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Calculating Model of Mass Action Concentrations for Mn-C Melts and Optimization of Thermodynamic Parameters

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Abstract: Based on the phase diagram, the coexistence theory of the metallic melt structure involving compound formation and the regularity of melts containing saturated phase, a calculating model of mass action concentrations for Mn-C melts was formulated. According to the activities (or activity coefficients γ_{Mn} and γ_C), obtained by the Unified Interaction Parameter Model (UIPM), the thermodynamic parameters $\Delta G^{\ominus}_{Mn_3C}$ and $\Delta G^{\ominus}_{Mn_5C_2}$ at higher temperatures (1628~1873 K) were optimized by the repeated try and error method. It is testified that $\Delta G^{\ominus}_{Mn_{23}C_6}$, $\Delta G^{\ominus}_{Mn_{15}C_4}$ (873~1273 K) and $\Delta G^{\ominus}_{Mn_7C_3}$ (298~1623 K), obtained at lower temperatures, can also be used at the above-mentioned higher temperatures. The calculated N_{Mn} and N_C agree well with a_{Mn} and a_C obtained by UIPM. This result shows that the deduced model can reflect the structural reality of Mn-C melts.

Key words: Mn-C melts; activity; coexistence theory; mass action concentration

Mn-C melts are the principal melts of ferromanganese production as well as ironmaking and steelmaking. Mn is both a reducing agent of extensive application and an alloy element adopted in large-scale productions. As Mn is popularly present in iron and steel melts, deep understanding of the thermodynamic properties of Mn-C melts is indispensable basis for investigating the structure and thermodynamic properties of multicomponent iron and steel melts. Hence Mn-C melts become one of the urgent subjects being studied by the metallurgists. As for the phase diagram, though there is still argument about the presence of peritectic $Mn_{15}C_4$ [1,2], the presence of 4 peritectics $Mn_{23}C_6$, Mn_3C, Mn_5C_2 and Mn_7C_3 has reached an identity of views. As regard the investigation of activity, some experimental results have been obtained in reference [3~6]. However, (1) their results are inconsistent with each other, (2) some of them concerned only to the activity of Mn, the others only to that of C, (3) all results were obtained at relatively lower temperatures (1628~1673 K). They are not suitable to be used in the field of ironmaking and steelmaking. According to the Unified Interaction Parameter Model (UIPM), Li and Morris [7] summarized the above experimental results into the following equations for evaluating the activity coefficients of Mn and C at different temperatures as follows:

$$\ln \gamma_{Mn} = \frac{1}{2} \cdot \frac{7530}{T} (\Sigma x_C)^2 - \frac{2}{3} \cdot \frac{97880}{T} (\Sigma x_C)^3 \quad (1)$$

$$\ln \gamma_C = -4 + \frac{5200}{T} + \left[\frac{1}{2} \cdot \frac{7530}{T} (\Sigma x_C)^2 - \frac{2}{3} \cdot \frac{97880}{T} (\Sigma x_C)^3\right] - \frac{7530}{T} (\Sigma x_C) - \frac{97880}{T} (\Sigma x_C)^2 \quad (2)$$

where Σx_C represents the sum of molar fraction of C in Mn-C melts. Using equations (1) and (2), the activities of Mn and C can be calculated.

In the respect of thermodynamic parameters, some useful results were reported in reference [8,9]. However, owing to the limited temperature range, whether they can be used at higher temperatures of ironmaking and steelmaking remains to be verified yet. The aims of the present paper is to formulate a calculating model of mass action concentrations for Mn-C melts on the basis of a_{Mn} and a_C evaluated by the above mentioned UIPM and to optimize thermodynamic parameters of the new model with the try and error method, so as to make it capable of calculating the mass action concentrations N_{Mn} and N_C, to broaden its temperature range of application, and to form the model based on the mass action law.

