Predication of Solubility of Titanium in Fe-Csat-Ti Melts by MIVM

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Abstract. The solubilities of Ti balanced with titanium carbide and titanium carbonitride in Fe-Csat-Ti melts were predicted by molecular interaction volume model (MIVM). In order to verify the present method, the activity of Si, Mn and Ti in Fe-C-Si, Fe-C-Mn and Fe-C-Ti melts were predicted by MIVM and compared with experimental data. The results indicate that the predicted values of Si, Mn and Ti activity by MIVM are in good agreement with the experimental data, and the predictive effect of this model is better than the Wagner formalism. Considering the fact that titanium carbonitride is a non-ideal solid solution, the solubilities of Ti were predicted. The results are in reasonable agreement with the experimental data, and the prediction effect of MIVM are of better stability and reliability. Therefore, its prediction results can be used as the reliable basis of thermodynamic study for liquid iron containing Ti, and the calculations can be performed to predict at which conditions the carbides or carbonitrides will form.

Keywords: liquid iron containing Ti, activity, solubility of Ti, molecular interaction volume model.

1. Introduction
The studies on the solubility of Ti and the critical conditions to form titanium carbide or carbonitride in liquid iron containing Ti are very significant for improving the vanadium titano-magnetite’s smelting theory in blast furnace and guiding blast furnace protection operating practices. The Wagner formalism is widely used in ferrous metallurgy to calculate the activity of each component in liquid iron at present [1]. However, the interaction parameters of Wagner formalism need to be determined by a complicated balance experiment of ternary system. In the published 448 first-order interaction parameters, 21% of the data are not reliable [2]. The first-order interaction parameters \( \varepsilon_{TC} \) and \( \varepsilon_{T} \) in liquid iron obtained by various researchers [1, 3-5] have great difference (as shown in Table 5). Since lack of reliable experimental data, there still don’t have a unified conclusion on these interaction parameters. Many scholars domestic and abroad have made lots of research on the solubility of Ti in...
liquid iron by using Wagner formalism. However, the obtained results of some researchers [6-9] are different by using different interaction parameters for Wagner formalism. There are uncertainties in their calculation. Therefore, it is very necessary to consider these factors comprehensively and to use a thermodynamic model with solid physical basis for these systems researched. Molecular interaction volume model (MIVM) has a certain physical meaning and satisfies thermodynamic consistency [10-11]. This model be able to predict thermodynamic properties of multicomponent liquid alloys by using only the experimental data of component activities or infinite activity coefficients in their sub-binary systems. This work considering the fact that titanium carbonitride is a non-ideal solid solution, and to predict the solubility of Ti in Fe-C-car-Ti melts by using MIVM. The results will have a certain reference value and guide role in the thermodynamics study of liquid iron containing Ti.

2. Brief Description of Models

2.1. Molecular interaction volume model

Based on statistical thermodynamics and theory of phase equilibrium of fluid, the expressions for configurational partition function and the excess Gibbs energy of liquids and their mixtures have been derived by Tao, thus establishing a thermodynamic model—MIVM [10]. According to MIVM, the activity coefficient of component $i$ in multicomponent system can be expressed as

$$
\ln \gamma_i = 1 + \ln \frac{V_{mi}}{\sum_{j=1}^{c} x_j V_{mj} B_{ij}} - \sum_{j=1}^{c} \frac{x_j V_{mj} B_{ij}}{\sum_{j=1}^{c} x_j V_{mj}} \left[ \frac{Z_i \sum_{j=1}^{c} x_j B_{ij} \ln B_{ij} + \sum_{j=1}^{c} Z_i x_j B_{ij} \ln B_{ij}}{\sum_{j=1}^{c} x_j B_{ij} \ln B_{ij}} \right]
$$

(1)

Where $x_i$, $V_{mi}$ and $Z_i$ are molar fraction, molar volume and the nearest molecule or first coordination number of component $i$, respectively; $c$ is component number; and the pair-potential energy interaction parameters $B_{ij}$ and $B_{ji}$ are defined as, respectively,

$$
B_{ij} = \exp\left[\frac{(\varepsilon_{ij} - \varepsilon_{ji})}{kT}\right] \quad B_{ji} = \exp\left[\frac{(\varepsilon_{ji} - \varepsilon_{ij})}{kT}\right]
$$

(2)

Where $\varepsilon_{ii}$, $\varepsilon_{jj}$ and $\varepsilon_{ij}$ are $i$-$i$, $j$-$j$, and $i$-$j$ systems pair-potential energies; $\varepsilon_{ij}$=$\varepsilon_{ji}$; $k$ is Boltzmann’s constant; and $T$ is the absolute temperature. From Eq. (1), MIVM is two-parameter model. Thus, the binary parameters $B_{ij}$ and $B_{ji}$ can be determined just requiring the experimental data of component activities or infinite activity coefficients in their sub-binary systems, then the thermodynamic properties of multicomponent systems can be predicted by MIVM ultimately.

