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Calculation models on the viscosity of CaO-SiO_2-TiO_2 slag system

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Due to the great importance of the smelting process, it is essential to establish a calculation model on the viscosity of the slag system containing titania. In this paper, the calculation models of mass action concentrations and viscosity for the CaO-SiO_2-TiO_2 slag system have been established according to the coexistence theory of the slag structure, as well as the referenced viscosities of CaO-SiO_2-TiO_2 at different temperatures and TiO_2 compositions. With the two models, corresponding calculated programs are made by means of programming language Matlab5.3, and the curves of viscosity of the TiO_2 concentration ($\eta TiO_2/\%$) at 1400°C, (R=0.9~1.0) are plotted. The results show that mass action concentrations of TiO_2 increases with increasing percentage of TiO_2, while the viscosity of CaO-SiO_2-TiO_2 system is decreased. The results show that the models are in good agreement with the experimental and referenced data. They also shows that the models are reasonable for the CaO-SiO_2-TiO_2 slag system.

Keywords: coexistence theory; CaO-SiO_2-TiO_2 slag system; viscosity ; calculation models.

Introduction

Any smelting process demands that molten slag has suitable viscosity. It is not only important for a successful smelting process, but is close related to mass transfer, and heat transfer velocity. Therefore, it affects reaction velocity, as well as lining life, whether molten bath is active or not[1–2].

Metallurgists have discussed how to use measured viscosity to derive model data to predict viscosity. In this, some results have been achieved. For slag containing titania however, solid points and suboxide containing titania will be easily produced during the viscosity measurement process. There is little literature on this.

Calculation model and result of mass action concentrations of components in slag

The purpose of the coexistence theory is to calculate mass action concentrations, namely activity. The main properties of the coexistence theory is as follows: (1) keeping strictly to mass action law; (2) obeying the three thermodynamic laws; and (3) using existing thermodynamic data. The paper uses the coexistence theory to produce mass action concentrations and viscosity models for CaO-SiO_2-TiO_2 slag system..

Structure units

For the slag system CaO-SiO_2-TiO_2, CaO-SiO_2, CaO-TiO_2, SiO_2-TiO_2 phase diagrams[5] are consulted. According to the coexistence theory of slag structure[4], the structure units are determined at 1464~1800°C in the slag: Ca_3SiO_5, Ca_2SiO_4, $CaSiO_3$, $Ca_3Ti_2O_7$, $CaTiO_3$, $CaTiSiO_5$ six compounds, as well as Ca^{2+}, O^{2-}, SiO_2, TiO_2 four simple ions and molecules.

Calculation model

Assuming $b = \Sigma X_{CaO}$, $a_1 = \Sigma X_{SiO_2}$, $a_2 = \Sigma X_{TiO_2}$; $N_1 = N_{CaO}$, $N_2 = N_{SiO_2}$, $N_3 = N_{TiO_2}$, $N_4 = N_{Ca_3SiO_5}$, $N_5 = N_{Ca_2SiO_4}$, $N_6 = N_{CaSiO_3}$, $N_7 = N_{Ca_3Ti_2O_7}$, $N_8 = N_{CaTiO_3}$, $N_9 = N_{CaTiSiO_5}$; $x = x_{CaO}$, $y_1 = x_{SiO_2}$, $y_2 = x_{TiO_2}$, $z = x_{Ca_3SiO_5}$, $w = x_{Ca_2SiO_4}$, $u = x_{CaSiO_3}$, $v = x_{Ca_3Ti_2O_7}$, $s = x_{CaTiO_3}$, $t = x_{CaTiSiO_5}$

where ΣX is the total molar fraction, b, a_1 and a_2 are the molar fractions of CaO, SiO_2, TiO_2 before reaction balance, respectively, N_i is mass action concentrations of some substance in molten metals, and x, y_1, y_2, z, w, u, v, s, and t are, respectively, equilibrium molecules for CaO, SiO_2, TiO_2, Ca_3SiO_5, Ca_2SiO_4, $CaSiO_3$, $Ca_3Ti_2O_7$, $CaTiO_3$, and $CaTiSiO_5$.

According to the coexistence theory, the following equations are obtained:

$CaO = Ca^{2+} + O^{2-}$

$N_1 = N_{Ca^+} + N_{O^{2-}} = 2x/\Sigma X, \quad x = 0.5N_1\Sigma X$

$N_2 = y_1/\Sigma X, \quad y_1 = N_2\Sigma X$

$N_3 = y_2/\Sigma X, \quad y_2 = N_3\Sigma X$

Then, according to these, chemical balance can be obtained as follows:

$(Ca^{2+}+O^{2-})+SiO_2 = CaSiO_3$

$K_1 = N_6/(N_1N_2) \qquad N_6 = K_1N_1N_2 \qquad u = K_1N_1N_2\Sigma X$

$\Delta G^o = -22476-38.52T$, J/mol[4] (1464~1800°C)

$3(Ca^{2+}+O^{2-})+SiO_2 = Ca_3SiO_5$

$K_2 = N_4/(N_1^3N_2) \qquad N_4 = K_2N_1^3N_2 \qquad z = K_2N_1^3N_2\Sigma X$

$\Delta G^o = -93366-23.03T$, J/mol[4] (1464~1800°C)

