VISCOSITY MEASUREMENTS AND ESTIMATION OF HIGH TiO_2 CONTAINING BLAST FURNACE SLAGS

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ABSTRACT

The viscosity for the blast furnace slag of the muti-components of CaO-MgO-Al_2O_3-SiO_2-TiO_2 had been measured in present study. A modified viscosity model, which was specially aimed to predict the viscosity of high TiO_2 containing BF slag was proposed based on the Urbain's model. The prediction results have been discussed and compared with that of the calculations by Urbain's model.

***Key Words**: Viscosity model, TiO_2, Urbain, blast furnace slags.*

INTRODUCTION

Iron making of tatanioferrite ore will produce lots of slag containing TiO_2. Therefore, the properties of slag containing TiO_2 are important for the iron making process. A number of people [See ref. 1 to 9] had evaluated the role of TiO_2 in the silicate melts. Most of the results showed that the effects of TiO_2 at the liquid region tended to decrease the viscosity in the ternary or higher order silicate systems in neutral conditions. But in reducing conditions, TiO_2 can be reduced and result in the rising of the viscosity of the slag. The previous study by G. Handfield *et al.* [3, 4] had found that titanium oxide such as TiO_2, Ti_2O_3 and TiO had a similar behavior to reduce the viscosity of the slag. The presence of titanium carbonitrides TiC or TiN, could be the reason to increase the viscosity during the reducing process.

In 2004, L. Zhang and S. Jahanshahi [10] extended their CSIRO's model to multi-component silicate slag containing TiO_2 and Ti_2O_3. The TiO_2 and Ti_2O_3 were treated as network modifiers similar to the alkaline oxides of CaO, MgO and MnO. Good agreement was obtained for the calculated value and the experimental data in the systems of the BF type slag containing high TiO_2 or Ti_2O_3, but the parameters of TiO_2 and Ti_2O_3 hadn't been published.

Urbain's model [11] is a well known viscosity model, which is based on the reliable experimental data for the parameters of the silicate systems. This model had been applied to lots of metallurgical slags and showed an reasonable predicting result, but for some kinds of slag, such as the high TiO_2 containing silicate systems, this modeling result showed a large error compared with the experimental data.

The present work was aimed to construct a model, which was extension with the Urbain's model, with the purpose of predicting the viscosity of the high TiO_2 containing BF type slag. In order to test the viscosity model, some viscosities of the BF type slag containing high TiO_2 had been measured.

EXPERIMENT

Materials and Preparation of Slags

The slag samples were prepared by mixing powders of reagent grade SiO_2, Al_2O_3, MgO, CaO and TiO_2.The reagent of CaO was pre-heated in a muffle at 1273 K, in case the existence of the compound of $CaCO_3$ and $Ca(OH)_2$. Some compositions of the slag are presented in Table 1. Each measurement, 140 g mixed powder was pressed into several pellets and added to the crucible.

Table 1: The composition of high TiO_2 containing BF slag (wt %)

Ref	No.	SiO_2	Al_2O_3	CaO	MgO	TiO_2
Xie *et al.* [1]	T 17	27.9	15.5	30.8	8.9	17.0
	T 25	25.2	14.0	27.8	8.0	25.0
	T 33	22.5	12.5	24.8	7.2	33.0
Vander colf and Howat[7]	A 5	23.65	11.2	18.675	18.675	24.8
	B 14	23.33	13.8	16.335	16.335	30.2
	C 23	19.19	16.82	13.405	13.405	37.2
The present study	T 20	26.2	15.0	28.2	10.0	20.0
	T 25	23.8	15.0	26.2	10.0	25.0
	T 35	19.0	15.0	21.0	10.0	35.0
	T 40	16.67	10.0	18.33	15.0	40.0

Apparatus for Viscosity Measurement

The viscosity was measured by the rotating cylinder method using a RTW-10 rotating viscometer as showed in Figure 1. The $MoSi_2$ heating elements were employed for heating the furnace. The spindle used in the experiments was made of molybdenum. The crucible was made of graphite covered by Mo sheet in the internal surface. The spindle and the crucible are showed in Figure 2.

