4th International Conference on Molten Slags and Fluxes, 1992, Sendai, ISIJ

A MODEL DESCRIBING THE AMPHOTERIC BEHAVIOUR OF AL^{3+} IN MOLTEN LIME-ALUMINA-SILICA TERNARY SYSTEM

JIANG Guochang, ZHANG Xiaobing,

Shanghai University of Technology, China

Synopsis: A model quantitatively describing the amphoteric behaviour of alumina was develpoed in this paper, based on the cell microstructure of slag. The calculation result is in an acceptable agreement with that of the experiment of Yamane et al.

Key Words: amphoteric behaviour, alumina, lime-alumina-silica system

1. Introduction

Alumina is a typical amphoteric compound frequently emerging in metallurgical slags, in magma as well as in many kinds of glasses. As a widely accepted view point, AlO_4^{5-} is acidic and AlO_6^{9-} is basic. Nevertheless, this is at utmost a qualitative concept. Even Gaye's Model[1,2] which is the most successful thermodynamic parameter model of slag right now, also avoids to directly and quantitatively describe how ($\%AlO_4^{5-}$) varies to follow the variation of slag composition. In order to elucidate the chemical activation of lime-alumina-silica slag, a model quantitatively describing the amphoteric behaviour of alumina in the molten slag was developed.

2. The modelling and the comparison of its results with the published data

The foundation of this model is the concept defined by us as cell theory of slag[3]. Namely, the microstructural unit of molten oxide slag is various kinds of i–O–j cells including that of i = j. And the chemical activation of molten slag is determined by the mole fraction (Y) of various i–O–j cells as well as their basic charateristics (B)–an index of the bonding energy of the cell, or say the activity coefficient of $O^{=}$ anion including in the cell. By means of XPS and so on, 9 kinds of i–O–j cells were detected in lime-alumina-silica ternary system as follows[4,5]:

cell	symbol	cell	symbol	cell	symbol
Si–O–Si	(11)	Si–O–Al_b	(13)	Al_a–O–Ca	(24)
Si–O–Al_a	(12)	Si–O–Ca	(14)	Al_b–O–Al_b	(33)
Al_a–O–Al_a	(22)	Al_a–O–Al_b	(23)	Ca–O–Ca	(44)

Al_a denotes the Al^{3+} in AlO_4^{5-}, Al_b denotes that in AlO_6^{9-}. Considerring a lot of modern thermodynamic parameter models are based on the assumption that various cell reactions:

$$(i-O-i)+(j-O-j)=2(i-O-j) \tag{1}$$

happen when multi-component slag is formed, it is reasonable to suppose the following cell reaction for lime-alumina-silica system:

$$N_C(44)+2N_S(11)+3N_AP_a(22)+3N_AP_b(33)=\alpha(12)+\beta(13)+\delta(14)+\varepsilon(24) \tag{2}$$

N_C, N_A, N_S denotes respectively the mole fraction of CaO, Al_2O_3, SiO_2. P_a and P_b denotes the relative ratio of Al_a and Al_b respectively, i.e. $P_a = 1 - P_b$, and

$$P_a = \frac{N_{22}}{3N_A} = \frac{N_{Al_a}}{2N_A} \tag{3}$$

α, β, δ and ε all are the stoichiometric parameters.

For the mass balancing of reaction (2), it was found the whole liquid region must be divided into three sub-regions.

(1). If $2N_S > (3N_A + N_C)$, it is the sub-region of high silica, or say silica is in excess, and $\varepsilon = 0$.

(2). If $3N_A > (2N_S + N_C)$, it is such a sub-region in which there is an excess alumina. Then $\delta = 0$.

