioned model have already been determined or verified during the formulation of the calculating models of mass action concentrations for Fe-Cr, Fe-P as well as Cr-P binary melts (in press). Only the standard free energy of CrP_2 formation has not seen yet in references. At the beginning of study,

the presence of CrP_2 in the melts was neglected, it gave unallowable errors in the calculated N_P compared with the measured a_P. So there has no choice, but to insert CrP_2 in the model. As to FeCrP, though there is the standard free energy of formation for this compound in reference [7], but it also gives visible errors during calculation. For this reason, equation (17) has been transformed to the following form [see equation (17a)] to optimize $K_9=K_{CrP_2}$ and $K_{10}=K_{FeCrP}$ by the use of 84 sets of the measured activities at different temperatures from reference [7].

$$1-(a+1)(N_1+N_2)-aN_3-K_1(2a+1)N_1N_2-2K_2aN_1N_3-3K_3aN_1^2N_3-4K_4aN_1^3N_3-2K_5aN_2N_3-3K_6aN_2^2N_3-4K_7aN_2^3N_3-K_8(5a-1)N_2^3N_3^2=K_9(3a-1)N_2N_3^2+3K_{10}aN_1N_2N_3 \quad (17a)$$

The result is

$$\lg K_9=\frac{25\,021.366}{T}-8.655 \qquad (r=1.0000)$$

From this, it gives

$$\Delta G^{\ominus}=-479\,274.51+165.778\,T \quad (\text{J/ mol, } 1\,469\sim 1\,821\text{ K}) \qquad (19)$$

Similarly

$$\lg K_{10}=\frac{8\,529.08\,675}{T}-0.5742 \qquad (r=1.0000)$$

$$\Delta G^{\ominus}=-163\,371.33+10.998\,T \quad (\text{J/mol, } 1\,403\sim 1\,826\text{ K}) \qquad (20)$$

The calculated mass action concentrations N_{fe} by using the optimized thermodynamic parameters at different temperatures (1 403 ~ 1 826 K) and compositions ($\sum x_{Fe}$= 0.059 ~ 0.801, $\sum x_{Cr}$= 0.054 ~ 0.789, $\sum x_P$ = 0.048 ~ 0.318) are compared with the measured a_{Fe} from reference [7] in **figure 1**. It is seen from this figure that the calculated results are in good agreement with those from reference [7]. Under the same conditions, the calculated mass action concentrations N_{Cr} are compared with the measured a_{Cr} as shown in **figure 2**. The agreement between them is also quite well.

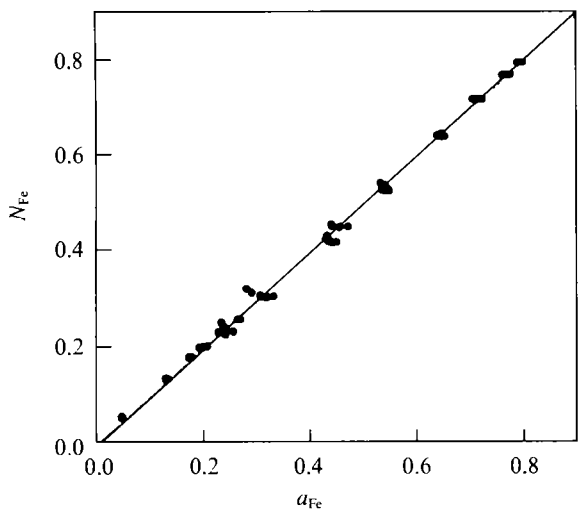

Figure 1 Comparasion of calculated N_{Fe} with a_{Fe} from reference[7] at different temperatures and compositions of the melts

