Nitride Capacities of $\text{CaO-Al}_2\text{O}_3\text{-CaF}_2$ Melts at 1773 K

Woo-Yong SHIN and Hae-Geon LEE

Pohang University of Science and Technology, San 31, Hyoja-Dong, Nam-Ku, Pohang 790-784 Korea.
E-mail: hglee@postech.ac.kr

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The nitrogen solubility of $\text{CaO-Al}_2\text{O}_3\text{-CaF}_2$ was studied at 1773 K. It was found that nitride capacity increased with increasing CaO content for a given $\text{CaF}_2/\text{Al}_2\text{O}_3$ ratio, decreased with increasing Al_2O_3 content for a given CaO/CaF_2 ratio, and increases with increasing CaF_2 content when the $\text{CaO}/\text{Al}_2\text{O}_3$ molar ratio was less than about 2, but became unaffected by CaF_2 content when the ratio exceeded about 2. These observations were interpreted that CaO depolymerized the Al_2O_3 network, allowing for nitrogen to exist as both free and non-bridging nitrides, and that CaF_2 assisted in depolymerization and hence increased nitrogen solubility, provided that there was a sufficient amount of network to be depolymerized. A diagram of iso-nitride capacity was drawn for the $\text{CaO-Al}_2\text{O}_3\text{-CaF}_2$ ternary system at 1773 K, and the nitride capacity was related to the optical basicity of the melt to obtain the following correlation equation:

$$\log C_N = 7.442A - 19.05$$

KEY WORDS: nitrogen; slag; solubility; nitride capacity; $\text{CaO-Al}_2\text{O}_3\text{-CaF}_2$ system.

1. Introduction

Nitrogen in steel may be considered as either an alloying element or as a harmful impurity, depending on its intended use. There have been two different approaches to the removal of nitrogen from steel: namely, the removal of nitrogen in its gaseous form (for instance, by vacuum degassing), and the removal of nitrogen by chemical processes (for example, by using slag). The removal rate of nitrogen in the gaseous form is sluggish, particularly in the presence of surface active elements such as oxygen or sulfur.¹⁾ The chemical process, *i.e.*, the dissolution of nitrogen into slag, has been examined by several investigators utilizing various slag systems to determine the solubility of nitrogen and hence the nitride capacity.²⁻²⁰⁾ There is a general consensus that nitrogen exists in slag either as a free nitride ion or as one incorporated with a network former in the slag. In the latter case, nitrogen will replace bridging or non-bridging oxygen, and the extent of the replacement will depend on the polymerization state of the slag. For aluminate melts such as $\text{CaO-Al}_2\text{O}_3$ slags in which Al_2O_3 is the network former, it is reported that nitrogen replaces oxygen combined in either a bridging or non-bridging form with aluminum.^{6,14)} A number of studies have been carried out by several investigators on the effect of CaF_2 on the nitrogen solubility of various slag systems. In slag systems such as CaO-CaF_2 where no network former exists, CaF_2 only acts as a diluent.⁵⁾ However, when a network former such as SiO_2 or Al_2O_3 is contained in a melt, two nitrogen dissolution mechanisms, *viz.*, one as a free nitride and the other as an incorporated nitride^{7,8,18)} have been discussed and generally accepted to hold. In the cases of $\text{CaO-SiO}_2\text{-CaF}_2$ ^{8,18)}

and $\text{CaO-Al}_2\text{O}_3\text{-CaF}_2$ ^{15,20)} slag systems, in which SiO_2 and Al_2O_3 act as network former, respectively, fluorine has been reported to liberate both oxygen ions and incorporated nitrides from the network. In the present study it has been attempted to elucidate the relative significance of each component in $\text{CaO-Al}_2\text{O}_3\text{-CaF}_2$ slag systems on the nitrogen solubility. Applicability of the optical basicity concept to the nitride capacity of this slag system is also examined.