1 Calculating Model

According to the phase diagram [1], there are 5 peritectics $Mn_{23}C_6$, $Mn_{15}C_4$, Mn_3C, Mn_5C_2 and Mn_7C_3 in Mn-C melts. On the basis of the coexistence theory of metallic melt structure involving compound formation [10], their structural units are Mn, C, $Mn_{23}C_6$, $Mn_{15}C_4$, Mn_3C, Mn_5C_2 and Mn_7C_3. Put (1) the composition of melts as $b = \Sigma x_{Mn}$, $a = \Sigma x_C$, (2) the equilibrium molar fraction of every structural unit expressed by the composition of Mn-C melts as $x = x_{Mn}$, $y = x_C$, $z_1 = x_{Mn_{23}C_6}$, $z_2 = x_{Mn_{15}C_4}$, $z_3 = x_{Mn_3C}$, $z_4 = x_{Mn_5C_2}$, $z_5 = x_{Mn_7C_3}$, Σx as the sum of all equilibrium molar fractions, and (3) the mass action concentration of every structural unit after normalization as $N_1 = N_{Mn}$, $N_2 = N_C$, $N_3 = N_{Mn_{23}C_6}$, $N_4 = N_{Mn_{15}C_4}$, $N_5 = N_{Mn_3C}$, $N_6 = N_{Mn_5C_2}$, $N_7 = N_{Mn_7C_3}$, then it gives

(1) Chemical equilibria.

$$23Mn_{(l)}+[C] = Mn_{23}C_{6(l)},$$

$$K_1 = \frac{N_3}{N_1^{23}N_2^6},\ N_3 = K_1N_1^{23}N_2^6,\ z_1 = K_1x^{23}y^6/(\Sigma x)^{28},$$

$$\Delta G^\ominus = -325333+76.20T\ (J/mol,\ 873\sim1273\ K) \quad (3)$$

$$15Mn_{(l)}+4[C] = Mn_{15}C_{4(l)},$$

$$K_2 = \frac{N_4}{N_1^{15}N_2^4},\ N_4 = K_2N_1^{15}N_2^4,\ z_2 = K_2x^{15}y^4/(\Sigma x)^{18},$$

$$\Delta G^\ominus = -179765+19.60T\ (J/mol,\ 873\sim1273\ K) \quad (4)$$

$$3Mn_{(l)} + [C] = Mn_3C_{(l)},$$

$$K_3 = \frac{N_5}{N_1^3N_2},\ N_5 = K_3N_1^3N_2,\ z_3 = K_3x^3y/(\Sigma x)^3,$$

$$\Delta G^\ominus = -30415.49+19.70T\ (J/mol,\ 298\sim1793\ K) \quad (5)$$

$$5Mn_{(l)} + 2[C] = Mn_5C_{2(l)},$$

$$K_4 = \frac{N_6}{N_1^5N_2^2},\ N_6 = K_4N_1^5N_2^2,\ z_4 = K_4x^5y^2/(\Sigma x)^6,$$

$$\Delta G^\ominus = -65516-0.333T\ (J/mol,\ 873\sim1273\ K) \quad (6)$$

$$7Mn_{(l)} + 3[C] = Mn_7C_{3(l)},$$

$$K_5 = \frac{N_7}{N_1^7N_2^3},\ N_7 = K_5N_1^7N_2^3,\ z_5 = K_5x^7y^3/(\Sigma x)^9,$$

$$\Delta G^\ominus = -171068.28+78.523T\ (J/mol,\ 298\sim1623\ K) \quad (7)$$

The transforming coefficient from soluble C to its saturated state (graphite):

$$[C] = C_{(gr)},\ L_{C[Mn]} = a_C/N_C \quad (8)$$

(2) Mass balance.

$$N_1+N_2+N_3+N_4+N_5+N_6+N_7-1 = 0 \quad (9)$$

$$b = x+23z_1+15z_2+3z_3+5z_4+7z_5 = \Sigma x(N_1+23N_3+15N_4+3N_5+5N_6+7N_7) \quad (10)$$

$$a = y+6z_1+4z_2+z_3+2z_4+3z_5 = \Sigma x(N_2+6N_3+4N_4+N_5+2N_6+3N_7) \quad (11)$$

From equations (10) and (11),

$$aN_1-bN_2+(23a-6b)N_3+(15a-4b)N_4+(3a-b)N_5+(5a-2b)N_6+(7a-3b)N_7 = 0 \quad (12)$$

The mass action concentration N_C' at C saturated state:

$$N_C' = L_{C[Mn]}N_C \quad (13)$$

Equations (3) ~ (13) are the calculating model of mass action concentrations for Mn-C melts, from which it is seen that (1) the temperature range is too low to be used in the conditions of ironmaking and steelmaking, and (2) in order to evaluate the mass action concentration N_C' at C saturated state, it is necessary to use $L_{C[Mn]}$, but the latter is unknown yet.