2.2. Wagner Formalism

Wagner formalism can be applied to calculate the activity of each component in liquid iron [1], and its expression is as follows:

$$
\ln \gamma_i = \ln \gamma_i^0 + \sum_{j=2}^{c} \varepsilon_{ij}^{(j)} x_j + \sum_{j=2}^{c} \rho_{ij}^{(j)} x_j^2 + \sum_{j=2}^{c} \sum_{j=3}^{c} \rho_{ij}^{(j)} x_j x_k
$$

(3)

The first-order interaction parameters and infinite dilution activity coefficients can be converted at various temperatures under the condition of regular solution assumptions, the transformational relations are as follows:

$$
\ln \gamma_i^0(T) = \frac{1873}{T} \times \ln \gamma_i^0(1873K) \quad \varepsilon_{ij}^{(j)}(T) = \frac{1873}{T} \times \varepsilon_{ij}^{(j)}(1873K)
$$

(4)
3. Determinations of MIVM Parameters

The Fe-C-Si, Fe-C-Mn and Fe-C-Ti systems includes seven sub-binary systems such as Fe-C, Fe-Si, Si-C, Fe-Mn, Mn-C, Fe-Ti and Ti-C, which have four carbonaceous systems. As is well known, the carbon activities in these sub-binary systems are relative to saturated solution of carbon in limited concentration range. In order to get a good fitting effect, the experimental activity of carbon, $a_{C,\text{sat}}$, need to be converted to activity $a_{C,(R)}$, which has the same standard state with Fe and Ti. The transformational relation is as follows [12]:

$$a_{i,(R)} = a_{i,\text{sat}} x_{i,\text{sat}}$$

Where $x_{i,\text{sat}}$ is the saturation of component $i$ at a certain temperature, which can be obtained from corresponding binary phase diagram. The values of carbon saturation for Fe-C, Si-C, Mn-C, and Ti-C systems are 0.211 (1873 K), 0.325 (3500 K), 0.273 (1700 K), and 0.722 (3500 K) [13-14], respectively.

3.1. Related Parameters of Pure Substances

The coordination number of component $i$ in liquid metal can be estimated by the following formula [15]:

$$Z_i = 4\sqrt{2\pi} \left( \frac{r_m^3 - r_0^3}{r_m^3 - r_0^3} \right) \rho_i r_m \exp \left( \frac{\Delta H_m (T_m - T)}{Z_c R T_m} \right)$$

Where $\rho_i = N_A / V_{mi}$ is the molecular number density of component $i$, $N_A$ is Avogadro constant, $V_{mi}$ is the molar volume of liquid metal $i$; $T_m$ and $\Delta H_m$ are the melting temperature and the melting enthalpy of component $i$, respectively; $Z_c=12$ is a close-packed coordination number; $T$ is the liquid metal temperature; $R$ is the gas constant; $r_0$ and $r_m$ are the beginning and first peak values of radial distance in a radial distribution function near its melting point of liquid metal $i$, respectively, and they can be estimated by the following formulae [15]:

$$r_0 = 0.918 d_{covi} \quad r_m = \sigma_i$$

Where $d_{covi}$ is atomic covalent diameter, and $\sigma_i$ is atomic diameter. Due to lack of thermodynamic data of liquid carbon, one can assume that the molar volume and coordination number of liquid carbon are independent of temperature. So they are approximately equal to the values at melting point of carbon. The related parameters [15-18] of pure substances are shown in Table 1, and the calculated results of coordination numbers at the temperatures of fitting are listed in Table 2.

