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THE EQUILIBRIUM OF NITROGEN BETWEEN GAS AND SLAG OR SLAG AND METAL

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Synopsis:The thermodynamic behaviour of nitrogen in gas-slag (lime-alumina-silica) system and slag-metal system is studied in this paper. The dissolving reaction of nitrogen from gaseous phase to the molten slag is

$$\frac{3}{2}O_{br} + \frac{1}{2}N_2 = N_{br} + \frac{3}{2}O_2$$

br denotes bridging. Based on this, the relationship between nitrogen capacity $C_{N^{3-}}$ and slag basicity can be elucidated. The relationships of $\gamma_{Si_{0.75}N}$ and γ_{AlN} vs. slag composition in lime-alumina and lime-silica binary systems, and the influence of temperature on them were discussed.

Key words: nitrogen; gas-slag reaction; slag-metal reaction

1.Introduction

The dissolution of nitrogen in slag is making itself a new reaserch focus in metallurgy. This results from several reasons. First, it is well known from steelmaking that slag can prevent nitrogen pickup of molten steel. Surely,this function concerns the dissolvability of nitrogen in slag. Second, a new technique idea about using slag in denitrogenation of steel was proposed in following the development of nitride ceramics. This undoubtly brings a lot of profit to the production of ultra pure ferrite stainless steel. Third, nitrogen is an important alloy element in austenite stainless steel. Perhaps, it will be an economic process that feeding nitrogen through slag. As a fundamental study this paper is devoted to the research of nitrogen behaviour in lime-alumina, lime-silica and lime-alumina-silica systems.

2.The experiment method and the results

Fig.1. shows the equipment used in this investigation. For the equilibrium experiment in gas-slag system graphite crucible was used. 5g slag material was put inside it. The atmosphere is $0.40CO-0.60N_2$ which is generally utilized as a standard for the calibration of analytical instruments. The flow rate of this gas was $4cm^3/s$. The reaction temperature was 1773, 1823 or 1873k. A pilot experiment was arranged to determine the time needed for equilibrium experiment. It was performed as adding some Si_3N_4 into $0.4CaO\cdot0.4SiO_2\cdot0.2Al_2O_3$ slag for making the intial (%N) to be either lower or higher than the estimated equilibrium value. Fig.2. indicates the approaching of nitrogen from both sides to each other needs about 14 hrs. Thus, experiment time was chosen as 18 hrs for gas-slag equilibrium. The results of gas-slag equilibrium experiment is shown in Table 1.

For the equilibrium experiment in slag-metal system alumina crucible was used.There were 5g

slag and 15g iron. At most, either 0.5% Si_3N_4 or 0.4% AlN was added in slag before experiment. Iron was killed with Si or Al, and its initial nitrogen content was lower than 0.02%. Ar atmosphere was used in this experiment. The time for this kind of experiment was determined according to Ito[1] and Inoue[2] et al, as 6 hrs. The results of equilibrium experiment in slag-metal is shown in Table 2.

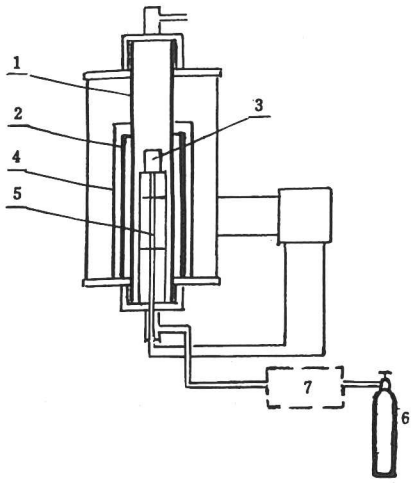

Fig.1.The experimental set
1.alumina tube 5.thermocouple
2.graphite heater 6.CO+nitrogen
3.graphite crucible 7.the set for gas
4.thermal insulation de-O_2, de-H_2O

Table 1.The results of gas-slag equilibrium experiment

temp.	slag(%)			(%N)	C_N^{3-}
(k)	CaO	SiO_2	Al_2O_3	exp.	($\times 10^{-13}$)
1823	55.0	45.0		0.63	4.78
1823	40.0	60.0		1.97	14.32
1823	40.0		60.0	0.28	2.14
1823	35.0		65.0	0.37	2.78
1823	40.0	40.0	20.0	0.92	6.92
1823	50.0	10.0	40.0	0.27	2.04
1823	30.0	40.0	30.0	1.38	10.47
1823	45.0	25.0	30.0	0.53	3.98
1823	55.0	45.0		1.24	9.32
1873	40.0		60.0	0.56	4.32
1873	50.0	10.0	40.0	0.60	4.49
1773	55.0	45.0		0.29	2.17
1773	40.0		60.0	0.13	0.98