2. Experimental

The experimental apparatus employed in the present study is given schematically in Fig. 1. A mixture of CaO (prepared by calcining CaCO_3), Al_2O_3 and CaF_2 , all of reagent grade, was placed in a graphite working crucible (14×10^{-6} m ID $\times 50 \times 10^{-6}$ m L). This mixture had a total weight of 3×10^{-3} kg. For investigation of effects of nitrogen and oxygen partial pressures, the working crucible containing the sample mixture was placed in a graphite protection crucible (30×10^{-3} m ID $\times 80 \times 10^{-3}$ L), and the whole crucible assembly was located at the uniform temperature zone of a vertical resistance heating furnace. For investigation of effect of slag compositions, a multiple number of working crucibles (5 crucibles in most cases) containing sample mixtures was placed in a graphite protection crucible (55×10^{-3} m ID $\times 80 \times 10^{-3}$ m L). A $\text{CO-N}_2\text{-Ar}$ gas mixture was blown at a flow rate of 200×10^{-6} m³ min⁻¹ using an alumina lance placed 2×10^{-2} m above the top of the protection crucible. CO gas was purified by being passed through silica gel and ascarite columns to remove moisture and CO_2 , respectively. Oxygen and moisture in N_2 and Ar gases were removed by passing through a Mg turn-

ings column (723 K) and silica gel column, respectively. The flow rate of each gas was accurately controlled using an electronic mass flow controller. A number of different

Fig. 1. Schematic diagram of the experimental apparatus.

gas mixtures were employed to examine the effects of nitrogen and oxygen partial pressures on the solubility of nitrogen in a slag. In the present study, the oxygen partial pressure was governed by the partial pressure of CO in the gas mixture, according to the following equilibrium:

The various compositions of gas mixtures and slags employed in the present study are given in **Table 1**, and slag compositions studied in the present work are shown in **Fig. 2**. The content of CaF_2 in the slag was found to decrease with time. It was also found that the CaF_2 content decreased rapidly in the first few hours (mostly in 5 hr), followed by the rate being slowed down substantially and becoming negligibly slow after about 10 hr. Therefore it was assumed that the rate of nitrogen absorption was much faster than the rate of CaF_2 loss in later times during equilibration for 18 hr, and hence the system was virtually in equilibrium as long as nitrogen dissolution was concerned. The slag compositions given in the above table and figure are the ones analyzed after equilibration for 18 hr by which the slags are assumed to have attained an equilibrium nitrogen content. Nitrogen in the slag was analyzed by the Kjeldahl method with titration using boric and sulfamic acids, and slag com-

Table 1. Experimental results of nitrogen solubility of $\text{CaO-Al}_2\text{O}_3\text{-CaF}_2$ at 1 773 K.