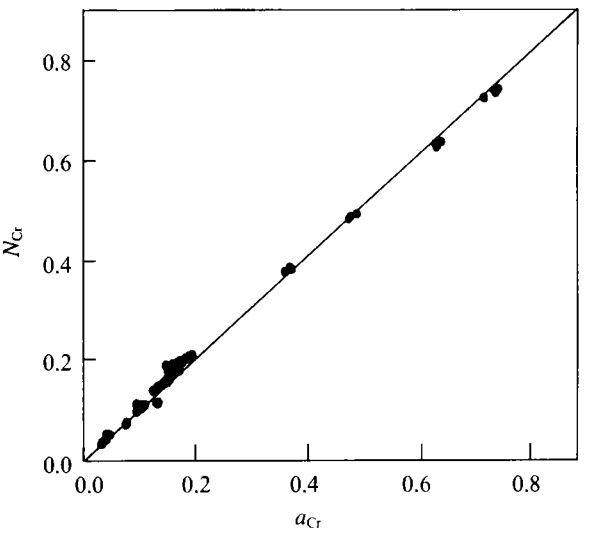

Figure 2 Comparasition of calculated N_{Cr} with a_{Cr} from reference[7] at different temperatures and compositions of the melts

In **figure 3** the calculated N_P are compared with a_P from reference [7] at different temperatures and compo sitions of the melts. Though the agreement between them is worse than that in figures 1 and 2, it is satisfactory.

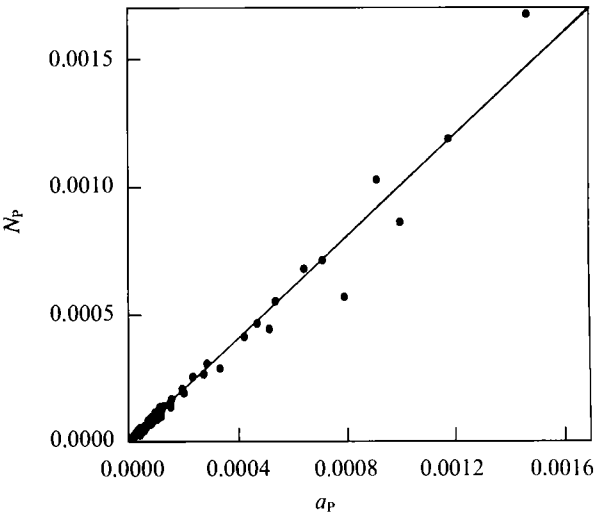

Figure 3 Comparasion of calculated N_P with a_P from reference[7] at different temperatures and compositions of the melts

The facts of the three figures show that the calculating model as well as the optimized thermodynamic parameters can reflect the structural reality of the melts, and can satisfy the requirement to estimate the mass action concentrations of Fe-Cr-P melts at differ-

-ent temperatures and compositions. They also confirm that in Fe-Cr-P melts, all chemical reactions obey the law of mass action, and there isn't any saturation phenomena for phosphorus solubility in Fe-Cr-P melts.

3 Conclusions

(1) According to the investigation results of Fe-Cr, Fe-P and Cr-P binary systems, reliable measured activities and thermodynamic parameters from reference sources as well as the coexistence theory of metallic melts structure involving compound formation, a calculating model of mass action concentrations for Fe-Cr-P melts has been formulated and some of its thermodynamic parameters have been optimized as follows:

$\Delta G^{\ominus}=-479274.51+165.778T$, (J/mol, 1469~1821 K)

$\Delta G^{\ominus}=-163371.33+10.998T$, (J/mol, 1403~1826 K)

The calculated results agree with practice, showing that the deduced model can reflect the structural characteristics of the melts.

(2) During the determination of the structural units of Fe-Cr-P melts, in addition to Fe, Cr, P, FeP, Fe_2P, Fe_3P, CrP, Cr_2P, Cr_3P, Cr_3P_2 and FeCrP, CrP_2 should be considered, otherwise, it would give serious error in the calculation of the mass action concentration N_P.

(3) In Fe-Cr-P melts, all chemical reactions obey the law of mass action, and there isn't any saturation phenomena for phosphorus solubility in Fe-Cr-P melts.

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[*continued from page* 10]

3 Conclusions

(1) The composition (mass fraction in %) of refining slag which has good foaming ability is CaO, 53.25; SiO_2, 17.75; MgO, 9; Al_2O_3, 15 and CaF_2, 5.

(2) The expression about Σ can be described as

$$\Sigma = 490\frac{\mu^{1.25}}{\rho^{0.56}\sigma^{0.68}g^{0.44}}.$$

It indicates that the viscosity of slag is the most important factor that influences the foaming index.

(3) The composition influence degree of refining slag on the foaming index is shown as $CaF_2 \rightarrow MgO \rightarrow Al_2O_3 \rightarrow$ basicity (CaO/SiO_2).

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