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NITRIDE CAPACITIES IN SLAGS

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Synopsis: Nitride capacities for various fluxes obtained by a newly developed technique of gas–slag equilibration are summarized as a function of temperature and slag composition. Activity coefficients of nitride, nitrogen distribution ratios between slag and liquid iron, and activities of SiO_2 and Al_2O_3 in $CaO-SiO_2-Al_2O_3$ system are discussed along with the refining characteristics of denitrogenization by using flux.

Key words: nitrogen, denitrogenization, distribution ratio, nitride capacity, slag

1. *Introduction*

There has been an increasing demand for low nitrogen steel products. However, nitrogen in liquid steel cannot be controlled to the same extent as sulfur can. Recently, studies on denitrogenization of liquid steel by using various fluxes have been made by measuring the nitride capacities[1-13], $C_{N^{3-}}(=(\text{mass-\%N})P_{O_2}^{3/4}/P_{N_2}^{1/2})$ and nitrogen distribution ratios between slag and metal[4,9,11-18].

The present paper deals with the dependence of nitride capacities on temperature and slag composition, activity coefficients of nitride, assessment of activities of Al_2O_3 and SiO_2 in $CaO-SiO_2-Al_2O_3$ system, and refining characteristics of denitrogenization. The data used in the present discussion were obtained by using a newly developed technique of gas–slag equilibration[8], in which partial pressures of oxygen and nitrogen are controlled by a $N_2-H_2-H_2O$ gas mixture.

2. *Basic consideration*

2.1 Nitride capacity

Based on the ionic gas–slag reaction given in Eq.[1]

$$1/2N_2 + 3/2\,(O^{2-}) = (N^{3-}) + 3/4O_2 \qquad [1]$$

nitride capacity, $C_{N^{3-}}$, is defined as

$$C_{N^{3-}} = (\text{mass-\%N})\, P_{O_2}^{3/4}/P_{N_2}^{1/2} = K_1\, a_{O^{2-}}^{3/2}/f_{N^{3-}} \qquad [2]$$

where K_1, $a_{O^{2-}}$, $f_{N^{3-}}$, and (mass–%N) represent the equilibrium constant for Eq.[1], the activity of O^{2-}, the activity coefficient of N^{3-} ion, and the concentration of nitrogen in the slag, respectively. The unit of partial pressure P_i is atm. It can be seen from Eq.[2] that $C_{N^{3-}}$ is a function of temperature and slag composition.

Dissolution of nitrogen in liquid iron can be expressed as

$$1/2\, N_2 = \underline{N}\ (1\ \text{mass-\%}) \qquad [3]$$

Equation [2] can be rewritten by using Eq.[3] as follows.

$$C_{N^{3-}} = L_N\, K_3\, P_{O_2}^{3/4}/f_N \qquad [4]$$

where L_N(=(mass–%N)/[mass–%N]), K_3, and f_N represent the nitrogen distribution ratio between slag and metal, the equilibrium constant for Eq.[3], and the activity coefficient of nitrogen relative to an infinite dilute 1 mass–% standard state, respectively.

When the oxygen partial pressure, P_{O_2}, is determined by the $\underline{Al}/(Al_2O_3)$ equilibrium given by Eq.[5],

$$2\underline{Al} + 3/2\ O_2 = Al_2O_3(s) \qquad [5]$$

equation [4] can be expressed as

$$L_N = C_N^{3-} \frac{f_N}{K_3} \left(\frac{K_5\, a_{Al}^2}{a_{Al_2O_3}} \right)^{1/2} \qquad [6]$$

2.2 Activity coefficient of nitride

Activity coefficients of nitride can be obtained from the results of slag-metal and gas-slag equilibration experiments. Let us consider AlN as an example for nitride.

Slag-metal equilibration: activity coefficient of AlN, γ_{AlN}, relative to pure solid can be derived from the following slag-metal reaction given by Eq.[7].

$$\underline{Al} + \underline{N} = AlN(s) \qquad [7]$$

$$\gamma_{AlN} = K_7\, a_{Al}\, a_N / X_{AlN} \qquad [8]$$

where K_7 and X_{AlN} represent the equilibrium constant for Eq.[7] and the mole fraction of AlN, respectively, and a_{Al} and a_N represent the activities of Al and N with respect to an infinite dilute 1 mass-% standard state, respectively.