| Table 1 The related parameters of the pure components [15-18] |
|-------------------------------------------------------------|
| $i$ | $V_{mi}$ / cm$^3$·mol$^{-1}$ | $\Delta H_m$ / KJ·mol$^{-1}$ | $\sigma_i$ / 10$^{-8}$cm | $r_0$/ 10$^{-8}$cm | $\gamma_{1873K}$ ($j=$Fe) |
| Fe | 7.94$[1+1.3\times10^{-4}(T-1809)]$ | 13.770 | 2.550 | 2.148 | - |
| Si | 11.1$[1+1.4\times10^{-4}(T-1685)]$ | 50.208 | 2.344 | 2.067 | 0.00132 [13] |
| C | 5.3 | - | 1.828 | 1.414 | - |
| Mn | 9.54$[1+0.56\times10^{-4}(T-1933)]$ | 12.058 | 2.732 | 2.148 | 1.0 [1] |
| Ti | 11.6$[1+0.56\times10^{-4}(T-1933)]$ | 14.600 | 2.920 | 2.424 | 0.077 [1] |

3.2. Pair-potential Energy Interaction Parameters $B_{ij}$ and $B_{ji}$

Since the infinite dilution activity coefficients for Fe-Si and Fe-Mn systems have some credibility, their binary parameters $B_{ij}$ and $B_{ji}$ can be determined by using infinite dilution activity coefficients
corresponded to \( i \) and \( j \). And if \( x_i \to 0 \), \( \gamma_i = \gamma_i^0 \); if \( x_j \to 0 \), \( \gamma_j = \gamma_j^0 \). Substituting them into Eq. (1) respectively, then we have

\[
\ln \gamma_i^0 = 1 - \ln \left( \frac{V_m B_{ji}}{V_{mi}} \right) - \frac{1}{2} \left( Z_i \ln B_{ji} + Z_j B_{ij} \ln B_{ij} \right)
\]

\[
\ln \gamma_j^0 = 1 - \ln \left( \frac{V_m B_{ij}}{V_{mj}} \right) - \frac{1}{2} \left( Z_j \ln B_{ij} + Z_i B_{ji} \ln B_{ji} \right)
\]

Above formula is a binary non-linear equation set about \( B_{ji} \) and \( B_{ij} \), it can be solved by graphical method or Newton iteration method. The infinite dilution activity coefficients of Fe-Si and Fe-Mn systems can be found from related references [1, 13-14], and the values are \( \gamma_{Fe,1873 \text{ K}}^0 = 0.0162 \), \( \gamma_{Si,1873 \text{ K}}^0 = 0.00132 \), \( \gamma_{Fe,1873 \text{ K}}^0 = 1 \), \( \gamma_{Mn,1873 \text{ K}}^0 = 1 \), respectively. It can be seen that the Fe-Mn melt is regarded as ideal solution approximately.

For the melts Fe-C, Si-C, Mn-C, Fe-Ti and Ti-C using two expressions of components \( i \) and \( j \) from Eq. (1), the binary parameters \( B_{ij} \) and \( B_{ji} \) can be determined by fitting experimental data [13-14] of activity of components in the \( i-j \) melts. The results are show in Table 2, where \( S_i \) and \( S_j \) are the standard deviation and relative error of activity of component \( i \) or \( j \), respectively. The formulae are as follows

\[
S_i^* = \left[ \frac{1}{m} \sum_{i=1}^{m} a_i \exp - a_i \text{pre} \right]^{1/2}
\]

\[
S_i = \left[ \frac{1}{m} \sum_{i=1}^{m} \left| a_i \exp - a_i \text{pre} \right| \right]^{1/2}
\]

Where \( a_i \exp \) and \( a_i \text{pre} \) are the experimental data [13-14] and the predicted of activity of component \( i \) respectively, and \( m \) is the number of experimental data.

In order to get the values of those binary parameters at various temperatures, one can assume that the \( -(\varepsilon_{ij} - \varepsilon_{ii})/k \) and \( -(\varepsilon_{ij} - \varepsilon_{jj})/k \) in Eq. (2) are independent of temperature. Then the Eq. (2) are the single-valued relationships between \( B_{ij} \) or \( B_{ji} \) and temperature \( T \). If the values of \( B_{ij} \) and \( B_{ji} \) have been known at a given temperature, then the values of \( B_{ij} \) and \( B_{ji} \) at other temperatures can be calculated by these relationships.