Table 2. The results of slag-metal-equilibrium experiment

temp.	slag(%)			N^{3-}	metal(%)			L_N
(k)	CaO	SiO_2	Al_2O_3		Si	Al	N	
1823	40.0	60.0		0.074	1.58		0.0062	11.92
1823	40.0	40.0	20.0	0.073	0.73		0.013	5.60
1823	40.0	50.0	10.0	0.081	1.51		0.0074	10.94
1823	30.0	40.0	30.0	0.061	0.74		0.011	6.03
1823	40.0	60.0		0.065	0.90		0.0085	7.65
1823	45.0		55.0	0.063		0.018	0.010	6.30
1823	40.0		60.0	0.065		0.017	0.007	9.29
1823	55.0		45.0	0.059		0.023	0.016	3.68
1823	45.0		55.0	0.041		0.012	0.019	2.16
1823	45.0		55.0	0.082		0.035	0.0075	10.93
1873	40.0	50.0	10.0	0.070	1.50		0.007	7.61
1873	55.0		45.0	0.035		0.18	0.019	1.84
1773	40.0	50.0	10.0	0.080	1.51		0.0054	14.81
1773	55.0		45.0	0.073		0.018	0.011	6.64

Note: $L_N = (\%N)/\%N$

The Kjeldahl method was used in these two experiments for analysing both (%N) and [%N]. So this paper does not concern (% CN^-), but (% N^{3-}).

3.Discussion

3.1. Gas-slag reaction

Under strong reduction atmosphere, nitorgen can dissolve in slag through a chemical reaction. Referring to this dissolving reaction, however, some contradictory points of view may be found in literatures. Summing up, there are two aspects. One is in what way the partial pressure of nitrogen affects the dissolvability. The other is in what state the nitorgen dissolving in slag

behaves. Davies[3] et al and Schwerdtfeger[4] et al reported that the relation of ($\%N^{3-}$) vs. partial pressure of nitrogen in equilibrium. As the idea of Davies, ($\%N^{3-}$) is in proportion to $(P_{N_2}/P_{O_2})^{1/2}$, however, Schwerdtfeger claimed it should be in proportion to $(P_{N_2}/P_{O_2})^{1/2}$. When the slag is in equlibrium with CO-N atmosphere and the partial pressure of nitrogen is high enough, the slag is saturated with Si_3N_4 and AlN. The chemical stoichiometry indicates that the reactions are

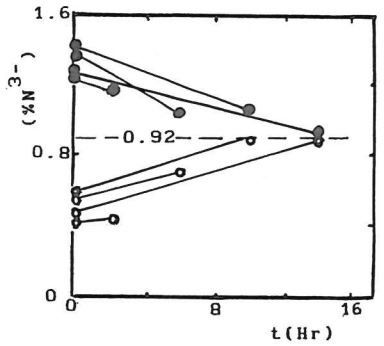

Fig.2.The variation of ($\%N^{3-}$) vs time under 1823k and (0.4 CO+0.6 N_2)

$$\frac{3}{4}SiO_2 + \frac{1}{2}N_2 = Si_{0.75}N + \frac{3}{4}O_2 \quad (1)$$

$$AlO_{1.5} + \frac{1}{2}N_2 = AlN + \frac{3}{4}O_2 \quad (2)$$

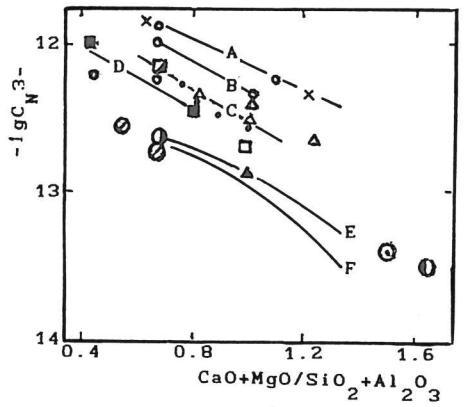

Fig.3.The relation between C_N3- and basicity

signal		ref.	experimental condition
○		this work	1823k,lime-alumina
□		this work	1823k,lime-silica-alumina(%40)
■		this work	1823k,lime-silica-alumina(%30)
◪		this work	1823k,lime-silica-alumina(%20)
×		this work	1823k,lime-silica
⊘		1)	1823k,lime-silica,lime-silica-alumina
△		1)	lime-silica-alumina-magnesia
•		3)	1823k,lime-silica-alumina(%20)
▲		8)	1873k,lime-alumina
◑		1)	1873k,lime-silica-alumina(sat.)
⊙		1)	1873k,lime-silica-magnesia(sat.)
◐		1)	1873k,lime(sat.)-alumina
line	A	sum up	1823k,lime-silica
	B	sum up	1823k,lime-silica-alumina(%10)
	C	sum up	1823k lime-silica-alumina(%20)
	D	sum up	1823k,lime-silica-alumina(%30)
	E	4)	1873k,lime-alumina
	F	8)	1823k,lime-alumina

