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ESTIMATING SULFIDE CAPACITIES FOR TERNARY SYSTEMS WITH LIMITED SOLUBILITY

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Abstract

In view of successful application of mass triangle model in thermophysical properties, in the current work, the mass triangle model was extended to evaluate sulfide capacities of ternary systems with limited homogeneous region. Four ternary systems of Al_2O_3-FeO-SiO_2, FeO-CaO-SiO_2, CaO-$CaCl_2$-CaF_2 and CaO-CaF_2-SiO_2 were chosen to calculate iso-sulfide capacity based on the limited boundary data. The good agreement between reference data and calculated data indicated that this model is feasible and will play an indispensable role in the future. Compared with optical basicity model, the results obtained by mass triangle model are still competitive when containing Cl^- and F^- in the molten slag due to lacking the optical basicity values.

Key words: Mass triangle model; Sulfide capacities; Optical basicity model

1. Introduction

The increasing demand for extremely clean steels has called for more efforts to decrease impurities to extra-low concentration. Sulfur is considered as a serious impurity which considerably deteriorates ductility and fatigue strength of steel materials [1-3]. Therefore, desulphurization which aims at improving the production of clean steels plays a crucial role in ladle metallurgy. Commonly, the desulphurization was

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processed in ladle refining processes at very high temperatures. The fundamental slag systems are FeO-CaO-SiO_2 and Al_2O_3-FeO-SiO_2. Moreover, with the development of hot metal pretreatment in recent years, more attention was focused on lowering Si, P, S contents before charging it to the basic oxygen furnace (BOF). The reagent used in this process is mainly composed of lime when desulfurization is required. For this reason, the evaluation of sulfide capacities of slags saturated with CaO, $CaCl_2$, CaF_2 or SiO_2 at a lower temperature would be more meaningful.

In order to further understand the desulfurization and process control, it is of the utmost importance to acquire knowledge of sulfide capacities of slags. Up to now, numerous experimental studies have been carried out to explore the sulfide capacities of slag systems in metallurgical processes. M. M. Nzotta [4] studied the sulfide capacities of "FeO-SiO_2 * MERGEFORMAT " melts with known sulfur and oxygen partial pressures in the temperature range of 1623 to 1723 K by the equilibrium measurement of gas-slag reaction. Meanwhile, Shiro Ban-ya [5] investigated the sulfide capacity of CaO-Al_2O_3-CaF_2 * MERGEFORMAT * slags at the temperature from 1823 to 1923 K. Kim Kärsrud [6] studied sulfide capacities of synthetic blast furnace slags at 1773 K. Recently, Simeonov et al [7] reported the sulfide capacity data for "FeO-MgO-SiO_2" slag at 1473 K and 1523 K in MgO crucibles. The sulfide capacities in the "FeO-MnO-SiO_2" system at 1823 K were determined by Hino and Fuwa [8]. Wang et al [9] have measured the sulfide capacities of CaO-SiO_2-CrO_x pseudo-ternary slags between 1823 K and 1923 K.

Parallely, evaluation methods also have been developed in these years. The optical basicity model, first addressed by Duffy and Igram [10], was then further modified by R. W. Young et al [11]. The Young model indicated below presented a satisfactory method for calculating sulfide capacities Cs as a function of optical basicity Λ, temperature T (K) and weight percent of some oxide components of the slag.

When $\Lambda < 0.8$, then:

$$\log C_s = -13.913 + 42.84\Lambda - 23.82\Lambda^2 - \\ -(11710/T) - 0.02223SiO_2 - 0.02275Al_2O_3 \quad (1)$$

When $\Lambda \geq 0.8$, then:

$$Cs = -0.6261 + 0.4808\Lambda + 0.7197\Lambda^2 + \\ +(1697/T) - (2587\Lambda/T) + 0.0005144FeO \quad (2)$$

However, limitations also have been placed on lacking the optical basicity values for chlorides and some transitional element oxides such as $CaCl_2$, Cr_2O_3.