### Table 2

| \( i-j \) | \( T / \text{K} \) | \( B_{ij} \) | \( B_{ji} \) | \( Z_i \) | \( Z_j \) | \( \pm S_i \) | \( \pm S_j \) | \( \pm S_i^* \) | \( \pm S_j^* \) | \( x_i \) |
|---|---|---|---|---|---|---|---|---|---|---|
| C-Fe | 1873 | 1.4760 | 0.6810 | 5.5 | 10.6098 | 37 | 0.0550 | 6 | 0.0540 | 0–0.2 |
| C-Mn | 1700 | 1.8780 | 0.6950 | 5.5 | 9.9636 | 56 | 0.0364 | 1 | 0.0124 | 0–0.2 |
| C-Si | 3500 | 0.7970 | 1.0190 | 5.5 | 4.2415 | 1 | 0.0010 | 0 | 0.0013 | 0–0.3 |
| C-Ti | 3500 | 1.9650 | 1.0250 | 5.5 | 9.6714 | 18 | 0.0021 | 1 | 0.0060 | 0–0.2 |
| Fe-Mn | 1873 | 0.9505 | 1.0400 | 5.5 | 9.6392 | - | - | - | - | 0–1.0 |
| Fe-Si | 1873 | 0.1815 | 2.4125 | 5.5 | 5.8723 | 24 | 0.0280 | 37 | 0.0220 | 0–1.0 |
| Fe-Ti | 2200 | 1.0956 | 1.2941 | 5.5 | 6.0697 | 10 | 0.0008 | 1 | 0.0021 | 0–1.0 |

### 4. Verification of MIVM in Fe-C-Si, Fe-C-Mn and Fe-C-Ti systems

The activities of components Si and Mn in Fe-C-Si and Fe-C-Mn melts are calculated by using Wagner formula, respectively. The first-order interaction parameters used are \( \varepsilon_{Si}^{(Si)} = 13.15 \), \( \varepsilon_{Si}^{(C)} = 9.7 \), \( \varepsilon_{Si}^{(Mn)} = 0.5 \), \( \varepsilon_{Mn}^{(Si)} = 0.5 \), \( \varepsilon_{Mn}^{(C)} = -2.7 \), \( \varepsilon_{Mn}^{(Mn)} = 0 \) at 1873 K [1, 16]. And the infinite dilution activity coefficients used are given in Table 1. These parameters at different temperatures can be converted by Eq. (4). The comparisons between the calculated values with partial experimental values of activity of components Si and Mn in Fe-C-Si and Fe-C-Mn melts are shown in Table 3 and Table 4, respectively, so that the readers can get reference and prove it. The relative error distributions between calculated values and
all the experimental data which can be searched are shown in Fig. 1 and Fig. 2. The total standard deviation and relative error of activity of component Si in Fe-C-Si melt predicted by MIVM are 0.00039 and 18%, while those calculated by Wagner formalism are 0.00048 and 55%, respectively. The total standard deviation and relative error of activity of component Mn in Fe-C-Mn melt predicted by MIVM are 0.025 and 6%, while those calculated by Wagner formalism are 0.074 and 11%, respectively. It can be seen from the results that in Fe-C-Si and Fe-C-Mn melts, the predicted values of Si and Mn activity of MIVM are in good agreement with experimental data [19-21], and the predictive effect of this model is significantly better than the calculated results of Wagner formalism. Therefore the prediction effect of MIVM are of better stability and reliability.

Table 3 Comparisons of calculated values with partial experimental data [19] of Si activity in Fe-C-Si melt

| T / K | xSi | xC | aSi,MIVM | aSi,Wagner | aSi,Exp |
|-------|-----|----|----------|------------|---------|
| 1693  | 0.2216 | 0.0373 | 0.004642 | 0.005402 | 0.004370 |
| 0.2162 | 0.0033 | 0.002903 | 0.003383 | 0.002370 |        |
| 0.1695 | 0.0210 | 0.001079 | 0.001626 | 0.001130 |        |
| 0.1525 | 0.0023 | 0.000519 | 0.000934 | 0.000600 |        |
| 1773  | 0.0615 | 0.0951 | 0.000198 | 0.000345 | 0.000196 |
| 0.0557 | 0.0864 | 0.000144 | 0.000263 | 0.000145 |        |
| 0.0282 | 0.1103 | 0.000063 | 0.000116 | 0.000068 |        |
| 0.0085 | 0.1799 | 0.000034 | 0.000055 | 0.000033 |        |