So it is difficult to apply the new model to calculate the mass action concentrations of Mn-C melts directly, and the following optimization of its thermodynamic parameters by the try and error method should be used.

2 Optimization of Thermodynamic Parameters

2.1 Main points

Take a lot of compositions of Mn-C melts, including 5 peritectics (*e.g.*, the composition of Mn_3C is Σx_{Mn}= 0.75, Σx_C= 0.25, *etc.*) as shown in the phase diagram, which are quantitatively enough and representative as samples for optimization, take the thermodynamic data at certain temperature from the new model as initial values of equilibrium constant, use a_{Mn} and a_C evaluated from equations (1) and (2) as standard values, and repeatedly change the values of equilibrium constant of 5 peritectics, so as to make the calculated N_{Mn} and N_C' identical respectively with a_{Mn} and a_C. Then the resulted 5 equilibrium constants of peritectics (and $\Delta G^\ominus$) should be the thermodynamic parameters suitable for higher temperatures of ironmaking and steelmaking.

2.2 Method of work

(1) Choose suitable amount of compositions of Mn-

C melts as samples.

(2) Change equilibrium constants of 5 peritectics one after another at certain temperature, and observe what is going on with the ratio $R_m = a_{Mn} / N_{Mn}$.

Its effect may be of three types: R_m increases with the increase of K_i; R_m decreases with the increase of K_i as well as R_m remains practically unchanged with the increase of K_i.

(3) Using different effect of changing equilibrium constant on R_m, consciously and repeatedly change different equilibrium constants (putting $K_i = K_{(i-1)} / R_m$ or $K_i = K_{(i-1)} \times R_m$), so as to make $R_m \approx 1$ ($0.97 < R_m < 1.015$) for the whole samples and R_C ($= a_C / N_C$) practically constant.

(4) Similarly, perform optimization at other temperatures till all samples at different temperatures are optimized.

3 Results and Discussion

3.1 Thermodynamic parameters

(1) New thermodynamic parameters optimized:

$$\begin{cases} \lg K_{Mn_3C} = \dfrac{2805.318}{T} - 0.2562 \quad (r = 1.0000) \\ \Delta G^{\ominus}_{Mn_3C} = -53729.29 + 4.907T \ \text{(J/mol, 1628~1873K)} \end{cases} \tag{14}$$

$$\begin{cases} \lg K_{Mn_5C_2} = \dfrac{3124.8895}{T} + 1.3809 \quad (r = 1.0000) \\ \Delta G^{\ominus}_{Mn_5C_2} = -59856.04 + 26.4506T \\ \text{(J/mol, 1628~1873 K)} \end{cases} \tag{15}$$

The relation between the coefficient of transforming soluble (in liquid Mn) C to its saturated state and temperature is shown in **figure 1**, which can also be expressed by equation (16).

$$\lg L_{C[Mn]} = \frac{4440.2964}{T} - 1.6381 \quad \text{(1628~1873 K)} \tag{16}$$

(2) It is shown by optimization that the following thermodynamic data from reference [8] can be used at higher temperatures:

$\Delta G^{\ominus}_{Mn_{23}C_6} = -325333 + 76.20T$ (J/mol, 873~1873 K);

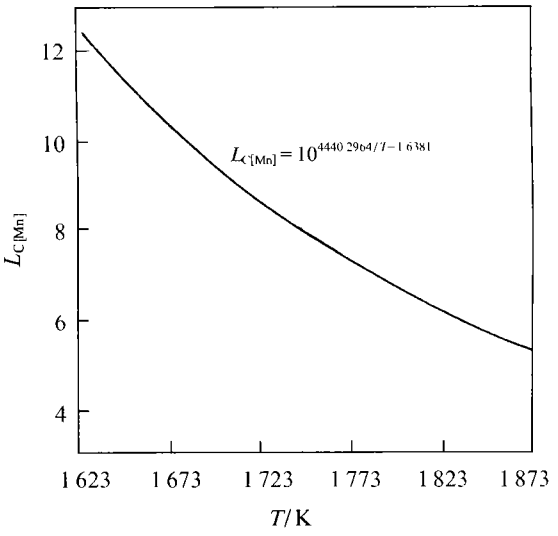

Figure 1 Relation between $L_{C[Mn]}$ and temperatures

$\Delta G^{\ominus}_{Mn_{15}C_4} = -179765 + 19.60T$ (J/mol, 873~1873 K).