Gas-slag equilibration: the reaction between gas and slags containing Al_2O_3 can be expressed as

$$1/2Al_2O_3(s) + 1/2N_2 = AlN(s) + 3/4O_2 \qquad [9]$$

The γ_{AlN} values can be evaluated from Eq.[10], using C_N^{3-} and $a_{Al_2O_3}$ values.

$$\gamma_{AlN} = K_9 \frac{a_{Al_2O_3}}{\alpha_{AlN}\, C_N^{3-}} \qquad [10]$$

where K_9 and α_{AlN} denote the equilibrium constant for Eq.[9] and X_{AlN}/(mass-%N), respectively.

If the values for $a_{Al_2O_3}$ are not available, the precipitation of AlN by lowering oxygen partial pressure gives the solubilities of AlN, which result in obtaining the γ_{AlN} values from Eq.[11] ; that is, assuming that Henry's law is valid up to the solubility limit.

$$\gamma_{AlN} = 1/X_{AlN} \qquad [11]$$

The solubilities of nitride can be estimated from the activity coefficients of nitride obtained from Eqs.[8] and [10] under the assumption that nitride obeys a dilute solution law.

3. *Experimental methods*

It is necessary for the dissolution of nitrogen into slags to control P_{O_2} at a considerably low level. In previous studies on nitride capacity, the following three experimental techniques have been used.

Slag-metal equilibration: P_{O_2} was controlled by the $\underline{Al}/(Al_2O_3)$ equilibrium, along with the control of P_{N_2} by a slag-metal equilibrium[16-18], or by the atmosphere of P_{N_2} =1 atm[3].

Gas-slag equilibration: slag was melted in a graphite crucible where a CO-N_2(-Ar) gas mixture controlled the P_{O_2} by the C/CO equilibrium[1,2,4-7,9]. A N_2-H_2-H_2O gas mixture was used for the control of P_{O_2} and P_{N_2} and the P_{O_2} values were measured using a solid electrolyte cell[8,10,11].

Gas-slag-metal equilibration: three phases equilibration was carried by using a CO- N_2(-Ar)[9] or N_2-H_2-H_2O[12,13] gas mixture.

4. *Dependence of C_N^{3-} on temperature and slag composition*

4.1. Temperature

In Fig. 1, the log C_N^{3-} values obtained by the present authors who used gas-slag[8,10,11] and gas-slag-liquid Cu[12,13] equilibration techniques, are plotted against reciprocal of temperature. These values were observed to increase almost linearly with decreased reciprocal of temperature. One can see that the C_N^{3-} values in the

$CaO-TiO_x$ system[13] are the highest of any of the other systems. Since the $C_{N^{3-}}$ values increase with increasing the content of nitride formers such as TiO_x, Al_2O_3, and SiO_2 at a given temperature, the effect of slag composition on $C_{N^{3-}}$ value should be examined at a specified concentration ratio of (basic oxide)/(nitride former). However, comparison at a given ratio cannot be made because of the limitation of having a liquid state at the experimental temperatures.

4.2. Slag composition

In Fig. 2, the log $C_{N^{3-}}$ values obtained at 1873 K are plotted against the sum of mole fraction of nitride formers, $X_{SiO_2} + X_{TiO_2} + 0.5\ X_{AlO_{1.5}}$, in which the coefficients of each oxide were determined by a trial and error method. It can be seen that the log $C_{N^{3-}}$ values increase with an increase of the content of nitride formers and those for CaO- based slags are greater than those for BaO- based slags at constant content of nitride formers. This may be interpreted by the stronger interaction of BaO with nitride former, compared with that of CaO at constant nitride former content, hence resulting in a decrease of $a_{O^{2-}}$ and an increase of activity coefficient of nitride ion, $f_{N^{3-}}$. The results for 32mass-%CaO-32mass-%Al_2O_3-36mass-%CaF_2[1] and $CaO-Al_2O_3-TiO_x$ systems[9] obtained by other investigators are also included in Fig. 2 for comparison. It can thus be concluded from these results that the increase of nitride former content is of crucial importance for high $C_{N^{3-}}$ values rather than the increase of basic oxide content.