As an alternative to optical basicity model, geometrical model could be a better choice. With the development of the technology of computer calculation, various geometric models provide considerable valuable data which are too difficult to obtain through the experiments. These geometric models such as Toop, Hillert, Muggianu and Kohler models are used to predict not only thermodynamic properties but also thermophysical properties for ternary and multicomponent systems from binary ones including chlorides and transitional element oxides. One of the promising geometrical models is mass triangle model proposed by Chou et al [12]

which applied limited data on the boundary of the homogeneous region to calculate the properties within it. Successful applications have been proved in evaluation of density [13], surface tension [14] as well as electrical conductivity in ternary system with limited solubility. In the present study, this model has been extended to evaluate one of the thermochemical properties, i.e. the sulfide capacities of several ternary systems with limited homogeneous phase region.

2. Theoretical fundamentals

In order to orient readers, the brief introduction of mass triangle model was presented here. As shown in Figure 1, it represents a system with a boundary of the homogeneous field. Chou proposed a new model called mass triangle model using limited data on the boundary of the homogenous to calculate properties within it [15].

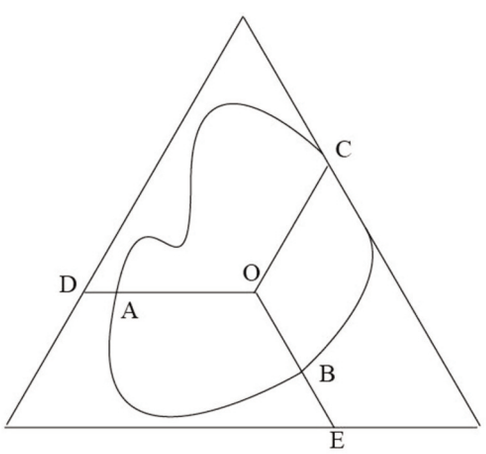

Figure 1. Schematic graph of ternary system with limited solubility region

As shown in Figure 1, the sulfide capacities at point O, C_o is expressed as the weight summation of the sulphide capacities of the other three points A, B and C.

$$C_o = W_A C_A + W_B C_B + W_C C_C \quad (3)$$

Three lines OD, OE and OC are drawn from the point O parallel to three sides and intersect the boundary of the homogenous phase region at A, B, C. The boundary in where C_A, C_B and C_C represent sulfide capacity at points A, B, C, respectively; W_A, W_B, and W_C are the weight factors corresponding to these three points.

The weight factors are determined by triangle area ratios.

$$W_A = \frac{S_{\Delta OBC}}{S_{\Delta ABC}} \quad (4)$$

If the sulfide capacities at points A, B, C are known, the sulfide capacities at any point within the homogenous solution region can be calculated. The detailed description of this new model can also be found in earlier papers [8, 9].

3. Results and discussion

3.1 Application to the Al_2O_3-FeO-SiO_2 system

In most steel-making practices, the knowledge of the sulfide capacities of FeO containing slags is valuable to master the desulfurization processes since FeO is an important component in these slags. However, due to experimental difficulties, especially at high temperatures, very few studies were carried out for the FeO containing slags. M. M. Nzotta et al [16] measured sulfide capacity for FeO-Al_2O_3-SiO_2 and FeO-CaO-SiO_2 system at 1873 K. Based on their experimental data, the sulfide capacity of FeO-Al_2O_3-SiO_2 was calculated

according to the mass triangle model, shown in Figure 2.