(3). In the middle content region,

$$\alpha = 2N_S - N_C - 3N_A + 6N_A P_a \tag{4}$$

$$\beta = 6N_A(1 - P_a) \tag{5}$$

$$\delta = 2N_S + N_C - 3N_A \tag{6}$$

$$\varepsilon = 3N_A + N_C - 2N_S \tag{7}$$

P_a is a thermodynamic variable, through $\frac{\partial(\triangle G_2^\circ)}{\partial P_a} = 0$ it should be determined. $\triangle G_2^\circ$ is the variation of the standard free energy of reaction (2). The model of Sastri et al also based on this consideration[6]. This corresponds to

$$\frac{\partial}{\partial P_a}\left\{\alpha\ln(B_{12}Y_{12}) + \beta\ln(B_{13}Y_{13}) - 3N_A P_a \ln(B_{22}Y_{22}) - 3N_A P_b \ln(B_{22}Y_{22}) - 3N_A P_b \ln(B_{33}Y_{33})\right\} = 0 \tag{8}$$

$$Y_{ij} = \frac{N_{ij}}{\sum N_0} = \frac{N_{ij}}{N_C + 2N_S + 3N_A} \tag{9}$$

Take $Y = a\psi$, ψ denotes the progression degree of the cell reaction. It depends upon the composition of the slag, so it should be a constant. Hence, the following can be deduced from Eq.(8).

$$\frac{\beta^2 P_a}{\alpha^2(1 - P_a)} = \frac{B_{12}^2 B_{22}}{B_{13}^2 B_{22}} = B \tag{10}$$

Here, the value of B was quoted from the theory of optical basicity. Namely, take $B_{33} = 0.80$, $B_{22} = 0.70$, $B_{13} = 0.65$ and $B_{12} = 0.56$. Among them B_{12} and B_{22} were evaluated based on the concept of "group optical basicity"[5].

According to this model, among the 4 $O^=$ anions coordinating an Al_a cation one is thought to form the so called complex bond with this Al_a. Meanwhile, this $O^=$ anion is no longer in two bond structure as (i–O–j), but is changed to be with triple bonds as ($\mathrm{i{-}O} <^{2}_{j}$), or (ij2)[3]. Using the following assumed relationship it may be converted to two bond structure cell.

$$(ij2) = 0.5(ij) + 0.5(i2) + 0.5(j2) \tag{11}$$

This complex bond does not take part in reaction (2). Thereby the P_a calculated from Eq.(10) has to be corrected, or say to add the effect of (ij2) on both sides of reaction (2). The total amount of complex bond is $2P_aN_A$. It was assumed that, in reactant side there are (222) and (232). And the proportion of their content equals P_a / P_b. In product side, the non-bridging O^- (O_{nbr}) containing in (14), (13) and (24) in turn to form complex bond with Al. Certainly, this coincides with the assumption of electroneutrality compensation by network modifier.

By means of the chemical shift displayed on X ray fluoroscope ($Al{-}K_{\alpha,1,2}$) Yamane et al investigated systematically the amphoteric behaviour of alumina in lime-alumina-silica slag[7]. The results of this model

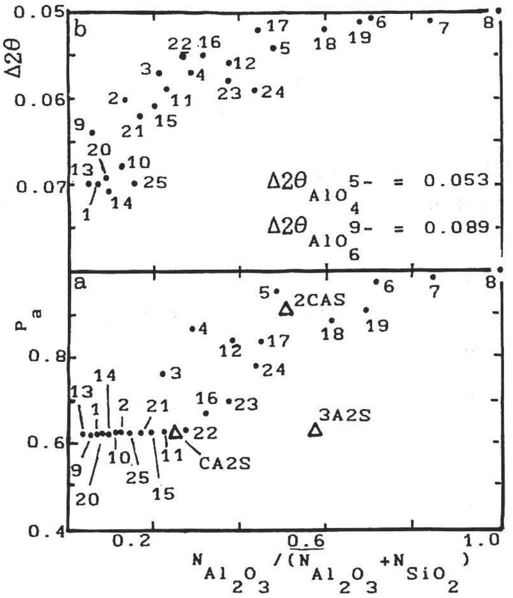

Fig.1.The comparison of the calculted results (a) and that of Yamane's experiment (b).
1--25 denote the sample number.

as shown in Fig.1 was found in an acceptable agreement with that of the experiment of Yamanee et al. The composition of the 25 samples and the boundaries of sub-regions are shown in Fig.2. Besides the 25 points, Fig.1 contains the calculation results on points corresponding to compounds 2CAS($2CaO-Al_2O_3-SiO$) or CA2S($CaO_2-Al_2O_3-2SiO_2$). Even though this model intends to describe molten slag, the calculation about 3A2S ($3Al_2O_3-2SiO_2$) solid mullite was also found to be agree with the experiment. Using an EPMA set, Hanada et al completed a fluoroscopy measure for a non crystalized film of 3A2S. It was indicated by them that P_a is about 60%[8]. The average coordination number is 4.3 to 4.7 for this glass pursuanting to the X ray diffraction-radial distribution function research of Morikawa et al[9]. In Fig.1 the calculation results about 2CAS, CA2S and 3A2S coincide with that of 25 points quits well.