$2(Ca^{2+}+O^{2-})+SiO_2 = Ca_2SiO_4$

$K_3 = N_5/(N_1^2N_2) \qquad N_5 = K_3N_1^2N_2 \qquad w = K_3N_1^2N_2\Sigma X$

$\Delta G^o = -100986-24.03T$, J/mol[4] (1464~1800°C)

$3(Ca^{2+}+O^{2-})+2TSiO_2 = Ca_3Ti_2O_7$

$K_4 = N_7/(N_1^3N_3^2) \qquad N_7 = K_4N_1^3N_3^2 \qquad \mathrm{v} = K_4N_1^3N_3^2\Sigma X$

$\Delta G^o = -207100-11.51T$, J/mol[6] (25~1400°C)*

$(Ca^{2+}+O^{2-})+TiO_2 = CaTiO_3$

$K_5 = N_8/(N_1N_3) \qquad N_8 = K_5N_1N_3 \qquad s = K_5N_1N_3\Sigma X$

ΔG^o = -79900-3.35T, J/mol[6] (25~1400°C)*

$(Ca^{2+}+O^{2-})+TiO_2 + SiO_2 = CaTiSiO_5$

$K_6 = N_9/(N_1N_2N_3) \qquad N_9 = K_6N_1N_2N_3 \qquad t = K_6N_1N_2N_3\Sigma X$

ΔG^o = -122591.2+-10.88T, J/mol[7] (25~1400°C)*

Where, K_i (i =1,2,3,…,26) is the equilibrium constant of the chemical reaction, and ΔG^o is the standard Gibbs free energy of formation (unit: J/mol).

According to mass balance, the following equations are obtained:

$N_1 + N_2 + N_3 + N_4 + N_5 + N_6 + N_7 + N_8 + N_9 = 1$

namely,

$$\begin{aligned}&N_1 + N_2 + N_3 + K_2N_1^3N_2 + K_3N_1^3N_2 + \\ &K_1N_1N_2 + K_4N_1^3N_3^2 + K_5N_1N_3 + \\ &K_6N_1N_2N_3 - 1 = 0\end{aligned} \qquad [1]$$

$$\begin{aligned}b &= \sum X_{CaO} \\ &= x + 3z + 2w + u + 3v + s + t \\ &= \sum X\begin{pmatrix}0.5 + 3K_2N_1^2N_2 + \\ 2K_3N_1N_2 + K_1N_2 + \\ 3K_4N_1^2N_3^2 + K_5N_3 + \\ K_6N_2N_3\end{pmatrix}N_1\end{aligned} \qquad [2]$$

$$\begin{aligned}a_1 &= \sum X_{SiO_2} \\ &= y_1 + z + w + u + t \\ &= \sum X\begin{pmatrix}1 + K_2N_1^3 + K_3N_1^2 + \\ K_1N_1 + K_6N_1N_3\end{pmatrix}N_2\end{aligned} \qquad [3]$$

$$\begin{aligned}a_2 &= \sum X_{TiO_2} \\ &= y_2 + 2v + s + t \\ &= \sum X\begin{pmatrix}1 + 2K_4N_1^3N_3 + \\ K_5N_1 + K_6N_1N_2\end{pmatrix}N_3\end{aligned} \qquad [4]$$

From Equation [2] and [3]:

$$\begin{aligned}&a_1 = \left(0.5 + 3K_4N_1^2N_3^2 + K_5N_3 + K_6N_2N_3 + K_1N_2\right) \\ &N_1 - b\left(1 + K_1N_1 + K_6N_1N_3\right)N_2 \\ &+\left(3a_1 - b\right)K_2N_1^3N_2 + \left(2a_1 - b\right)K_3N_1^2N_2 = 0\end{aligned} \qquad [5]$$

From Equations [2] and [4]:

$$\begin{aligned}&a_2 = \left(0.5 + 3K_4N_1^2N_2 + 2K_3N_1N_2 + K_6N_2N_3 + K_1N_2\right) \\ &N_1 + \left(3a_2 - 2b\right)K_4N_1^3N_3^2 \\ &+\left(a_2 - b\right)K_5N_1N_3 - b\left(1 + K_6N_1N_2\right)N_3 = 0\end{aligned} \qquad [6]$$

From Equation [2]:

$$\sum X = b \Big/ \begin{pmatrix}0.5 + 3K_2N_1^2N_2 + 2K_3N_1N_2 + K_1N_2 + \\ 3K_4N_1^2N_3^2 + K_5N_3 + K_6N_2N_3\end{pmatrix}N_1 \qquad [7]$$

Thus, the calculation models of mass action concentrations will be expressed by the Equations [2],[5],[6] and [7].

Mass action concentrations of other components in the slag are given by the expressions:

$N_4 = K_2N_1^3N_2$, $N_5 = K_3N_1^2N_2$, $N_6 = K_1N_1N_2$, $N_7 = K_4N_1^3N_2^3$, $N_8 = K_5N_1N_3$, $N_9 = K_6N_1N_2N_3$.