(3) It is concluded that the thermodynamic data from reference [9] can be used at higher temperatures too:

$\Delta G^{\ominus}_{Mn_{23}C_6} = -171068.28 + 78.523T$ (J/mol, 873~1873 K).

3.2 Comparison of calculated mass action concentrations with activities

Calculated mass action concentrations N_{Mn} and N'_C are compared with a_{Mn} and a_C evaluated by UIPM at different temperatures as shown in **figures 2 and 3**. It is seen that the agreement between N_{Mn} and a_{Mn} as well as N'_C and a_C at different temperatures and compositions of melts is quite good. This in turn shows that the

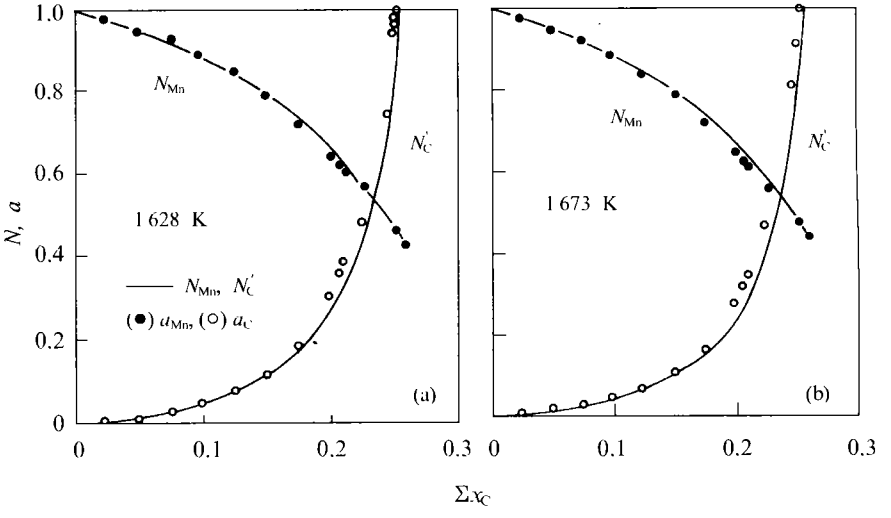

Figure 2 Comparison of N_{Mn} and N'_C with a_{Mn} and a_C at (a) 1628 K and (b) 1673 K

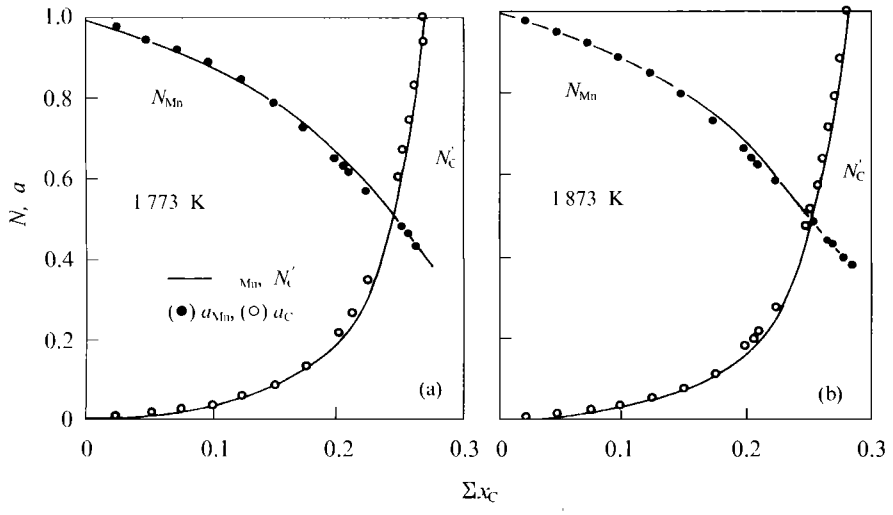

Figure 3 Comparison of N_{Mn} and N_C' with a_{Mn} and a_C at (a) 1773 K and (b) 1873 K

aforementioned model can reflect the structural characteristics of Mn-C melts, the thermodynamic data obtained by optimization are applicable at higher temperatures and the foregoing try and error method is a practical and effective measurement.