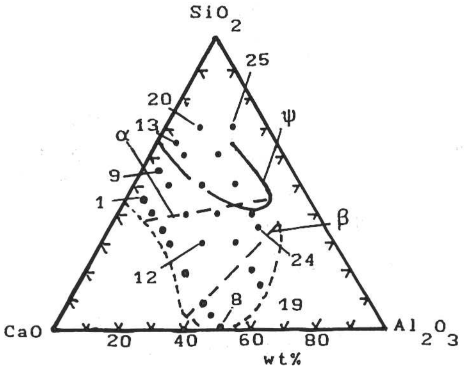

Fig.2.The composition of Yamane's smaple and the boundaries of 3 sub-regions.
Note:α--the boundary of high Silica region
β--the boundary of high alumina region
ψ--the galss formation region
1 to 25--sample number

This diagram also exhibits the characteristics of three sub-regions. Pursuanting to this model, almost all alumina behaves as AlO_4^{5-}, if it is in the high alumina sub-region. But in high silica sub-region P_a for various examined points is about 62%, this gets some difference with the experiment of Yamane et al.

3. Discussion

(1). This paper is devoted to a thermodynamic parameter model. The merit of this way is the possibility to discuss easily the influences of some factors, comparing to doing this based on experiment. Fig.3 exhibits the effect of $N_A/(N_A+N_S)$ under the condition of constant N_C. Fig.4 indicates the influence of N_C/N_A in the case of a constant N_S. Fig.5 displays that of N_C/N_S when N_A is constant. The revealed relationship points out P_a in molten lime-alumina-silica is determined not by the individual factor, but by the contents of three components.

(2). In a quite long period, the researches on the amphoteric behaviour of alumina were limited mainly for soda ash-alumina-silica glasses. It was claimed that $Al_a/(Al_a+Al_b)$ and $\%O_{nbr}$ in these glasses get an abrupt change at $N_{Al}/N_{Na}=1.0$. Although in recent years some measurements based on advanced instruments still support this view point$^{8)}$, there are also some experiments argue against this view point. In fact, this view point was initially proposed to explain the variation of some physical properties of the melt in following the variation of N_{Al}/N_{Na}. However, it was proved that many physical properties do not have an abrupt change seriously at $N_{Al}/N_{Na}=1.0$, but the turning points disperse inside a range of composition$^{10)}$. Dingwell found during his research on the pseudo binary system of $Na_2Si_2O_5$–$Na_4Al_2O_5$ that the viscosity of this system is a function of $N_{Al}/(N_{Al}+N_{Si})$. And the minimum of viscosity emerges when $N_{Al}/(N_{Al}+N_{Si})=0.2-0.3$, or say $N_{Al}/N_{Na}=0.17-0.23^{11)}$.

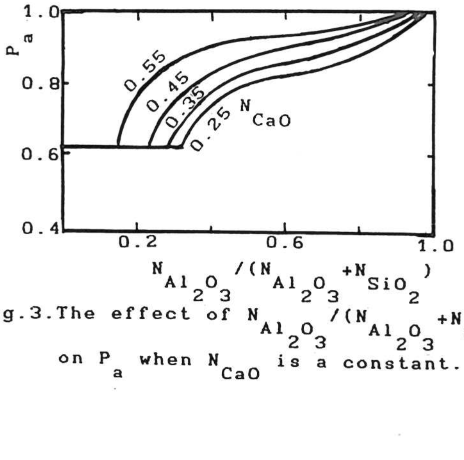

Fig.3.The effect of $N_{Al_2O_3}/(N_{Al_2O_3}+N_{SiO_2})$ on P_a when N_{CaO} is a constant.