	Run No.	Gas partial pressures, atm			Slag compositions							%N	logC _N
		N ₂	CO	Ar	Mass %			Mole fraction					
					(CaO)	(CaF ₂)	(Al ₂ O ₃)	X _{CaO}	X _{CaF₂}	X _{Al₂O₃}			
Effect of O ₂ pressure	O-1	0.35	0.25	0.40	43.0	21.3	35.7	0.552	0.196	0.252	0.145	-13.10	
	O-2	0.35	0.35	0.30	42.2	21.5	35.3	0.548	0.200	0.252	0.110	-13.22	
	O-3	0.35	0.45	0.20	42.5	22.2	35.3	0.546	0.205	0.249	0.096	-13.28	
	O-4	0.35	0.65	-	43.1	21.7	35.2	0.552	0.200	0.248	0.040	-13.66	
Effect of N ₂ pressure	N-1	0.25	0.35	0.40	42.4	22.3	35.3	0.545	0.206	0.249	0.092	-13.22	
	N-2	0.35	0.35	0.30	43.5	21.3	35.2	0.557	0.196	0.248	0.115	-13.20	
	N-3	0.45	0.35	0.20	42.5	22.2	35.3	0.546	0.205	0.249	0.120	-13.23	
	N-4	0.65	0.35	-	42.3	22.2	35.5	0.544	0.205	0.251	0.154	-13.21	
Effect of Slag composition	S-1	0.35	0.35	0.30	24.8	30.3	44.9	0.348	0.305	0.347	0.072	-13.40	
	S-2	0.35	0.35	0.30	25.8	54.2	20.0	0.341	0.514	0.145	0.180	-13.01	
	S-3	0.35	0.35	0.30	26.3	69.7	4.0	0.335	0.638	0.028	0.587	-12.49	
	S-4	0.35	0.35	0.30	26.9	41.4	31.7	0.363	0.401	0.236	0.116	-13.20	
	S-5	0.35	0.35	0.30	28.5	31.5	40.0	0.390	0.310	0.301	0.087	-13.32	
	S-6	0.35	0.35	0.30	28.9	20.0	51.0	0.405	0.202	0.393	0.053	-13.54	
	S-7	0.35	0.35	0.30	29.0	46.6	24.4	0.382	0.441	0.177	0.110	-13.22	
	S-8	0.35	0.35	0.30	29.3	25.2	45.5	0.405	0.250	0.346	0.064	-13.46	
	S-9	0.35	0.35	0.30	30.5	45.2	24.3	0.399	0.425	0.175	0.116	-13.20	
	S-10	0.35	0.35	0.30	31.2	45.2	23.6	0.407	0.424	0.169	0.108	-13.23	
	S-11	0.35	0.35	0.30	31.4	56.9	11.7	0.399	0.519	0.082	0.345	-12.72	
	S-12	0.35	0.35	0.30	31.8	33.1	35.1	0.424	0.318	0.258	0.061	-13.47	
	S-13	0.35	0.35	0.30	35.0	43.2	21.8	0.449	0.398	0.154	0.216	-12.93	
	S-14	0.35	0.35	0.30	36.6	28.2	35.2	0.480	0.266	0.254	0.110	-13.22	
	S-15	0.35	0.35	0.30	36.9	38.7	24.4	0.472	0.356	0.172	0.164	-13.05	
	S-16	0.35	0.35	0.30	37.6	44.8	17.6	0.474	0.405	0.122	0.272	-12.83	
	S-17	0.35	0.35	0.30	39.6	35.4	25.0	0.502	0.323	0.175	0.147	-13.09	
	S-18	0.35	0.35	0.30	40.2	24.6	35.2	0.520	0.229	0.251	0.115	-13.20	
	S-19	0.35	0.35	0.30	41.3	31.2	27.5	0.524	0.284	0.192	0.136	-13.13	
	S-20	0.35	0.35	0.30	43.9	30.5	25.6	0.549	0.274	0.176	0.168	-13.04	
	S-21	0.35	0.35	0.30	43.9	31.5	24.5	0.549	0.283	0.168	0.200	-12.96	
	S-22	0.35	0.35	0.30	44.1	25.8	30.1	0.557	0.234	0.209	0.164	-13.05	
	S-23	0.35	0.35	0.30	44.4	30.4	25.2	0.554	0.273	0.173	0.193	-12.98	
	S-24	0.35	0.35	0.30	44.7	27.0	28.3	0.561	0.243	0.195	0.212	-12.94	
	S-25	0.35	0.35	0.30	45.1	14.5	40.4	0.508	0.134	0.286	0.0091	-14.30	
	S-26	0.35	0.35	0.30	45.5	20.3	34.2	0.577	0.185	0.239	0.140	-13.11	
	S-27	0.35	0.35	0.30	49.1	22.7	28.2	0.606	0.202	0.192	0.178	-13.01	
	S-28	0.35	0.35	0.30	49.5	23.2	27.3	0.610	0.205	0.185	0.223	-12.91	
	S-29	0.35	0.35	0.30	50.9	18.5	30.6	0.628	0.164	0.208	0.214	-12.93

Fig. 2. Slag compositions studied in the present work (The phase diagram is after Chatterjee *et al.*²²⁾).