Dependence of $C_{N^{3-}}$ on slag composition can be basically explained by the dependence of activity coefficient of nitride and activity of nitride former on slag composition, as is evident from Eq.[10]. The $C_{N^{3-}}$ values observed at the slag compositions of $X_{CaO}/X_{Al_2O_3} > 1$ in the $CaO-Al_2O_3$ system[8] decrease with an increase of X_{CaO}. This may be explained by the fact that the $a_{Al_2O_3}$ values[19] decrease much faster than the γ_{AlN} values (see Fig. 3) with increasing the CaO content, which leads to an decrease in $C_{N^{3-}}$ values.

The $C_{N^{3-}}$ values observed at the slag compositions of $X_{basic\ oxide} / X_{TiO_x} < 1$ in $BaO-TiO_x$[12] and $CaO-TiO_x$[13] systems decrease with an increase of basic oxide. This may be due to the fact that the γ_{TiN} values (see Fig. 3) increase and the a_{TiO_x} values decrease with an increase in the basic oxide content, which results in an decrease of $C_{N^{3-}}$ value.

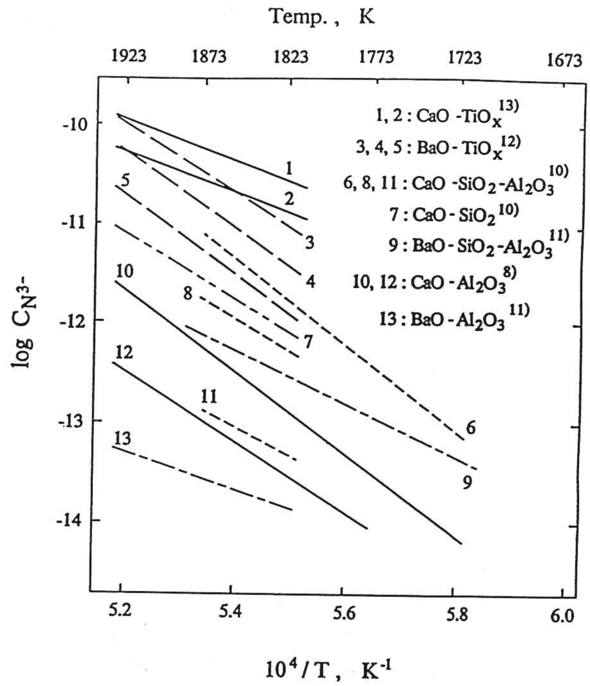

Fig.1 Nitride Capacities for various fluxes obtained by gas-slag and gas-slag-metal equilibration techniques.

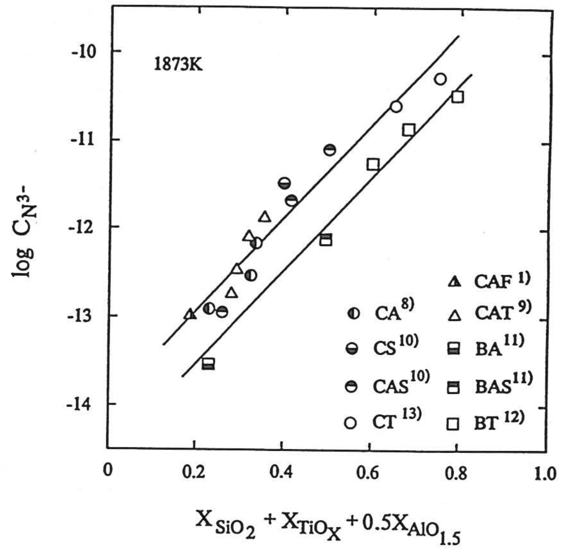

Fig.2 Dependence of nitride capacities on slag compositions; A:Al_2O_3, B:BaO, C:CaO, F:CaF_2, S:SiO_2, T:TiO_X.

Martinez and Sano[2,5,6] and Fruehan and his co-workers[4,7] discuss in detail the dependence of $C_{N^{3-}}$ on slag compositions, by postulating that nitrogen can dissolve into slag as "free nitride" at high basicities by Eq.[1] and "incorporated nitride" with the network for acidic slags by Eq.[12].

$$1/2N_2 + 2(O^-) = (N^-) + 1/2(O^{2-}) + 3/4O_2 \qquad [12]$$

It should be noted that their interpretation is based on the assumption that the activity coefficient of nitrogen is independent of slag composition.