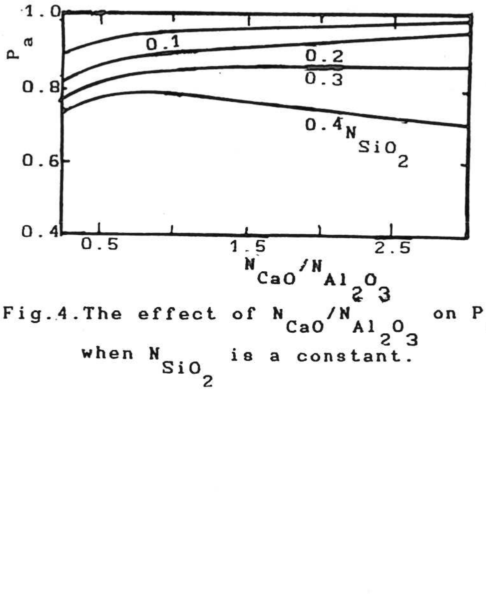

Fig.4.The effect of $N_{CaO}/N_{Al_2O_3}$ on P_a when N_{SiO_2} is a constant.

According to this result, it is difficult to expect that there are a simple and distinct relationship between the physical properties and N_{Al}/N_{Na}. Provided, the more direct factor effecting on physical properties is the polymerization of the microsturctural units in the melt.

(3). What is the differences between the amphoteric behaviour of alumina in soda ash-alumina-silica glasses and that in the whole liquid region of lime-alumina-silica? Yamane et al made a comparison of lime-alumina-silica and magnesia-alumina-silica, and claimed the difference of the effects of Ca and Mg is not distinguishable$^{7)}$. In contrast, many researchers keep different point of view. Mysen indicated that Al^{3+} and Si^{4+} involved in the tetrahedra network of soda ash- alumina- silica can change their site randomly$^{11)}$. In that of lime-alumina-silica, however, distinguishable ordering appears. This results from the influence of various basic cations on the stability of bond in tetrahedra$^{11)}$. DE Jong et al gave a similar comment$^{12)}$. Furthermore, Appen and Varshal claimed that AlO_4^{5-} and AlO_6^{9-} coexisted in lime-alumina-silica and only AlO_6^{9-} is contained in magnesia-alumina-silica[3] The result of this model is probably valid only for lime-alumina-silicasystem. At present, with this model it is impossible to distinguish the difference of the effects of Na^+, Ca^{2+} and Mg^{2+}. It is thought that they should cause a change in the evaluation of B, especially of B_{12} in Eq(11).

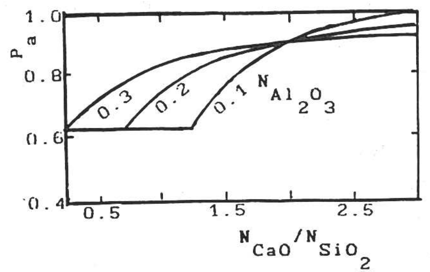

Fig.5.The effect of N_{CaO}/N_{SiO_2} on P_a when $N_{Al_2O_3}$ is a constant.

On the other hand, it is reasonable to find some similar feature about the amphoteric behaviour of alumina in either soda ash-alumina-silica or lime-alumina-silica. As aforementioned, the feature of the amphoteric behaviour of alumina is that a slower change in following the variation of N_{Al}/N_{Na}, except in the region adjacent to the turning point. Similar to this, the slope of the curve in Fig.4 is quite small. Pursuanting to this model, as shown in Fig.3 and 4, a more intensive effect of $N_A/(N_A+N_S)$ under a constant N_C was revealed comparing to that of N_A/N_C under a constant N_S. This can be understood based on Mysen's idea, as even in lime-alumina-silica, $N_A/(N_A+N_S)$ is an approximation of the proportion of Al and Si in tetrahedra network.

(4). As shown in Fig.5, the curves meet together almost at a point. It was interested in finding the similar result of Sastri et al[6]. When they investigated the effect of N_A under a constant N_C/N_S, they also found the curves almost meet together at a point.