Table 4 Comparisons of calculated values with partial experimental data [20-21] of Mn activity in Fe-C-Mn melt

| T / K | xMn | xC | aMn,MIVM | aMn,Wagner | aMn,Exp |
|-------|-----|----|----------|------------|---------|
| 1736  | 0.2203 | 0.1482 | 0.1556 | 0.1431 | 0.1610 |
| 0.3912 | 0.2453 | 0.2330 | 0.1915 | 0.2170 |        |
| 0.3600 | 0.0536 | 0.3263 | 0.3080 | 0.3390 |        |
| 1773  | 0.0727 | 0.1109 | 0.0545 | 0.0530 | 0.0550 |
| 0.1521 | 0.0394 | 0.1389 | 0.1359 | 0.1400 |        |
| 0.2529 | 0.1701 | 0.1739 | 0.1557 | 0.1780 |        |
| 1823  | 0.0754 | 0.1511 | 0.0520 | 0.0496 | 0.0520 |
| 0.2164 | 0.2165 | 0.1345 | 0.1187 | 0.1150 |        |
| 0.3951 | 0.2291 | 0.2564 | 0.2093 | 0.2350 |        |
| 1673  | 0.6277 | 0.1841 | 0.4579 | 0.3598 | 0.4600 |
| 0.7435 | 0.1160 | 0.6430 | 0.5237 | 0.6500 |        |
| 0.9369 | 0.0425 | 0.9191 | 0.8240 | 0.9400 |        |
Fig. 1 The relative error distributions between the calculated values and the experimental data of Chipman and JI-Chunlin [19] of Si activity in Fe-C-Si melt.

Fig. 2 The relative error distributions between the calculated values and the experimental data of Enokido [20] and Tanaka [21] of Mn activity in Fe-C-Mn melt.

Activity data for Ti in the Fe-C-Ti system are rather limited. A activity coefficient of Ti in Fe-C$_{sat}$= 1.3%Ti ($x_{Fe}=0.7783$, $x_{C,sat}=0.2090$, $x_{Ti}=0.0127$) melt was determined by Y Morizane et al. through measuring the solubility of Ti in carbon-saturated iron in equilibrium with titanium carbide, and the value is 0.023 (reference state: 1 mass pct titanium) at 1773 K [22]. Under similar conditions, the
results obtained by Yun Li et al. is 0.03 (reference state: 1 mass pct titanium) [7]. While the predicted value of the activity coefficient of Ti by MIVM is 0.026 (reference state: 1 mass pct titanium) at same condition. Obviously, the predicted values by MIVM are in good agreement with the experimental values.

The part of first-order interaction parameters of Wagner formula obtained by different researchers are given in Table 5. It can be seen that the published interaction parameters about Ti in liquid iron exist great differences. Since lack of reliable experimental data of activity, there is no unified conclusion in this field at present. Thus, the Wagner formalism is not applicable for the study of liquid iron containing Ti.

Based on a good prediction effect of MIVM in liquid iron containing Si, Mn and Ti, the thermodynamic properties of liquid iron containing Ti predicted by present method have certain credibility and reference value. And the results obtained can be used as a reliable basis in the studies of thermodynamics of liquid iron containing Ti, which fill the deficiency of experimental data.

### Table 5 The parameter values of $\varepsilon^{(Ti)}_0$ and $\varepsilon^{(C)}_0$ by different researchers [1, 3-5]

| $\varepsilon^{(Ti)}_0$ | $T$ / K | Reference sources | $\varepsilon^{(C)}_0$ | $T$ / K | Reference sources |
|------------------------|---------|-------------------|------------------------|---------|-------------------|
| 9.0                    | 1873    | Chipman           | -8.9                   | 1773    | Sumito            |
| 2.7                    | 1873    | Fruehan           | -11.94                 | 1873    | Guo et al        |
| 8.3                    | 1873    | Suzuki et al.     | -9.6826                | 1873    | Wang et al.       |
| 5.7                    | 1873    | Smellie et al.    | -9.9256                | 1773    | Wang et al.       |
| 2.8                    | 1873    | Wagner et al.     | -7.3                   | 1873    | Reference         |
| 10.5                   | 1873    | Furukawa et al.   | -14.0                  | 1873    | Reference         |
| 9.61                   | 1873    | Janke et al.      | - -                    | -       | -                 |
| 104.7                  | 1873    | Morita et al.     | - -                    | -       | -                 |
| 4.67                   | 1873    | Guo et al.        | - -                    | -       | -                 |