Viscosity Measurement

The crucible filled with the as-prepared slag pellets was placed into the furnace and heated to 1823 K. The molten slag was held at 1823 K for half an hour, and then the rotating spindle at a speed of 200 rpm was dipped into the slag on the position of 10 mm above the bottom of the crucible. The viscosity was measured during the cooling process with cooling rate of 2 K/min until the viscosity started to rise sharply. Then the furnace was heated up and repeated again.

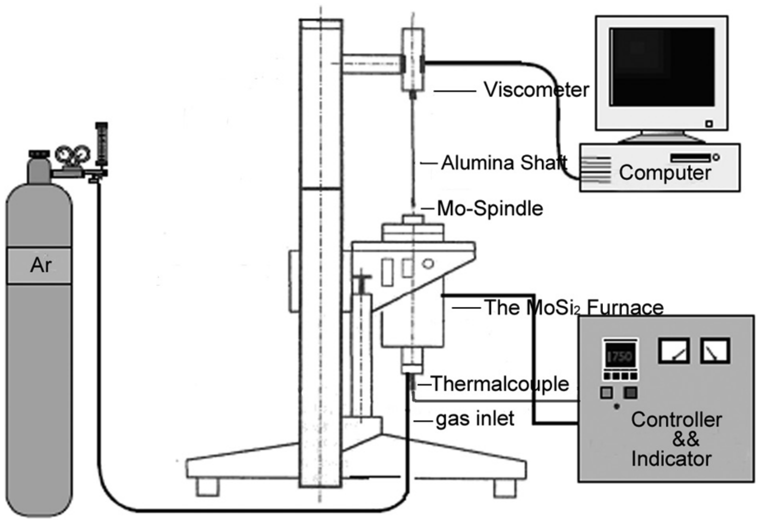

Figure 1: Experimental arrangement

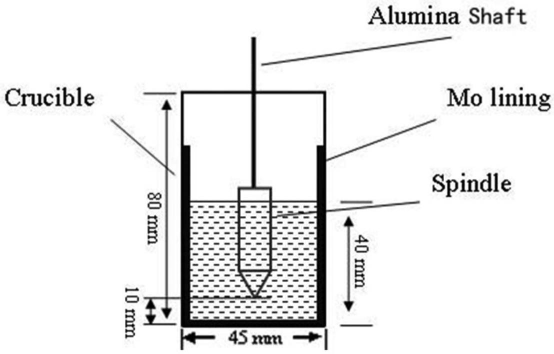

Figure 2: Crucible and Spindle

VISCOSITY MODELING

Urbain's Model

Urbain [11] proposed a classical classification, namely, all cations had been distributed into three kinds:

- Glass former, modifier and amphoteric
- Glass former: cations such as Si^{4+},Ge^{4+},P^{5+},etc.
- Modifier: cations of Na^{+},K^{+},Mg^{2+},Fe^{2+},Cr^{3+},Ti^{4+},etc.
- Amphoteric: cations Al^{3+} and Fe^{3+}.

An hypothetic ternary TO_2-A_2O_3-MO was adopted to calculation the equivalent mole fraction.

- T is a cation in a tetrahedral position: TO_4,
- A is an amphoteric cation: A^{3+},
- M is a modifier cation (M^{++}) associated with one oxygen ionic.

An empirical equation to predict the viscosity was proposed as follows:

$$\eta = A \cdot T \cdot \exp(1000 \cdot B/T) \quad (1)$$

$$-\ln A = m \cdot B + n \quad (2)$$

$$m = 0.29,\ n = 11.57$$

where, η is the viscosity, T is the temperature in K, the parameters A or B in Equations (1) and (2) are calculated from the experimental data. The parameters A and B have a linear relationship as shown in Equation (2), where m and n are deduced from the parameters A and B.