Fig. 3. Change in nitrogen content in the melt over time at 1773 K.

positions were determined by both wet and XRF analyses. The time required for attaining equilibrium between the slag and gas phases was determined by measuring the change of the nitrogen content in a slag over time (see Fig. 3). It was found that the system reached equilibrium in about 10 hr at 1773 K. Therefore the system was held for 18 hr at 1773 K after which the crucible assembly was quickly removed from the furnace and quenched by dipping it into water in a shallow bath. Care was taken to prevent water from flowing into the crucible.

3. Results and Discussion

3.1. Nitride Capacity

Experimental results of the present study are summarized in Table 1. Gaseous nitrogen may dissolve in a molten slag either in the form of free nitride (N^{3-}) according to the reaction represented by Eq. (2):

or in the form of a non-bridging nitrogen (N^-) according to the reaction represented by Eq. (3):

or in the form of a bridging nitrogen (N^o) according to the reaction represented by Eq. (4):

where O^o represents a bridging oxygen, O^- a non-bridging oxygen and O^{2-} a free oxygen ion. When the reactions represented by Eqs. (3) and (4) are compared, the reaction with non-bridging oxygen (O^-), Eq. (3), is more favorable since the reaction involving bridging oxygen (O^o) requires a high activation energy.⁶⁾ Therefore, both free and non-bridging nitrides are thought to coexist in a slag. By using α as the fraction of nitrogen existing in the form of free nitride to the total nitrogen, Eqs. (2) and (3) can be combined to form Eq. (5), given in the following:

The equilibrium constant of the above reaction can be expressed by the following Eq. (6):

$$K_5 = \frac{a_{N^{3-}}^\alpha a_{N^-}^{(1-\alpha)} P_{O_2}^{3/4}}{a_{O^{2-}}^{(2\alpha-1/2)} a_{O^-}^{2(1-\alpha)} P_{N_2}^{1/2}} \quad \text{.....(6)}$$

where K_5 is the equilibrium constant of the reaction represented by Eq. (5), $a_{N^{3-}}$ and a_{N^-} are the activities of free and non-bridging nitrides, respectively, $a_{O^{2-}}$ and a_{O^-} are the activities of free and non-bridging oxygen ions, respectively, P_{N_2} and P_{O_2} are the partial pressures of nitrogen and oxygen, respectively, in the gas phase. It can be seen that the above equation is reduced to the equilibrium constant expression for the reaction of Eq. (2) with α being equal to unity, and to the equilibrium constant expression for the reaction of Eq. (3) with α being equal to zero.

Nitride capacity (C_N) is now defined by incorporating the mass balance of nitrogen ions, viz., $(\%N^{3-}) = \alpha(\%N)$, and $(\%N^-) = (1-\alpha)(\%N)$, into Eq. (6) and rearranging it as follows:

$$C_N = \frac{(\%N)P_{O_2}^{3/4}}{P_{N_2}^{1/2}} = \frac{K_5 a_{O^-}^{2(1-\alpha)} a_{O^{2-}}^{(2\alpha-1/2)}}{f_{N^{3-}}^\alpha f_{N^-}^{(1-\alpha)} \alpha^\alpha (1-\alpha)^{(1-\alpha)}} \quad \text{.....(7)}$$

In the above equation, $(\%N)$ is the solubility of nitrogen in a slag expressed in terms of the total nitrogen concentration in mass percent in the slag. It is thus the sum of mass percents of both free nitride ($\%N^{3-}$) and non-bridging ones ($\%N^-$). $f_{N^{3-}}$ and f_{N^-} are the activity coefficients of N^{3-} and N^- in the slag, respectively. It is clear from Eq. (7) that ni-

Fig. 4. Effect of oxygen partial pressure on nitrogen solubility of CaO–Al₂O₃–CaF₂ melts at 1 773 K.

Fig. 5. Effect of nitrogen partial pressure on nitrogen solubility of CaO–Al₂O₃–CaF₂ melts at 1 773 K.

tride capacity (C_N) is dependent on the slag system only at a given temperature. Nitride capacities were calculated for different slag compositions with the results being given in Table 1.