(5). Iwamoto reported the measurement of $Na_2O-4.7\ SiO_2-XAl_2O_3(X=0-1.2)$ by means of Raman spectroscopy[13]. Two wave-peaks were shown at 950 and $1100cm^{-1}$. Mysen indicated these two wave-peaks respond to the existence of O_{nbr}[11]. And Furukawa et al claimed the wave-peak at $950cm^{-1}$ relates to the O_{nbr} resulting from alumina[14]. Thus, Iwamoto's result is an evident for O_{nbr} existence when $N_{Al}/N_{Na}=1.0$. Certainly, this is in contrast with the assumption of electroneutrality compensation for AlO_4^{5-}.

In inorganic chemistry, alumina is such a typical element preferring to form complex bond. If suggest the fourth bond of Al_a as a complex bond, then no need for the electroneutrality compensation! Based on this consideration, P_a was determined in this model not pursuanting to electroneutrality but in accordance with the minimum of the standard free energy variation of the cell reaction.

(6). Based on the X ray diffraction-radial distribution function method, Mysen claimed that there are only AlO_4^{5-} in the melt of CA2S[11]. This is different from the present model.

So far it is not scarce to find some contrary reports in the field, to which this paper refers. The reliability of either the instrument and the procedure of the measurement, or the sampling way may be the determining factors for the contradiction. Perhaps, during sampling the over heating of the melt and the following quenching rate play significant roles. Nowadays it is important to approach to the reality from both sides: theoretical modelling and experimental technology.

4. Conclusion remarks

(1). A thermodynamic parameter model is proposed in this paper. It was used in quantitatively description of the amphoteric behaviour of alumina in lime-alumina-silica molten slag. The calculation results are in an acceptable agreement with that of the experiment of Yamane et al. The main points of this model are: $\%Al_a/(\%Al_a+\%Al_b)$ is determined according to the minimum of the standard free energy variation of the cell reaction, and every Al_a contains one complex bond.

(2). The claculation based on this model indicates that the content of 3 conponents in lime-alumina-silica slag all effect $\%Al_a$. This seems to be a deeper discussion on the amphoteric behaviour of alumina.

(3). Based on this model, it is possible to further go on the calculation of the concentration of various cells in lime-alumina-silica slag and its bonding basicity.

Acknowledgement:

This paper is supported by The Foundation of National Natural Science of China

Reference:

1 H.Gaye, J.Welfringer:Proceedings of 2nd Intern. Symp. on Metallurgical Solags & Fluxes, Lake Tahoe, Nevada, Nov. 1984;357–375.
2 J.Lehmann, H.Gaye, W.Yamada, T.Matsumiya:Proceedings of 6th IISC, Nagoya, Japan, Oct.1990;vol.1, 256–263.
3 Jiang Guochang, Xu Kuangdi, Wei Shoukun: Some Advances on the Theoretical Research of Slag to be published.
4 K.Mizoguchi, M.Yamane, Y.Kaneko, Y.Suginohara:J.of JIM **448** 1(1984)12,1179–1186.
5 J.A.Duffy, M.D.Ingram:J.Non–Cryst. Solids, **421** 1(1976)373–410.
6 P.Sastri, A.K.Lahiri:Proceedings of 2nd Intern. Symp. on Metallurgical Slags & Fluxes, Lake Tahoe, Nevada, Nov. 1984;377–391.
7 M.Yamane, M.Okuyama:J.Non–Cryst. Solids **452** 1(1982);217–22.
8 T.Hanada, T.Aikawa, N.Soga:J.Non–Cryst. Solids **450** 1(1982);397–405.
9 H.Morikawa, S.I.Miwa, M.Miyake, F.Marumo, T.Sato:J.Am. Caremic Soc. **465** 1(1982);78–81.
10 B.M.J. Smets, T.P.A. Lommen:Phy. & Chem. of Glasses **422** 1(1981);6,158–162.
11 B.O.Mysen:Structure and Properties of Silicate Melts, Elsevier Sci. Publishers B.V. 1988;48–59, 79–91, 116–141.
12 B.H.W.S, DE Jong, C.M.Schramn, V.E.Parziale, Geochimica Acta **447** 1(1988);1223–1236.
13 N.Iwamoto:Bull.of JIM **416** 1(1977);11,771–777.
14 T.Furukawa, W.B.White:J.Non–Cryst. Solids **438** 1 & **439** 1(1980);87–92.