### 5. Prediction of Solubility of Titanium

The existing form of titanium mainly are elementary substance dissolved in hot metal, titanium carbide and titanium carbonitride in blast furnace smelting process. When there is no nitrogen exist, the following reaction will be occurred.

$$[Ti]_{Fe} (\text{pure liquid})+[C]_{Fe} (\text{sat})=TiC(s)$$ (10)

When there is nitrogen exist, the following reactions will be occurred

$$[Ti]_{Fe} +(1-x)[C]_{Fe} + \frac{x}{2}N_2 =Ti(C_{1-x},N_x)$$ (11)

Where the unknown number $x$ can represents the molar fraction of titanium nitride in the titanium carbonitride solid solution. The Reaction (11) can be divided into two reactions as follows:

$$[Ti]_{Fe} (\text{pure liquid})+[C]_{Fe} (\text{sat})=TiC_{Ti(C_{1-x},N_x)}(\text{pure solid})$$ (12)

$$[Ti]_{Fe} (\text{pure liquid})+\frac{1}{2}N_2 (g)=TiN_{Ti(C_{1-x},N_x)}(\text{pure solid})$$ (13)

Where TiC$_{Ti(C_{1-x},N_x)}$ and TiN$_{Ti(C_{1-x},N_x)}$ are dissolved states of titanium carbide and titanium nitride in titanium carbonitride solid solution, respectively. Then the free energy for Reactions (10), (12) and
(13), $\Delta G^{\theta}_{10}$, $\Delta G^{\theta}_{12}$, and $\Delta G^{\theta}_{13}$ can be determined by linear combination of the reactions listed in Table 6, and have the following results: $\Delta G^{\theta}_{10}$=-203419+22.182$T$, $\Delta G^{\theta}_{12}$=-354919+102.892$T$.

| Reactions                                      | $\Delta G^{\theta}$ / J·mol$^{-1}$ |
|------------------------------------------------|-------------------------------------|
| Ti(s)+C(s)=TiC(s)                             | -184800+12.55$T$ [1]               |
| Ti(s)+1/2N$_2$(g)=TiN(s)                     | -336300+93.26$T$ [1]               |
| Ti(s)=[Ti]Fe(pure liquid)                    | 18619-9.632$T$ [18]               |
| C(s)=[C]Fe(sat)                              | 0                                  |
| TiC(s)=TiC$_{TiCN}$ (pure solid)             | 0                                  |
| TiN(s)=TiN$_{TiCN}$ (pure solid)             | 0                                  |

Table 6 Equations for free energies of selected reactions

Under the condition of without nitrogen, according to Reaction (10) we obtain:

$$\Delta G^{\theta}_{10} = -RT \ln \frac{a_{Ti}^{\theta}}{a_{Ti} a_{C}^{\theta}} = -RT \ln \frac{1}{\gamma_{Ti} x_{Ti}}$$  \hspace{0.5cm} (14)

Rearranging Eq. (14), the following equation can be get:

$$\gamma_{Ti} x_{Ti} - \exp \left( \frac{\Delta G^{\theta}_{10}}{RT} \right) = 0$$  \hspace{0.5cm} (15)

Under the condition of nitrogenous atmosphere, according to the Reactions (12) and (13), we can get:

$$\Delta G^{\theta}_{12} = -RT \ln \frac{a_{Ti}^{\theta}}{a_{Ti} a_{C}^{\theta}} = -RT \ln \frac{\gamma_{TiC} x_{TiC}}{\gamma_{Ti} x_{Ti}}$$  \hspace{0.5cm} (16)

$$\Delta G^{\theta}_{13} = -RT \ln \frac{a_{Ti}^{\theta}}{a_{Ti} a_{N}^{\theta}} = -RT \ln \frac{\gamma_{TiN} x_{TiN}}{\gamma_{Ti} x_{Ti} P_{N2}^{\theta}}$$  \hspace{0.5cm} (17)

Combining Eq. (16), Eq. (17) and $x_{TiC}+x_{TiN}=1$, the following equation can easily be obtained.