5. *Activity coefficient of nitride*

Activity coefficients of nitride are plotted against mole fraction of basic oxide in Fig. 3. The γ_{TiN} values in the $BaO-TiO_X$[12] and $CaO-TiO_X$[13] systems are calculated from the results obtained in gas-slag-liquid Cu equilibration experiments given by Eq.[13].

$$\underline{Ti}(\text{in Cu}) + 1/2N_2 = TiN(s) \qquad [13]$$

$$\gamma_{TiN} = K_{13}\,\gamma_{Ti}\,X_{Ti}\,P_{N_2}^{1/2}/X_{TiN} \qquad [14]$$

where K_{13} represents the equilibrum constant for Eq.[13], The value for γ_{Ti} was obtained in gas-slag-liquid Cu. The γ_{AlN} values in $BaO-Al_2O_3$[11] and $CaO-Al_2O_3$[16] systems are calculated from the results of slag-metal equilibration experiments using Eq.[8], whereas the $\gamma_{Si_{3/4}N}$ values are obtained from the results of gas-slag experiments[10] using the equation similar to Eq.[10] with respect to $Si_{3/4}N$. It can be seen that the values for γ_{AlN} and $\gamma_{Si_{3/4}N}$ decrease with an increase in the CaO content, whereas those for TiN increase with an increase in the CaO or BaO content. These results are consistent with the previous observation that activity coefficients of CaS in binary silicate and aluminate systems, had the maximum values at the compositions with the minimum values for the free energy of mixing[20].

Furthermore, it can be said from the order of activity coefficients of nitride that the activity coefficient of nitride is strongly influenced by the interaction between nitride former and basic oxide ; the order of activity coefficients of nitride is in line with the order of the standard heat of formation[21] of basic oxide-nitride former compound.

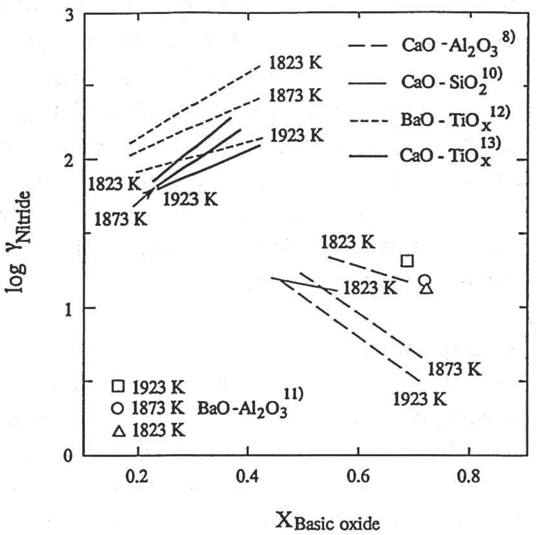

Fig.3 Dependence of activity coefficients of nitride on slag composition.

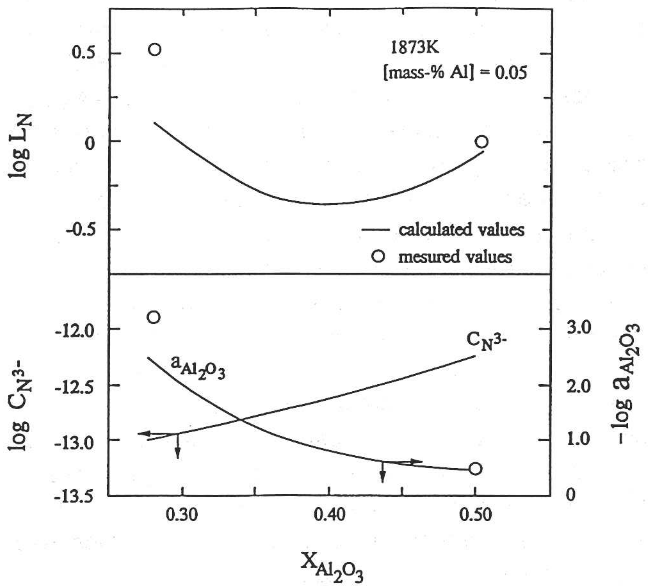

Fig.4 Variations of L_N, C_N^{3-}, and $a_{Al_2O_3}$ with slag composition in $CaO-Al_2O_3$ system.