3.2. The Effects of Oxygen and Nitrogen Partial Pressures

Equation (7) predicts that the logarithm of nitrogen solubility ($\%N$) is linearly proportional to the logarithm of the oxygen partial pressure with a slope of $-3/4$, and to the logarithm of nitrogen partial pressure with a slope of $1/2$ for a given slag composition at a given temperature. **Figure 4** shows the effect of oxygen partial pressure on nitrogen solubility for a given nitrogen partial pressure ($P_{N_2}=0.35$ atm.). A linear relationship is clearly visible, with a slope of -0.72 which is close to the theoretical value of -0.75 . **Figure 5** shows the dependence of nitrogen solubility on nitrogen partial pressure. An excellent linear relationship is clearly seen as having a slope of 0.5 which fits well with the theoretical value. These agreements prove that experimental results obtained in the present study truly represent the equilibrium values of nitrogen solubility in the slag.

Fig. 6. Effect of CaO content on the nitride capacity of CaO–Al₂O₃–CaF₂ melts at 1 773 K.

3.3. The Effect of Slag Compositions

In the case of multicomponent systems like the one in the present study, thermodynamic behavior of a component is influenced by other components in the system and hence it is often difficult to discuss the effect of each component separately on thermodynamic behaviors, such as nitrogen solubility of a system. However, proper imposition of a certain restriction to the variation of slag compositions may provide a meaningful method for understanding the effects of individual components. **Figure 6** shows the change in nitride capacity defined by Eq. (7) with CaO content in the slag. In this figure CaF₂ and Al₂O₃ contents are indicated by the CaF₂/Al₂O₃ molar ratio (with a ± 0.25 tolerance range), and different ratios are distinguished by using different symbols. Although there is some scattering of data points, the nitride capacity shows a general trend towards an increase by increasing the CaO content. This trend is particularly clear when the change in nitride capacity *versus* the CaO mole fraction is viewed for a particular CaF₂/Al₂O₃ ratio, *i.e.*, the same symbols. The vertical scatter of data points for a given CaO mole fraction is seen to reflect the effects of CaF₂ and Al₂O₃. It is also clear that, the larger the CaF₂/Al₂O₃ ratio, the larger the nitride capacity is for a given CaO content. This implies that CaF₂ is more effective than Al₂O₃ in increasing nitrogen solubility. In order to compare the relative effects of CaF₂ over Al₂O₃, the change in nitride capacity with the CaF₂/Al₂O₃ ratio at CaO saturation (*i.e.*, the CaO activity being fixed at unity) is given in **Fig. 7**. It is clear that nitride capacity increases with increasing the CaF₂/Al₂O₃ molar ratio at a unit CaO activity. Martinez *et al.*¹⁵ reported similar results that the total nitrogen solubility increased with increasing the CaF₂ mole fraction in the CaO–Al₂O₃–CaF₂ system with the CaO activity fixed at 0.6 at 1 773 K. They claimed that this was mainly due to an increase of free nitrides (N^{3-}) with increasing CaF₂ content, and also cited a previous suggestion²² that the interaction of fluorine ions with other ions and polyions in the melt became strong with increasing the content of network forming elements. Sohn *et al.*²⁰ also observed that nitride capacity increased by increasing the CaF₂/Al₂O₃ molar ratio in the CaO–Al₂O₃–CaF₂ system with CaO satu-

Fig. 7. Effect of $\text{CaF}_2/\text{Al}_2\text{O}_3$ molar ratio on nitride capacity of $\text{CaO}-\text{Al}_2\text{O}_3-\text{CaF}_2$ melts with CaO saturation at 1773 K.