In order to get a complete picture of Mn-C melts, the variations of mass action concentrations with C content Σx_C for all structural units at 1673 K are given in **figure 4**. In the figure, N_{Mn_3C} and $N_{Mn_5C_2}$ have comparatively larger values, so they are shown by the left hand side ordinate; while $N_{Mn_{23}C_6}$, $N_{Mn_{15}C_4}$ and $N_{Mn_7C_3}$ have much smaller values, they are represented by the right hand side ordinate after multiplication respectively by 10^8 and 10^5.

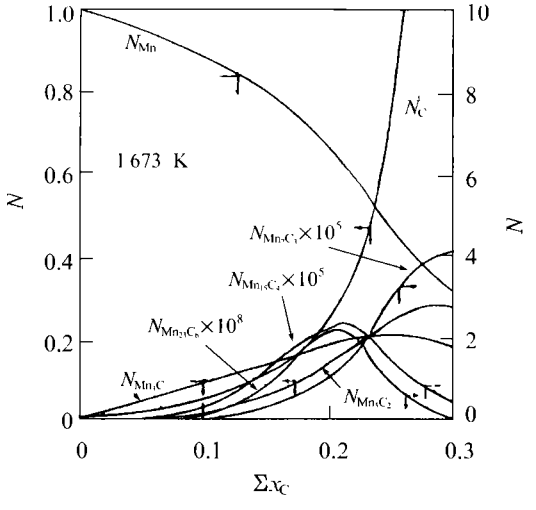

Figure 4 Variations of mass action concentrations with C content Σx_C for all structural units at 1673 K

4 Conclusions

(1) The calculating model of mass action concentrations for Mn-C melts was formulated. The agreement between N_{Mn} and a_{Mn} as well as N_C' and a_C at different temperatures and compositions of melts is quite good. This shows that the model can reflect the structural characteristics of Mn-C melts.

(2) The new thermodynamic parameters applicable at higher temperatures are obtained by the try and error method as

$$\Delta G^{\ominus}_{Mn_3C} = -53729.29+4.907T \text{ (J/mol, 1628~1873K)}$$

$$\Delta G^{\ominus}_{Mn_5C_2} = -59856.04+26.4506T \text{ (J/mol, 1628~1873K)}$$

$$\lg L_{C[Mn]} = \frac{4440.2964}{T} - 1.6381 \text{ (1628~1873K)}$$

(3) It is shown that the temperature range of thermodynamic parameters $\Delta G^{\ominus}_{Mn_{23}C_6}$, $\Delta G^{\ominus}_{Mn_{15}C_4}$ and $\Delta G^{\ominus}_{Mn_7C_3}$ can also be expanded to the temperatures of ironmaking and steelmaking.

References

1 T B Massalski, J L Murray, L N Bennett, *et al.* Binary Alloy Phase Diagrams, Vol 1. American Society for Metals, Metals Park, Ohio, 1986. 575

2 H Baker, H Okamoto, S D Henry, *et al.* ASM Handbook Alloy Phase Diagrams Vol 3. The Materials Information Society, 1992. 111

3 R Gee, T Rosenqvist. Scan J Metall, 1976, 5(2): 57

4 A Tanaka. Trans JIM, 1979, 20(8): 516

5 A Katsnelson, F Tsukihashi, N Sano. ISIJ International, 1993, 33(10): 1045

6 R Ni, Z Ma, S Wei. Steel Research, 1990, 61(3): 113

7 H Li, A Morris. Met & Mater Trans, 1997, 28B(4): 553

8 S Du, S Seetharaman, L I Staffansson. Met Trans, 1988, 19B(6): 951

9 O Knacke, O Kubaschewski, K Hesselmann. Thermochemical Properties of Inorganic Substances. Second Edition. Springer-Verlag, Verlag Stahleisen, 1991.

10 J Zhang. J Univ of Sci and Tech Beijing (in Chinese), 1990, 12(3): 201