$$\gamma_{Ti} x_{Ti} \left[ \frac{1}{\gamma_{TiC}^{\theta}} \exp \left( \frac{\Delta G^{\theta}_{12}}{RT} \right) + \frac{P_{N2}^{\theta}}{\gamma_{TiN}^{\theta}} \exp \left( -\frac{\Delta G^{\theta}_{13}}{RT} \right) \right] = 0$$  \hspace{0.5cm} (18)

For the Eq. (15) and Eq. (18), $x_{Ti}$ is the minimum mole fraction of titanium to form titanium carbide or titanium carbonitride in Fe-C$_{sat}$-Ti melt; $\gamma_{Ti}$ is the activity coefficient of Ti relative to pure liquid titanium, and it is a function of mole fraction of each component $x_i$ and temperature $T$; $P_{N2}$ is the nitrogen partial pressure; $\gamma_{TiC}$ and $\gamma_{TiN}$ represent the activity coefficients of titanium carbide and titanium nitride in titanium carbonitride solid solution, respectively. The ideal solution model has often been employed to describe the thermodynamic behavior of titanium carbonitride solid solution, namely, $\gamma_{TiC}^{\theta}$=1, $\gamma_{TiN}^{\theta}$=1. But a non-ideal behavior of the titanium carbonitride solid solution has been represented in several reports. Jung I J and Kang S obtained the activity curves of titanium carbide and titanium nitride in titanium carbonitride solid solution at 1700 K and 2100 K [23-24]. The results are shown in Fig. 3, and they exhibit strong negative deviations from ideal solution behavior and small effect of the temperature.
Fig. 3 The activities of TiC and TiN in Ti(C_{1-x},N_{x}) at 1700 K and 2100 K

Fig. 4 A application example of graphic method for Eq. (22)

Fitting the activity curves at 1700 K in Fig. 3, the following equations can be obtained. (Gaussian fitting)

\[ \gamma_{\text{TiC}} = -3.018 \exp \left( -\frac{(x+0.5699)^2}{0.3595} \right) + 10.18 \exp \left( -\frac{(x+1.694)^2}{1.8879} \right) \]  
(19)

\[ \gamma_{\text{TN}} = 1.001 \exp \left( -\frac{(x-0.9995)^2}{0.6176} \right) \]  
(20)

Where \( x \) is the molar fraction of titanium nitride in the titanium carbonitride solid solution, so it is the same with the value in molecular formula Ti(C_{1-x},N_{x}). From Eq. (19) and Eq. (20), \( \gamma_{\text{TiC}} \) and \( \gamma_{\text{TN}} \) are only a function of \( x \) if the effects of temperature are not considered. Substituting Eq. (19) and Eq. (20) into Eq. (18), the Eq. (18) will be an equation containing unknown quantities \( x_{\text{Fe}}, x_{\text{c}}, x, T \) and \( P_{\text{N2}} \). The solubility of carbon (mass percent) as a function of temperature in liquid iron containing Ti can be expressed as [1]:

\[ w[C]_{\text{sat}} = 1.34 + 2.54 \times 10^{-3}t + 0.17w[\text{Ti}] \]  
(21)

Where \( w[C]_{\text{sat}} \) is solubility of carbon in molten iron, namely maximum mass percent of carbon dissolved in molten iron; \( t \) is centigrade temperature; \( w[\text{Ti}] \) mass percent of titanium dissolved in molten iron. Converting Eq. (21) concentration unit, we can obtain the mole fraction of saturated
carbon, $x_{C,sat}$, and its a function of $x_{Ti}$ and $T$. The mole fraction of Fe can be calculated by equation $x_{Fe}=1-x_{Ti}-x_{C,sat}$. It can be seen that $x_{C,sat}$ and $x_{Fe}$ are functions of the $x_{Ti}$ and $T$. Then the Eq. (15) and Eq. (18) are nonlinear equation containing only one unknown quantity $x_{Ti}$ at a given temperature, nitrogen partial pressure and composition of carbonitride solid solution. Let $f_1(x_{Ti})$, $f_2(x_{Ti})$ be, respectively

$$f_1(x_{Ti}) = \gamma_{Ti}x_{Ti} - \exp\left(\frac{\Delta G_{10}^{0}}{RT}\right)$$

$$f_2(x_{Ti}) = \frac{1}{\gamma_{Ti}} \exp\left(-\frac{\Delta G_{10}^{0}}{RT}\right) + \frac{P_{N2}^{0.5}}{\gamma_{Ti}} \exp\left(-\frac{\Delta G_{10}^{0}}{RT}\right)$$