Fig. 8. Effect of CaF_2 content on nitride capacity of $\text{CaO}-\text{Al}_2\text{O}_3-\text{CaF}_2$ melts at 1773 K.

ration. Assuming that nitrogen existed in the slag as free nitride (N^{3-}), they claimed that addition of CaF_2 decreased the activity coefficient of nitride ($f_{\text{N}^{3-}}$) and hence increased the nitride capacity (see Eq. (7)). In order to see the effect of CaF_2 on nitrogen capacity, the experimental results of the present study were rearranged in Fig. 8 so that the nitride capacity was plotted against the CaF_2 mole fraction. It is seen that when the $\text{CaO}/\text{Al}_2\text{O}_3$ molar ratio is low (≤ 1.5), the nitride capacity increases with increasing CaF_2 content in the melt. When the $\text{CaO}/\text{Al}_2\text{O}_3$ molar ratio is high (≥ 2.0), however, nitride capacity is seen to barely increase with increasing CaF_2 content. Sohn *et al.*²⁰⁾ made a similar suggestion that CaF_2 would have no effect on nitrogen solubility in the CaO -rich region in $\text{CaO}-\text{Al}_2\text{O}_3-\text{CaF}_2$ melts. Figure 9 shows the variation of nitride capacity against the $\text{CaO}/\text{Al}_2\text{O}_3$ molar ratio. It can be seen that the nitride capacity increases with increasing $\text{CaO}/\text{Al}_2\text{O}_3$ ratio. The result that the extent of data point scatter increases as the $\text{CaO}/\text{Al}_2\text{O}_3$ ratio is decreased is due to the effect of CaF_2 as seen in Fig. 8.

In Fig. 10 the effect of Al_2O_3 on nitride capacity is shown. Nitride capacity decreases with increasing Al_2O_3 content regardless of the CaO/CaF_2 molar ratio. It is also

Fig. 9. Effect of $\text{CaO}/\text{Al}_2\text{O}_3$ molar ratio on the nitride capacity of $\text{CaO}-\text{Al}_2\text{O}_3-\text{CaF}_2$ melts at 1773 K.

Fig. 10. Effect of Al_2O_3 content on nitride capacity of $\text{CaO}-\text{Al}_2\text{O}_3-\text{CaF}_2$ melts at 1773 K.

seen that nitride capacity increases by increasing the CaO/CaF_2 ratio for a given Al_2O_3 content. Martinez *et al.*¹⁵⁾ examined the change of the nitrogen solubility of $\text{CaO}-\text{Al}_2\text{O}_3-\text{CaF}_2$ melts with a fixed CaF_2 content ($X_{\text{CaF}_2}=0.2$) at 1773 K, and reported somewhat different results in that total nitride content in the melt showed one maximum and two minima as the Al_2O_3 mole fraction increased from 0.2 to 0.4. They attributed this trend to a change in the activity of free oxygen ions due to changes in the alumina structure. However, they did not discuss these changes in alumina structure in detail.

All observations discussed above may be summarized as follows:

- 1) Nitride capacity increases with increasing CaO content for a given $\text{CaF}_2/\text{Al}_2\text{O}_3$ concentration ratio.
- 2) Nitride capacity decreases with increasing Al_2O_3 content for a given CaO/CaF_2 concentration ratio.
- 3) Nitride capacity increases with increasing CaF_2 content when the $\text{CaO}/\text{Al}_2\text{O}_3$ molar ratio is less than about 2, but becomes unaffected by CaF_2 content when the ratio exceeds about 2.

Fig. 11. Effect of the CaO activity on nitride capacity of CaO–Al₂O₃–CaF₂ melts at 1773 K.

An interpretation of the above observations in view of the types of nitrides in the melt, *i.e.*, free nitrides (N^{3-}) and non-bridged nitrides (N^-) incorporated with the network, is now in order. It is known that Al₂O₃ is amphoteric, and acts as a network former or acidic in CaO–Al₂O₃ melts. By increasing the CaO proportion and adding CaF₂ the following is therefore expected to occur:

- 1) With an increase of CaO in the melt, the extent of network depolymerization increases and hence more oxygen becomes available in the form of free oxygen ions (O^{2-}) and non-bridging oxygen ions (O^-). This leads to an increase in nitrogen dissolution in the form of free nitrides (N^{3-}) according to Eq. (2) and also as non-bridging nitrides (N^-) according to Eq. (3).^{7,8,23)}
- 2) As CaO in the melt increases further, the amount of free oxygen ions increase and hence the relative proportion of free nitrides increases.
- 3) CaF₂ assists in depolymerization,^{8,15,18,24)} and hence increases nitrogen solubility, provided that there is a sufficient amount of network to be depolymerized.
 - When the CaO/Al₂O₃ ratio is low, a substantial amount of oxygen still remains fully bound in the network and hence the addition of CaF₂ effectively liberates this oxygen to form free oxygen ions. This leads to an increase in the nitrogen solubility, *i.e.*, nitride capacity (see Figs. 8 and 9).
 - If the CaO/Al₂O₃ ratio is sufficiently high and the network has been substantially depolymerized, there is not much oxygen left bound in the network and hence the addition of CaF₂ exerts little influence on increasing the amount of free oxygen ions. Therefore nitrogen solubility barely increases with increasing the CaF₂ content in this compositional region (see Figs. 8 and 9).
- 4) Assuming that the activity of CaO in the melt is representative of the basicity of the melt, *i.e.*, the activity of O^{2-} , nitride capacity is expected to be proportional to CaO activity to the power of $(2\alpha - 1/2)$, where α is a function of depolymerization of the network defined earlier and varies from zero to unity (refer to Eq. (7)). When the melt is highly depolymerized, *i.e.*, high in

Fig. 12. Iso-nitride diagram of CaO–Al₂O₃–CaF₂ melts at 1773 K.

CaO content, the value of α approaches unity and hence nitride capacity will be closely proportional to CaO activity to the power of 3/2. As CaO activity decreases, the value of α also decreases and so does the power. **Figure 11** shows the variation of nitride capacity *versus* CaO activity. These CaO activities were obtained by extrapolating the data reported in the literature at 1700 K²⁵⁾ by applying regular solution assumption. It is clearly seen that nitride capacity increases with increasing the CaO activity. The vertical scatter in the figure is mainly due to the effect of the CaF₂/Al₂O₃ ratio—the higher the ratio, the higher the nitride capacity for a given CaO activity. In the region of high CaO activity ($\log a_{CaO} > -0.4$) in particular, the slope is close to the theoretical value of 3/2. This indicates that the value of α is unity in Eq. (7) and therefore nitrogen dissolves mainly as free nitride in this compositional region. As the CaO activity decreases, however, the slope tends to decrease as well, meaning that the value of α becomes smaller and the relative proportion of non-bridging nitride according to Eq. (3) gradually increases.

As the present study measured the nitride capacity over a wide range of compositions, an attempt has been made to construct a diagram of iso-nitride capacity with results being given in **Fig. 12**. The effects of individual components on nitrogen solubility in different compositional regions are clearly visible, and this figure is considered as a graphical summary of all experimental findings in the present study.

3.4. Application of Optical Basicity

Nitrogen dissolution in oxide melts requires electrons as nitrogen exists in an ionic state in the melts. Therefore, the nitrogen solubility or nitride capacity of a melt should be closely related to the electron donor power of the melt. As the optical basicity concept is also based on electron donor power,²⁶⁾ nitride capacity is expected to have a close rela-

Fig. 13. Correlation between nitride capacity and optical basicity of CaO–Al₂O₃–CaF₂ melts with different optical basicities for CaF₂ at 1773 K.

Fig. 14. Optimum correlation between nitride capacity and optical basicity of CaO–Al₂O₃–CaF₂ melts at 1773 K.

tionship with the optical basicity of the melt. In the present system, the optical basicity is given by the following Eq. (8):

$$\Lambda = \frac{\Lambda_{\text{CaO}}x_{\text{CaO}} + 3\Lambda_{\text{Al}_2\text{O}_3} + 2\Lambda_{\text{CaF}_2}x_{\text{CaF}_2}}{x_{\text{CaO}} + 3x_{\text{Al}_2\text{O}_3} + 2x_{\text{CaF}_2}} \quad \text{.....(8)}$$

where Λ is the optical basicity of the melt, Λ_i the optical basicity of component i , x_i the mole fraction of component i .