6. *Nitrogen distribution ratio between slag and metal*

Distribution ratios for nitrogen (L_N) and sulfur (L_S) in the $CaO-Al_2O_3$ system[16] are estimated using Eqs.[6] and [15], respectively at constant Al content in liquid iron of [mass-%Al] = 0.05

$$L_S = C_S^{2-}\frac{f_S}{K_S}\left(\frac{K_5\,a_{Al}^2}{a_{Al_2O_3}}\right)^{1/3} \qquad [15]$$

where K_S and f_S represent the equilibrium constant for the sulfur dissolution into liquid iron and the activity coefficient of sulfur, respectively. The results are shown in Figs. 4 and 5. The log L_N values versus $X_{Al_2O_3}$ relationship shows the concave curve due to the different dependence of C_N^{3-} and $a_{Al_2O_3}$ on the Al_2O_3 content, while the log L_S value shows the continuous decrease with an increase in the Al_2O_3 content due to the opposite dependence of C_S^{2-} and $a_{Al_2O_3}$ on the Al_2O_3 content.

Nitrogen distribution ratios obtained by Al_2O_3-containing slags and liquid iron are plotted against the Al content in logarithmic form in Fig. 6, indicating that nitrogen distribution ratios increase with an increase of Al content.

7. Assessment of activities of Al_2O_3 and SiO_2 in $CaO-SiO_2-Al_2O_3$ system

The values for $a_{Al_2O_3}$ and a_{SiO_2} were evaluated based on the results of C_N^{3-} values obtained by gas-slag experiments and those of L_N values obtained by slag-metal experiments. These results are compared with the reported values of Rein and Chipman[19].

$CaO-Al_2O_3$ system[16] : the values for activity of Al_2O_3 saturated with Al_2O_3 ($a_{Al_2O_3}$(A)) and CaO ($a_{Al_2O_3}$(C)) crucibles are plotted in Fig.7, along with the values of Rein and Chipman($a^*_{Al_2O_3}$)[19]. The values of $a_{Al_2O_3}$(A) are in good agreement with the Rein and Chipman's values, but the values of $a_{Al_2O_3}$(C) are considerably different from their values.

$CaO-SiO_2$ system[17] : the values for activities of SiO_2 saturated with a CaO crucible are shown in Fig. 7, together with the values of Rein and Chipman. The results obtained at 1823 and 1873 K agree well with their values.

$CaO-SiO_2-AlO_{1.5}$ system[18] : the activities of SiO_2 and $AlO_{1.5}$ saturated with CaO and Al_2O_3 crucibles are shown in Fig. 8, in which the values for a_{SiO_2} and $a_{AlO_{1.5}}$ saturated with a CaO crucible are different from those of Rein and Chipman to a significant degree.

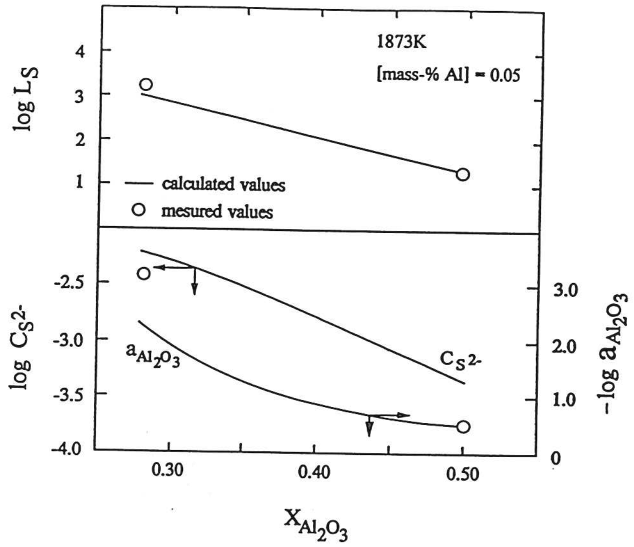

Fig.5 Variations of L_S, C_S^{2-}, and $a_{Al_2O_3}$ with slag composition in $CaO-Al_2O_3$ system.