The values of $x_{Ti}$ can be solved by graphic method. Namely, set $x_{Ti}$ as the x-coordinate and $f(x_{Ti})$ as the y-coordinate, then we can obtain a function curve for Eq. (22) or Eq. (23) by giving a range of continuous values of $x_{Ti}$. Then the x-coordinate value of point of intersection between the curve and transverse axis are required result. For example, for the Fe-C$_{sat}$-Ti melt, the function curve of Eq. (22) at 1650 K are plotted in Fig. 4, then the value of $x_{Ti}$ can be obtained to be 0.004535; similarly, the function curves of Eq. (23) are plotted in Fig. 5 under the conditions of ideal solution assumption and non-ideal solution ($x=0.5$), and the values of $x_{Ti}$ can be obtained to be 0.000964 and 0.000646, respectively.

The comparisons of the solubilities of Ti balanced with titanium carbide predicted by MIVM with the experimental data in Fe-C$_{sat}$-Ti melts are shown in Fig. 6. From Fig. 6 it is seen that the experimental values of solubility of Ti balanced with titanium carbide obtained by other researchers a little differ from the prediction of this work. However, all the results show a same law as the temperatures change. And there also exist bigger differences in the results of other researchers.
The minimum titanium contents predicted to form titanium carbonitride from Fe-Csat-Ti melt as a function of temperature at 1.0 atm of nitrogen are shown in Fig. 7. The previous research results and experimental data are shown in the same figure. It can be seen that the present results are closer to the experimental data than previous prediction results, and it show that adopting the non-ideal behavior of titanium carbonitride are more reasonable than using the ideal solution model. From the calculation results it can also be found that the solubilities of Ti balanced with titanium carbonitride is related to the composition of titanium carbonitride solid solution. Since the compositions of solid solution obtained by various researchers are different in their experiment, so maybe that is the reason why there are some deviations among these experimental data. The results calculated by using $x=0.7$ and $x=0.9$ are not presented in this paper, but the curves of those are in between the curves of $x=0.5$ and $x=0.1$ listed in Fig. 7. A specific composition of the solid solution, Ti (C_{0.5},N_{0.5}), was reported to exhibit the highest stability. So Ti (C_{0.5},N_{0.5}) can be more easily formed in blast furnace smelting process.
Fig. 8 Solubilities of Ti balanced with titanium carbonitride in Fe-Csat-Ti melt as a function of temperature under different nitrogen partial pressures (x=0.5)

Fig. 9 Solubilities of Ti balanced with titanium carbonitride in Fe-Csat-Ti melt as a function of nitrogen partial pressure under different temperatures (x=0.5)

The conditions under which the carbonitrides, Ti(C0.5,N0.5), will form in liquid iron determined by present method are shown in Fig. 8 and Fig. 9. From them, it is can be seen that as the temperature rising or the nitrogen partial pressure decreasing the solubility of Ti increases. When actual Ti contents are higher than the values of solubility of Ti obtained, the carbonitrides will be formed and precipitated in liquid iron.

Based on the reliability and applicability of MIVM, a series of results obtained have certain credibility. In actual production, these results are meaningful to improve and perfect the vanadium titanomagnetite’s smelting theory in blast furnace and to guide the blast furnace protection operating practices.

6. Conclusion
The activity of Si, Mn and Ti in Fe-C-Si, Fe-C-Mn and Fe-C-Ti melts were predicted by MIVM, respectively. The predicted values are in good agreement with the experimental data, and the
predictive effect of this model is better than the Wagner formalism. The results show that MIVM has good prediction effect, stability and reliability.

Considering the fact that titanium carbonitride is a non-ideal solid solution, the solubilities of Ti balanced with titanium carbide and carbonitride in Fe-Cur-Ti melt were predicted by MIVM. The predicted values are in reasonable agreement with the experimental data, and the solubility of titanium increases with increasing temperature or decreasing nitrogen partial pressure. The results obtained will have a certain reference value and guide roles in vanadium titanomagnetite’s smelting in blast furnace and blast furnace protection operating practices.

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