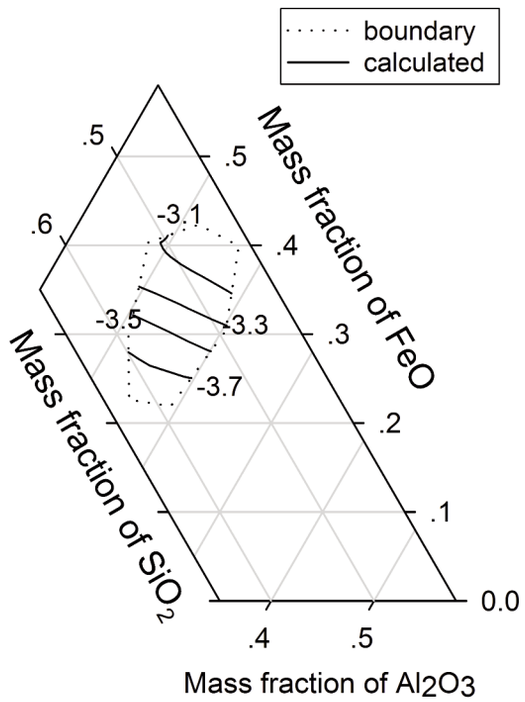

Figure 2. Sulfide Capacities in logarithm of Al_2O_3-FeO-SiO_2 system at 1873 K

Four sulfide capacity contour lines were obtained. In this case, the lowering trends of the sulfide capacities by the addition of SiO_2 as well as the replacement of FeO by Al_2O_3 are presented as expected.

3.2 Application to the FeO-CaO-SiO_2 system

In the case of FeO-CaO-SiO_2 system at 1773 K, boundary data were still using the experimental values provided by M. M. Nzotta [16], the sulfide capacity of this system was evaluated. Seven sulfide capacity contour lines were shown in Figure 3.

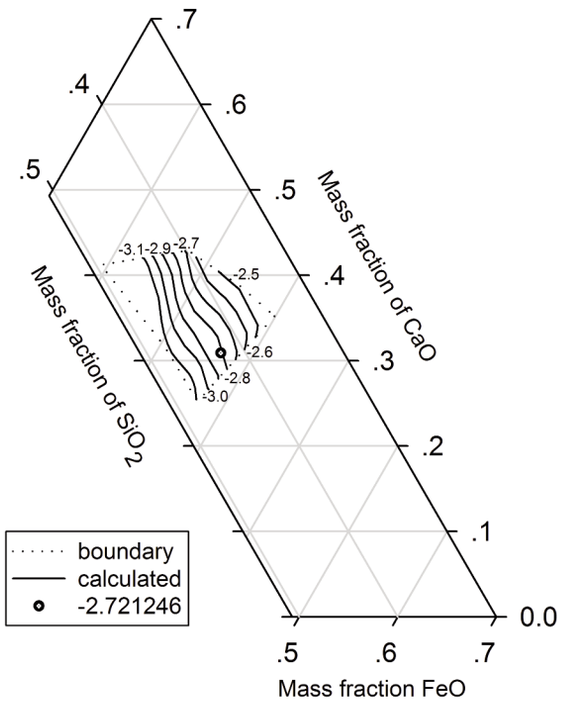

Figure 3. Sulfide Capacities in logarithm of FeO-CaO-SiO_2 system at 1773 K

As seen in this figure, the increase in the SiO_2 content or the decrease of FeO content resulted in the sharp decrease of sulfide capacities while the influence of CaO can be ignored.

In order to compare the effectivity of this new model, one reference data (a circle in Figure 3) located within the middle miscible area was used for comparison as shown in Table 1. The deviation of calculation results with experimental data was measured by the error rate, defined as eq. (5). The error rate was referred to as the percentage of incorrect recognitions for each data, as showed in the equation below:

$$\text{Error rate} = \frac{calculated\ data - reference\ data}{reference\ data} \quad (5)$$

Table 1 Comparison between the calculated sulfide capacities using new model and optical basicity method and the reference values in the FeO-CaO-SiO_2 system at 1773 K

Composition (mass%)			Reference data (log Cs)	Mass triangle model		Optical basicity method	
FeO	CaO	SiO_2		log Cs	Err.%	log Cs	Err.%
0.266	0.309	0.425	-2.721	-2.82	3.68	-2.43	-10.7

It was demonstrated that this new model worked very well in predicting sulfide capacity for the FeO-CaO-SiO_2 system, while the deviation of optical basicity method went up to -10.7%.