B is calculated from a polynominal equation, which was shown in Equations (3) and (4),

$$B = B_0 + B_1 \cdot X + B_2 \cdot X^2 + B_3 \cdot X^3 \quad (3)$$

$$B_i = a_i + b_i \cdot \alpha + c_i \cdot \alpha^2 \quad (4)$$

with i=0, 1, 2, 3.

$$X=N(TO_2)\ \alpha = MO/(MO+A_2O_3)$$

$N(TO_2)$ is the mole fraction of TO_2

$$MO= \sum \text{(mole frac. of the modifier oxides)}$$

$$A_2O_3= \sum \text{(mole frac. of the amphoteric oxides)}$$

The parameters of the ternary SiO_2-Al_2O_3-CaO and SiO_2-Al_2O_3-MgO were listed in Table 2.

Table 2 The parameters of ternary SiO_2-Al_2O_3-CaO and SiO_2-Al_2O_3-MgO

i	a(i)		b(i)		c(i)	
	Mg	Ca	Mg	Ca	Mg	Ca
	0	13.2	15.9	41.5	-18.6	-45
	1	30.5	-54.1	-117.2	33	130
	2	-40.4	138	232.1	-112	-298.6
	3	60.8	-99.8	-156.4	97.6	213.6

Present Model

The previous study [See ref. 1 to 9] indicated the effect of TiO_2 tended to decrease the viscosity of the silicate melts. The present model is an extension to the Urbain's model. The role of TiO_2 was considered as a network modifier. Based on the analysis and review of the experimental data [5, 6] in TiO_2 containing silicate systems of CaO-TiO_2-SiO_2 and CaO-TiO_2-Al_2O_3-SiO_2, the parameters of TiO_2 were introduced. According to the reliable experimental data [5, 6, 12, 13, 14, 15], the present parameters were determined as follows.

$$\eta = A\bullet T\bullet \exp(1000\bullet B/T) \tag{5}$$

$$-\ln A = m\bullet B+n \tag{6}$$

$$m = 0.338,\ n = 11.179$$

Where, the Equations (5) and (6) are just as the same as Equations (1) and (2), except for the value of the parameters m, n and A, B.

The parameter B is represented by a similar polynomial equation which is shown in Equation (7):

$$B= \frac{x_{Ca}}{x_{Ca}+x_{Mg}+x_{Ti}}\bullet(a_{Ca}+b_{Ca}\bullet X+c_{Ca}\bullet X^2+d_{Ca}\bullet X^3)+$$

$$\frac{x_{Mg}}{x_{Ca}+x_{Mg}+x_{Ti}}\bullet(a_{Mg}+b_{Mg}\bullet X+c_{Mg}\bullet X^2+d_{Mg}\bullet X^3)+$$

$$\frac{x_{Ti}}{x_{Ca}+x_{Mg}+x_{Ti}}\bullet(a_{Ti}+b_{Ti}\bullet X+c_{Ti}\bullet X^2+d_{Ti}\bullet X^3)+$$

$$\alpha\bullet(a_1+b_1\bullet X+c_1\bullet X^2+d_1\bullet X^3)+\alpha^2\bullet(a_2+b_2\bullet X+c_2\bullet X^2+d_2\bullet X^3) \tag{7}$$

Where, X, x_{Ca}, x_{Mg} and x_{Ti} are the mole fractions of SiO_2, CaO, MgO, TiO_2, respectively. α

is defined as $\frac{x_{Al}}{x_{Ca} + x_{Mg} + x_{Ti} + x_{Al}}$, x_{Al} is the mole fraction of Al_2O_3. ai bi ci di are calculation parameters.

The parameters of a, b, c, d in present calculation were listed in Table 2.