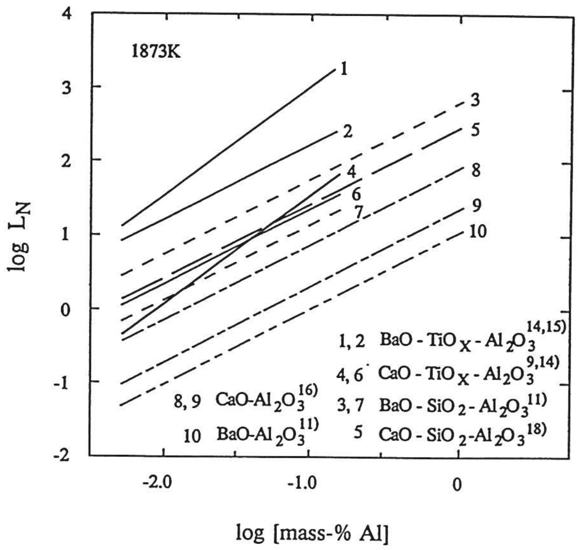

Fig.6 Nitrogen distribution ratios between slag and metal as a function of Al content in liquid iron.

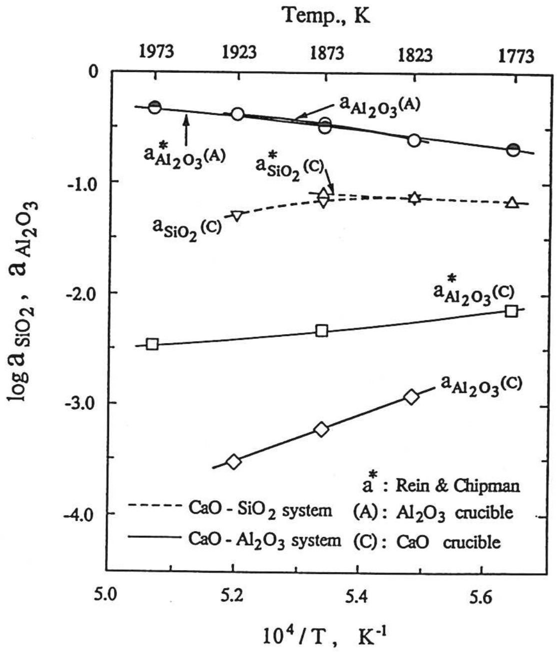

Fig.7 Activities of SiO_2 and Al_2O_3 in $CaO-SiO_2$ and $CaO-Al_2O_3$ systems saturated with CaO and Al_2O_3 crucibles.

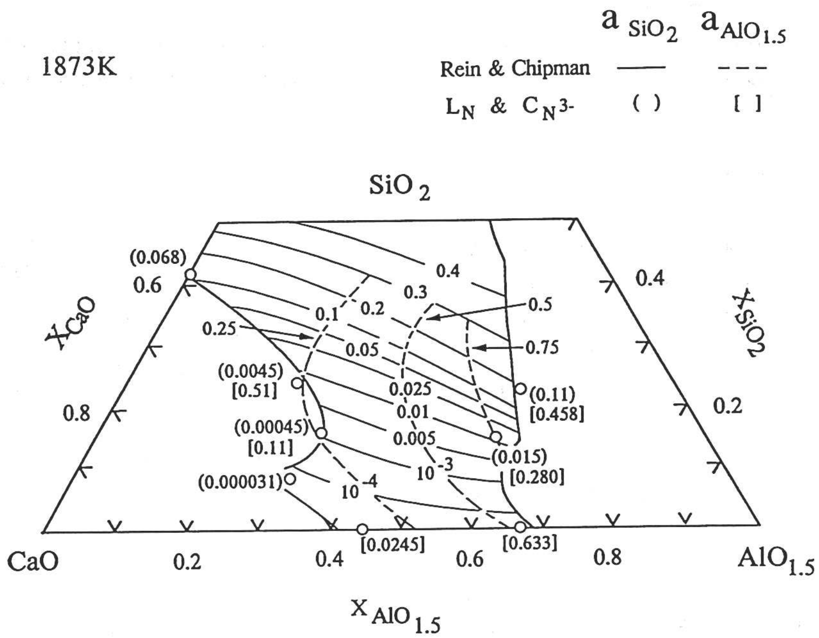

Fig.8 Activities of SiO_2 and $AlO_{1.5}$ in CaO–SiO_2–$AlO_{1.5}$ system saturated with CaO and Al_2O_3 crucibles.

8. Summary

The nitride capacities for various fluxes obtained by a gas–slag equilibration technique are summarized based on the recent data obtained by the authors. The results for activity coefficients of nitride, L_N, and activities of SiO_2 and Al_2O_3 in CaO–SiO_2– Al_2O_3 system are discussed.

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