3.3 Application to the CaO-CaF_2-SiO_2 system

CaF_2 was applied in desulfurization slag in order to decrease the melting point of corresponding slags. The typical ternary system is CaO-CaF_2-SiO_2. Katsujiro et al [17] measured sulfide capacities of CaO-CaF_2-SiO_2 in the temperature range of 1473 K-1623 K. According to their work, the sulfide capacities contours were evaluated based on the new model, as shown in Figure 4.

The sulfide capacities showed a drastic increase with the increase of CaO/SiO_2 ratio. Meanwhile, the increasing CaF_2 in slags also increases sulfide capacities, which suggests the important role of CaF_2 in the desulfurization.

In this case, several reference data (circles in Figure 4) located within the middle miscible were used for comparison as shown in Table 2.

It was demonstrated that mass triangle model works better in view of the deviations of both mass triangle model and optical basicity model, in spite of the three relatively large deviations in the case of mass triangle model. The possible reason of the larger deviation occurred in the case of optical basicity method was due to this model was developed for slags in higher temperature range. Moreover, the optical basicity model used in this system had seven relatively large deviations. The optical basicity values used for CaO, CaF_2 and SiO_2 were 1.0, 0.43, 0.46 respectively and the sulfide capacities for this system were calculated using eq. (1) and eq. (2) as shown in the introduction.

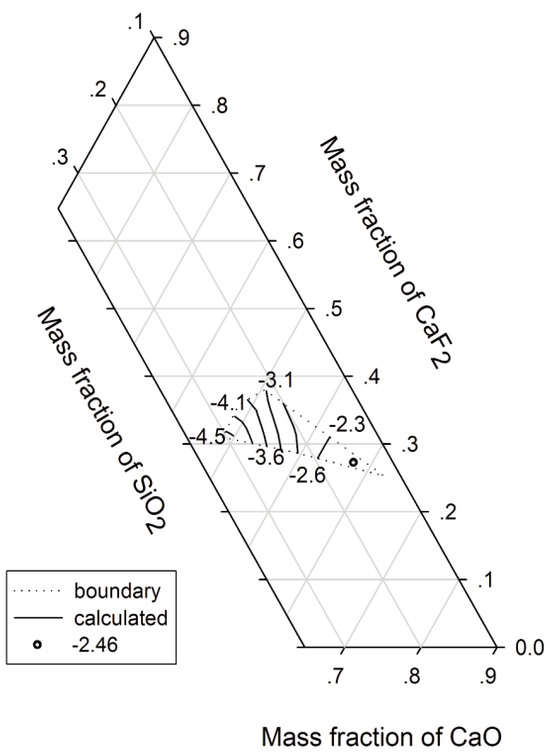

Figure 4. Sulfide Capacities in logarithm of CaO-CaF_2-SiO_2 system at 1523 K

Table 2 Comparison between the calculated sulfide capacity using new model and optical basicity method and the reference values in the CaO-CaF_2-SiO_2 system

Composition (mass%)			T/K	Reference data (log Cs)	Mass triangle model		Optical basicity method	
CaO	CaF_2	SiO_2			log Cs	Err.%	log Cs	Err.%
0.39	0.4	0.21	1473	-3.44	-3.55	3.21	-4.12	19.77
0.43	0.37	0.2	1473	-3.26	-3.41	4.699	-3.93	20.55
0.575	0.273	0.152	1523	-2.46	-2.35	-4.45	-2.89	17.48
0.426	0.347	0.227	1573	-2.48	-3.17	27.7	-3.45	39.11
0.43	0.3	0.27	1623	-3.16	-3.39	7.39	-3.29	4.11
0.443	0.325	0.232	1623	-2.54	-3.34	31.5	-3.24	27.56
0.481	0.29	0.229	1623	-2.19	-3.11	41.8	-2.96	35.16
0.551	0.256	0.193	1623	-2.23	-2.2	-1.268	-2.402	7.71