Table 2: The parameters in present model

	Ca	Mg	Ti	1	2
a	45.2	55.9	82.9	138.3	759.2
b	-154.9	-303.8	-911.6	626.6	-4824.6
c	267.8	666.6	3620.1	-78.1	8405.8
d	-117.7	-409.4	-4346.6	-630.1	-4439.5

MODELING RESULT AND DISCUSSION

Figure 3 shows the comparison between the calculated viscosity using the present model and the experimental data [5, 6] for the systems of $CaO\text{-}TiO_2\text{-}SiO_2$ and $CaO\text{-}TiO_2\text{-}Al_2O_3\text{-}SiO_2$. It can be seen that the calculated results have a good agreement with the measured data.

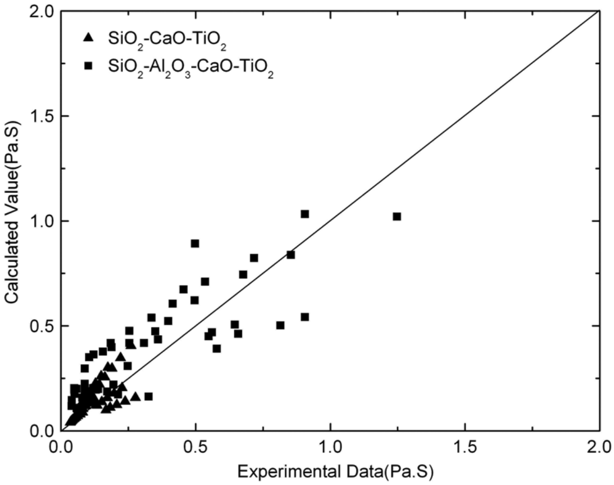

Figure 3: Comparison between the calculated viscosity and the experimental data [5, 6] using the present model

In order to compare the present model with Urbain's model the viscosities of the same slag were calculated using the Urbain's model, which is showed in Figure 4. Because in Urbain's calculation, there are no corresponding parameters for calculation in the binary system of $TiO_2\text{-}SiO_2$, simplified calculation was adopted. From the Figure 4, it can be seen that Urbain's model tends to give a lower value compared to the experimental data.

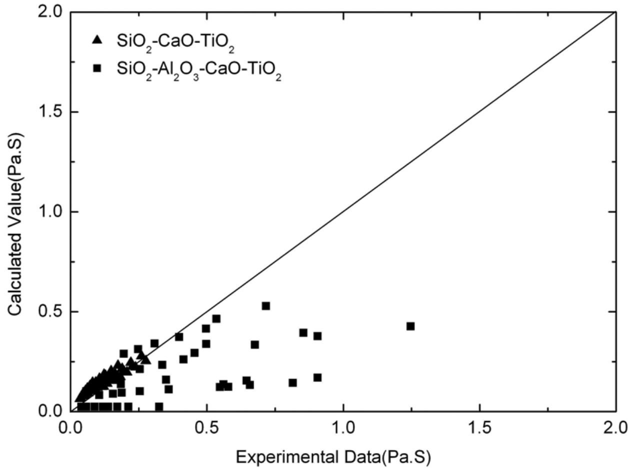

Figure 4: Comparison between the calculated viscosity and the experimental data [5, 6] using the Urbain's model

Xie *et al.* [1] and Van der Colf *et al.* [7] both had measured the viscosity of the BF type slags of CaO-MgO-TiO_2-Al_2O_3-SiO_2 systems under neutral conditions respectively. The content of TiO_2 in their studied covered a similar range of 17-33 wt% and 24.8-30.2 wt% (except for one composition of 37 wt% TiO_2 in Van der Colf et al's study). In order to test the present model, the authors also measured the viscosity of BF type slags of CaO-MgO-TiO_2-Al_2O_3-SiO_2 systems containing TiO_2 with a range of 20-40 wt% under neutral atmospheres. The detailed compositions are listed in Table 1. Some comparison between the calculation viscosity and the measured data are showed in Figures 5-7.