Λ_{CaO} and $\Lambda_{\text{Al}_2\text{O}_3}$ are 1.0 and 0.605, respectively.²⁷⁾ However, two different values have been reported for Λ_{CaF_2} , viz., 0.43 and 0.67.^{27,28)} Using these values in Eq. (8), the optical basicity of each slag composition studied in the present work was computed, and then the nitride capacity was plotted against the optical basicity in Fig. 13. The correlation between nitride capacity and optical basicity is not thought to be good, although a slightly better correlation is exhibited by using $\Lambda_{\text{CaF}_2} = 0.67$. As fluorine is considered to

Fig. 15. Correlation between nitride capacity and optical basicity of CaO–Al₂O₃–CaF₂ melts with different optical basicities for CaF₂ with data from Sohn *et al.*²⁰⁾ at 1723 K.

modify the structure of a slag in a complex manner, and this in turn affects the ability of a slag to react with a specific element,^{8,24)} the optical basicity of CaF₂ may be system-dependent. In this regard, an attempt was made to find a value of Λ_{CaF_2} which results in the best correlation between nitride capacity and the slag optical basicity. The value of 0.835 for Λ_{CaF_2} was found to have the best fit, with the result shown graphically in Fig. 14. Compared to the results in Fig. 13, it is clear that the new value of $\Lambda_{\text{CaF}_2} = 0.835$ shows a much better correlation. Linear regression of this correlation offers the following relationship:

$$\log C_N = 7.442\Lambda - 19.05 \quad \text{.....(9)}$$

In order to check the validity of the new value of Λ_{CaF_2} , the work of Sohn *et al.*²⁰⁾ which reports the nitride capacity of a number of different slag compositions in the CaO–Al₂O₃–CaF₂ system at 1723 K, was analyzed using optical basicity, with the result shown in Fig. 15. It is remarkable that, while the use of reported values for Λ_{CaF_2} , viz., 0.43 and 0.67, shows poor correlations, applying the new value (0.835) obtained by the present study results in a much improved correlation.

The above analysis proves that in a CaO–Al₂O₃–CaF₂ melt CaF₂ acts much more basic than reported, and hence effectively assists in the depolymerization of Al₂O₃ network in the melt as discussed earlier.

In summary the concept of the optical basicity can be applicable to the nitrogen solubility of CaO–Al₂O₃–CaF₂ melts, but with the value of 0.835 for Λ_{CaF_2} .

4. Conclusions

The nitrogen solubility of CaO–Al₂O₃–CaF₂ was studied at 1773 K with experimental observations summarized as follows:

- 1) Nitride capacity increases with increasing CaO for a given CaF₂/Al₂O₃ ratio.
- 2) Nitride capacity decreases with increasing Al₂O₃ for a given CaO/CaF₂ ratio.
- 3) Nitride capacity increases with increasing CaF₂ when the CaO/Al₂O₃ molar ratio is less than about 2, but be-

comes unaffected by CaF_2 content when the ratio exceeds about 2.

The above observations are interpreted that CaO depolymerizes the Al_2O_3 network, allowing for the existence of nitrogen as both free and non-bridging nitrides, and CaF_2 assists in depolymerization and hence increases nitrogen solubility, provided that there is a sufficient amount of network to be depolymerized.

A diagram of iso-nitride capacity is drawn for $\text{CaO}-\text{Al}_2\text{O}_3-\text{CaF}_2$ ternary system at 1773 K, and nitride capacity is related to the optical basicity of the melt and the following correlation equation is obtained:

$$\log C_N = 7.442A - 19.05$$

where A is the optical basicity of the melt, given by

$$A = \frac{x_{\text{CaO}} + 1.815x_{\text{Al}_2\text{O}_3} + 1.670x_{\text{CaF}_2}}{x_{\text{CaO}} + 3x_{\text{Al}_2\text{O}_3} + 2x_{\text{CaF}_2}}$$

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