3.4 Application to the CaO-$CaCl_2$-CaF_2 system

In order to select proper reagents in hot metal pretreatment, it is vital to obtain the thermodynamic data of the melts at lower temperatures. However, the data for sulfide capacity of molten slag is still scarce, especially containing with Cl^- and F^- whose abilities of holding elements like S have been found by few reports [18-22]. Simeon et al [23] have measured sulfide capacity of CaO-$CaCl_2$-CaF_2 at 1373 K. Based on the boundary data provided by Simeon, the sulfide capacities based on mass triangle model were calculated as shown in Figure 5.

It shows that the sulfide capacities increased with the replacing chloride by fluoride at constant content of CaO. At the same time, the sulfide capacities increased slightly with increasing CaO content at the constant ratio of CaF_2/$CaCl_2$ since the lime content mainly defined the basicity of slag.

Similarly, two reference data (circles in Figure 5) located within the middle miscible area have been selected for comparison as shown in Table 3.

The maximum error rate is 1.04% and the minimum error rate is 0.798%. It was demonstrated that mass triangle model works

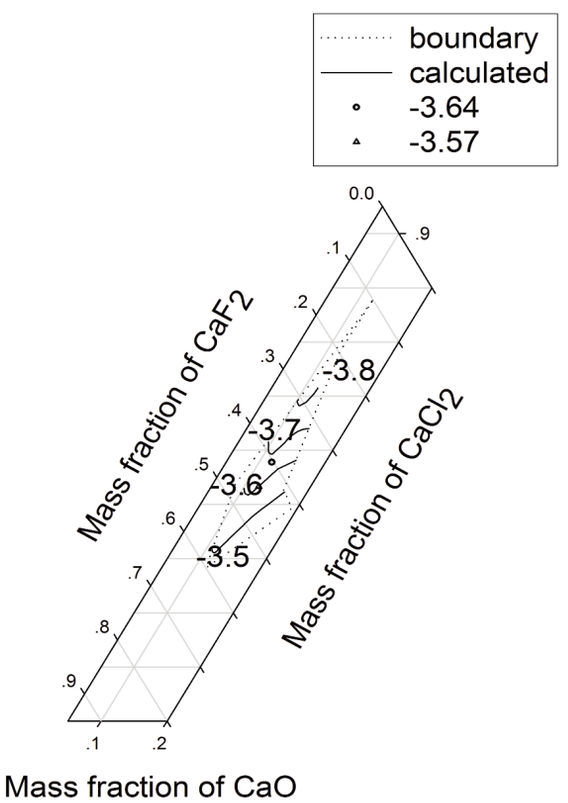

Figure 5. Sulfide capacities in logarithm of CaO-$CaCl_2$-CaF_2 system at 1373 K

Table 3 Comparison between the calculated sulfide capacities using new model the reference values in the CaO-$CaCl_2$-CaF_2 system at 1373 K

Composition (mass%)			Reference data (log Cs)	The new model	
CaO	$CaCl_2$	CaF_2		log Cs	Err. %
0.118	0.438	0.444	-3.64	-3.67	0.798
0.122	0.433	0.445	-3.57	-3.61	1.04

very well in predicting sulfide capacity for the CaO-$CaCl_2$-CaF_2 system. However, since the optical basicity values for $CaCl_2$ are not available, optical basicity method can not be used to calculate sulfide capacities for this system.