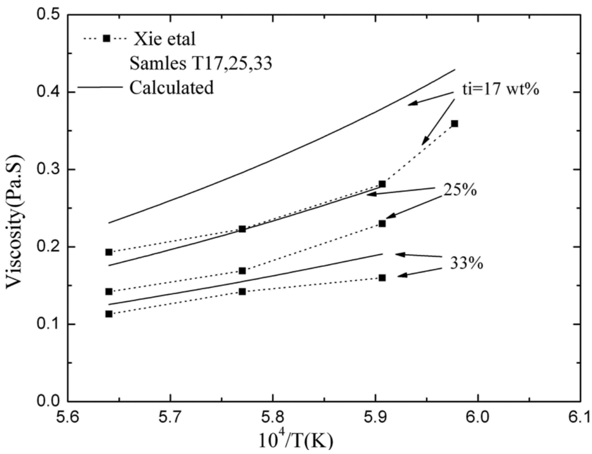

Figure 5: Comparison between the calculated viscosity and the experimental data from Xie *et al.*

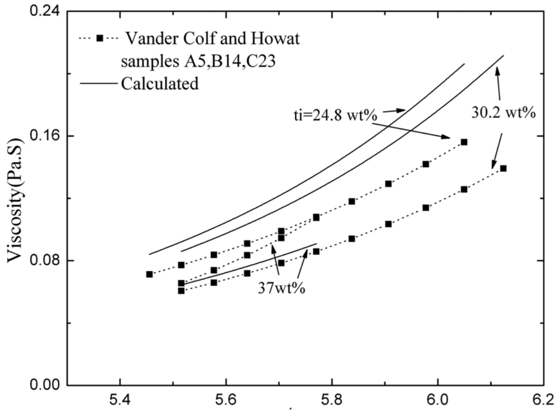

Figure 6: Comparison between the calculated viscosity and the experimental data from Vander Colf and Howat

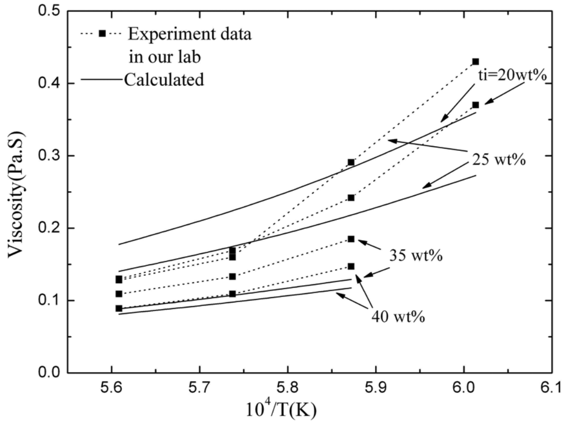

Figure 7: Comparison between the calculated viscosity and the experimental data in present work

Figures 5-7 show the comparison between the calculated values and the experimental data with the different amount of TiO_2. Figure 5 shows the comparison between the calculated values and the data from Xie et al's study [1]. Figure 6 and 7 show the comparison between the calculated results and the experimental data from Van der Colf et al's study [7] and the present study, separately. As can be seen, the present calculation gave reasonable viscosity estimation for the experimental data in Figures 5-7. All the calculations and the experimental data showed that viscosity of the slag was decreased with the increase of the TiO_2 addition, although the calculated values are consistently higher than the experimental data.

Handfield *et al.* [4] have investigated the influence of TiO_2, Ti_2O_3 and TiO additions on the viscosity of the blast furnace slag in the Steel Company of Canada. The compositions of the BF slag were 35% CaO, 37% SiO_2, 18% MgO, 4% Al_2O_3, 1.7% K_2O, 1.2% TiO_2, 1.2% S, 0.4% MnO, 0.2% Fe0 and 1.3% others. The addition amount of TiO_2 is 0%, 2%, 5%, 10%, 15% and 20% in mass percent, separately. The data in fully liquid region are chosen for comparison of the present modified model and Urbain's model. The results are showed in Figure 8. The calculations of the present modified model are better agreement with the experimental data than that of Urbain's result. In the present modified Urbain's model, the authors considered the role of TiO_2 in the silicate melts using the corresponding parameters, which gave a better result for predicting.