Thus, we can calculate mass action concentrations of components in slag at different temperatures and composites by using the above calculation models. The results of N_{TiO_2} are shown in Table I.

From Table I, we can see it is in agreement with N_{TiO_2}=0.0709 and measured data a_{TiO_2} =0.06 when the percent of TiO_2 is 20% or so[8].

Calculation model of viscosity

According to the mass action concentration calculation model of the $CaO-SiO_2-TiO_2$ slag system, the function is established between mass action concentration of structure units and corresponding literature values[5] under different temperatures and compositions. The calculation model of viscosity is regressed by the Arrhenius equation and document[9], and calculated mass action concentrations data as follows:

$$\eta = A_o \exp\sum_{i=1}^{n}\left(A_i + \frac{B_i}{T}\right)N_i \qquad [8]$$

this is,

$\ln\eta = C_0 + \Sigma C_iN_i$

Where ln $A_0 = C_0$, $C_i = A_i + \frac{Bi}{T}$ (i=1,… ,9), T is temperature (unit: K), Ni is mass action concentration of structure units and Ci°, Ai and Bi are respectively regression coefficients. The function is regressed by Matlab5.3. The results are shown in Table II.

Table I
Mass action concentrations of titania in the $CaO-SiO_2-TiO_2$ slag system

Number	CaO	SiO_2	TiO_2	N_{TiO_2}	
	Wt,%	Wt,%	Wt,%	1400°C	1500°C
1	22.80	24.70	52.50	0.3711	0.3791
2	24.70	25.30	50.00	0.3248	0.3434
3	28.00	27.00	45.00	0.2543	0.2742
4	29.32	30.68	40.00	0.2137	0.2295
5	31.81	33.19	35.00	0.1628	0.1813
6	34.00	36.00	30.00	0.1246	0.1412
7	34.50	36.50	29.00	0.1170	0.1344
8	36.20	35.80	28.00	0.1052	0.1191
9	35.75	38.25	26.00	0.0985	0.1132
10	36.40	38.10	25.50	0.0937	0.1089
11	37.70	37.30	25.00	0.0866	0.0992
12	37.35	38.15	24.50	0.0863	0.0997
13	37.90	39.10	23.00	0.0785	0.0918
14	38.97	39.53	21.50	0.0702	0.0814
15	39.80	39.40	20.80	0.0649	0.0753
16	40.60	39.40	20.00	0.0600	0.0709

Table II
Regression data of TiO_2 viscosity (η)

Temper-ature/K	Regression coefficient									
	C_0	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9
1673.15	17	-1193	-27	-17	-19100	139	-27	-28	-31	37
1773.15	-5.8	1287.2	17.9	3.1	640	-48.1	2.7	-224.7	20.9	-25.8

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*Apply to those data temporarily

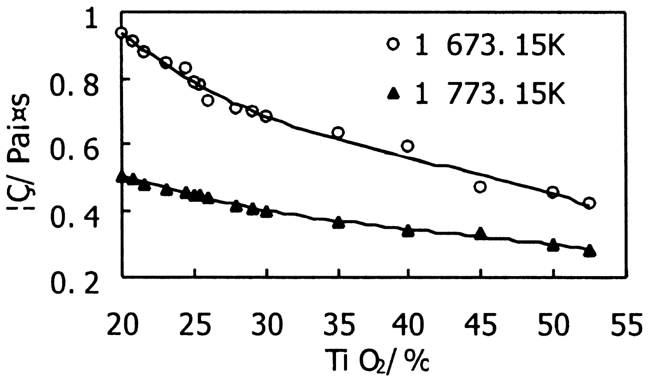

Figure 1. Viscosity curve of CaO-SiO$_2$-TiO$_2$ slag system

As is shown in Figure 1, compared with previous data[5], correlation coefficients r=0.9988(1673.15K), r=0.9979 (1773.15K) are calculated by Matlab. Due to different temperatures, C_0 obviously varies.

Calculation results and discussion

From Table II, under the binary R=0.9~1.0, when the per cent of $a_{TiO_2}=0.06$ is 20% or so, the results show $N_{TiO_2}=0.0709$ is in agreement with.

In CaO-SiO$_2$-TiO$_2$ slag system, viscosity decreases with the increase in TiO$_2$ per cent. During the smelting of titanium-vanadium in blast furnace and a reducing atmosphere, however, slag has a higher viscosity if TiO$_2$ exceeds 25% in the molten slag. The reason is that TiO$_2$ is reduced to compound with high melting points: TiC(m: 3140°C), TiN(m:2930°C)and Ti (C°, N).

Conclusions

- The mass action concentration calculation model and viscosity calculation model are established, according to the coexistence theory of slag structure and document value under different temperatures and compositions for the CaO-SiO$_2$-TiO$_2$ ternary slag system. Calculated data is consistent with literature values.
- With increasing TiO$_2$ per cent in slag, the mass action concentration increases. It is in agreement with practice.
- With increasing TiO$_2$ per cent in slag, viscosity of slag decreases.
- Temperature is key to viscosity. If the temperature rises, viscosity decreases, and running quality is good.

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