4. Conclusion

In view of the great importance of sulfide capacities in industry practice, it was essential to obtain reliable values from both experimental and theoretical. In theoretical aspect, optical basicity model is widely used in this field. However, with the development of hot-metal treatment, optical basicity model faced great challenges due to lacking the theoretical optical basicity of fluorides and chlorides. As a promising alternative, mass triangle model has been demonstrated its flexibility and reliability not only in high temperature cases, CaO-SiO_2-FeO, FeO-Al_2O_3-SiO_2 etc. but also in lower temperature cases with containing F^- and Cl^- : CaO-CaF_2-SiO_2, CaO-CaF_2-$CaCl_2$. Thus, based on the present study, mass triangle model is a powerful tool in evaluating sulfide capacities of ternary systems with miscible gap.

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References

[1] Ž. Živković, N. Mitevska, I. Mihajlović, Đ. Nikolić, J. Min. Metall. Sect. B-Metall. 45(1) B (2009) 23.

[2] F. Habashi, J. Min. Metall. Sect. B-Metall. 45(1) B (2009) 1.

[3] C. B. Shi, X. M. Yang, J. S. Jiao, C. B. Shi, C. Li, H. J. Guo, ISIJ Int., 50(10) (2010) 1362.

[4] M. M. Nzotta, S. C. Du, S. Seetharaman, ISIJ Int., 39(7) (1999) 657.

[5] S. Ban-ya, M. Hobo, T. Kaji, T. Itoh, M. Hino, ISIJ Int., 44(11) (2004) 1810.

[6] K. Kärsrud, Scand. J. Metall., 13(3) (1984) 144.

[7] S. R. Simeonov, R. Sridhar, J. M. Toguri, Metall. Mater. Trans. B, 26(2) B (1995) 325.

[8] M. Hino, T. Fuwa, Proc. 3rd International Iron and Steel Congress. ASM&ISS, AIME, Chicago, 1978, p.321-326.

[9] L. J. Wang, S. Seetharaman, Metall. Mater. Trans. B, 41(2) B (2010) 367.

[10] J. A. Duffy, M. D. Ingram, J. Am. Chem.

Soc., 93(24) (1971) 6448.

[11] R. W. Young, J. A. Duffy, G. J. Hassall, Z. Xu, ISIJ Int., 19(3) (1992) 201.

[12] K. C. Chou, Proc. CALPHAD XXIII meeting, Madison, Wisconsin, USA, 1994, p.315-321.

[13] L. J. Wang, S. L. Chen, K. C. Chou, Y. A. Chang. Computer Coupling of Phase Diagrams and Thermochemistry, 29(2) (2005) 149.

[14] L.J. Wang, K.C. Chou, S.L. Chen, Y. A. Chang, Z. Metallkd., 96(8) (2005) 948.

[15] K. C. Chou, X. M. Zhong, K. D. Xu, Metall. Mater. Trans. B, 35(4) B (2004) 715.

[16] M. M. Nzotta, S. C. Du, S. Seetharaman, Metall. Mater. Trans. B, 30(6) B (1999) 909.

[17] K. Susaki, M. Maeda, N. Sano, Metall. Mater. Trans. B, 21(1) B (1990) 121.

[18] M. Muraki, H. Fukushima, N. Sano, Tetsu-to-Hagané, 71(6) (1985) 693.

[19] A. Mckague, A. McLean, I. D. Sommerville, Proc. Fifth Int. Iron and Steel Congress, Washington DC, USA, 1986, 6, p.493-497.

[20] H. Inoue, Y. Shigeno, M. Tokuda, M. Ohtani, Tetsu-to-Hagané, 69(1983) 210.

[21] A. M. Cameron, J. Cook, P. Grieveon, Int. Symp. Physical Chemistry of Iron and Steelmaking, CIM, Toronto, Canada, 1982, p.1.3-1.17.

[22] L. J. Wang, S. Seetharaman, Metall. Mater. Trans. B, 41(2) B (2010) 367.

[23] S. Simeonov, T. Sakai, M. Maeda, Metall. Mater. Trans. B, 23(3) B (1992) 325.