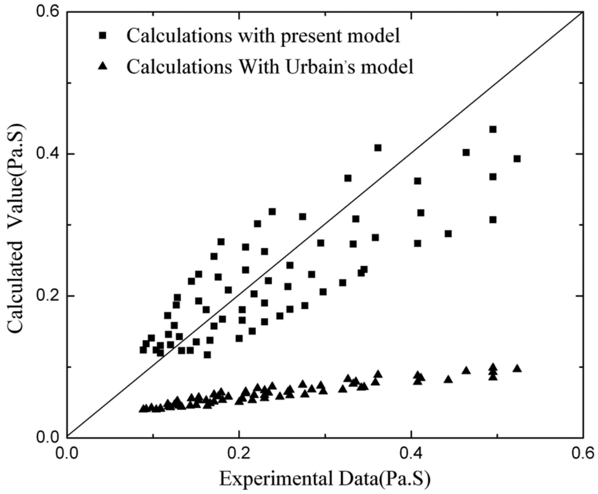

Figure 8: Comparison of the present modified model and Urbain's model with the calculated viscosity and the experimental data in BF slag containing TiO_2

CONCLUSIONS

The viscosities were measured by synthesizing the BF type slags containing high TiO_2 in present study. The content of TiO_2 has reached 40 wt% in the BF type slags. An extended model was reconstructed on the base of Urbain's model by analyzing the reliable data of TiO_2 containing silicate systems. A serial of comparisons showed that the present model could accurately predict the viscosity of high TiO_2 containing blast furnace slags. Both the calculations and the experimental data indicated that the viscosity was decreased along with the increased amount of TiO_2 in the BF slags.

ACKNOWLEDGEMENTS

This work was financially supported by Natural Science Foundation of China (No. 50174026 and 50425415) and National Basic Research Program of China (973 Program: 2007CB613608).

REFERENCES

Xie, D., Mao, Y., Guo, S. & Zhu, Y. (1986). Iron and Steel, v21(1),pp. 6-11. [1]

Xie, D., Mao, Y., Guo, S. & Zhu, Y. (2004). VII International Conference on Molten slags Fluxes and Salts, South Africa. Inst.,Min.Metall, pp. 43-50. [2]

Handfield, G., Charette, G. G. & Lee, H. Y. (1971). *Light Metals*, New York, pp. 591-601. [3]

Handfield, G., Charette, G. G. & Lee, H. Y. (1972). *Journal of Metals*, v24(9), pp. 37-40. [4]

Dingwell, D. B. (1992). American Mineralogist, Vol. 77, pp. 270-274. [5]

Ohno, A. & Ross, H. U. (1963). Canadian Metallurgical Quarternay, v2(3), pp. 327-333. [6]

Vander Colf, J. & Howat, D.D. (1979). J.South Africa. Inst.Min.Metall, (11), pp. 255-263. [7]

Schenck, H. & Frohberg, M. G. (1962). Arch.Eisenhuttenw, Vol. 33, pp. 421-425. [8]

Frohberg, M. G. & Weber, R. (1965). Arch.Eisenhuttenw, Vol. 36, pp. 477-80. [9]

Zhang, L. & Jahanshahi, S. (2004). VII International Conference on Molten slags Fluxes and Salts, South Africa. Inst., Min.Metall, pp. 51-56. [10]

Urbain, G. (1987). Steel Research, 58, pp. 111-115. [11]

Bockris, J. O. M., Mackensie, J. D. & Kitchener, J. A. (1955). Trans.Farad.Soc, 51, pp. 1734-1748. [12]

Kozakevitch, P. (1960). Rev.Metall.Paris, 57, pp. 149. [13]

Urbain,G., Bottinga,Y. & Richet, P. (1982). Geochim.et Cosmo. Acta 46, pp. 1061-1072. [14]

Urbain, G., Cambier, F., Deletter, M. & Anseau, M. R. (1981). Trans. J. B.Ceram. Soc.80, pp. 139-141. [15]