Hence, so far the view point of Schwerdtfeger is the generally accepted one. And it was thought that the dissolving reaction should be

$$\frac{1}{2}N_2 + \frac{3}{2}(O^{=}) = (N^{3-}) + \frac{3}{4}O_2 \tag{3}$$

Then the nitrogen capacity was defined as

$$C_{N^{3-}} = (\%N^{3-})\frac{P_{O_2}^{3/4}}{P_{N_2}^{1/2}} \tag{4}$$

The $C_{N^{3-}}$ listed in Table 1 was evaluated pursuanting to Eq.(4). Fig.3 shows the relation of these $C_{N^{3-}}$ values together with the results quoted from literatures[1,3,4,8] vs. slag basicity. It was indicated by Ito and others that this curve is contrary to Eq.(3).

The key problem here is in what state the nitrogen dissolves in slag. Several different opinions were suggested. It is well known, in Si_3N_4, AlN nitride ceramics nitorgen exists in the cell of Si-N-Si or Al-N-Al. Furthermore, a TEM investigation claimed that Si_2N_2O was found inside high nitrogen bearing Ca-Si-Al-O-N and Mg-Si-O-N systems[5]. This proves that the dissolving nitrogen is existed in Si-N-Si cell in these systems. According to these reports, the nitrogen dissolving reaction in lime-alumina-silica slag is thought to be the follows

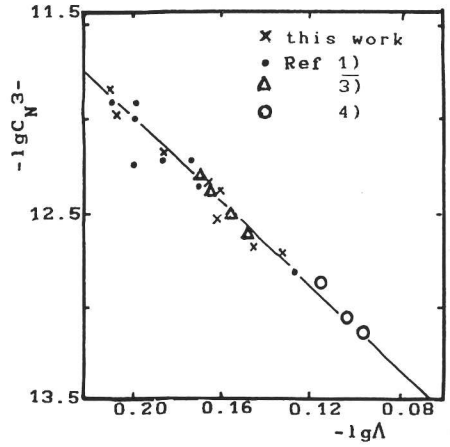

Fig.4.The relation of C_N^{3-} vs.optical basicity, under 1823k.

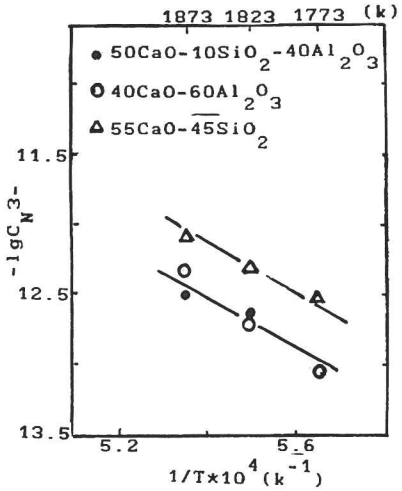

Fig.5. the effect of temperature on C_N^{3-}

$$\frac{3}{2}O_{br} + \frac{1}{2}N_2 = N_{br} + \frac{3}{4}O_2 \tag{5}$$

br denotes bridging. Then, based on the concept of bonding basicity[6] the nitrogen capacity should be defined as

$$C_{N^{3-}} = (\%N^{3-})\frac{P_{O_2}^{3/4}}{P_{N_2}^{1/2}} = \frac{K_{(5)}(B_{O_{br}}Y_{O_{br}})^{3/2}}{\gamma_{N^{3-}}} \tag{6}$$

$B_{O_{br}}, Y_{O_{br}}$ is the basicity charateristics and mole fraction of the bridging $O^{=}$ anion respectively. As the following Fig.6, in lime-alumina binary slags $\gamma_{N^{3-}}$ is constant. On ther other hand, it was

proved[6] in these slags $\gamma_{N^{3-}}$ is in proportion with $(B_{O_{br}} Y_{O_{br}})^{3/2}$. This is an evidence for the correction of reaction (5). Mulfinger[7], Shimoo[8] et al and Davies et al all considered that the dissolving nitrogen is in N_{br} state.

3.2. The effect of optical basicity and temperature on nitrogen capasity.

The effect of optical basicity (Λ) on $\gamma_{N^{3-}}$ is shown in Fig.4. Both the results of this experiment and some literature informations are involved in this relation, and it gives Eq.(7) for 1823k.

$$\lg C_{N^{3-}} = -11.5\lg\Lambda - 14.28 \tag{7}$$

As the bonding basicity is a revision of optical bsicity, so Eq.(7) coincides with Eq.(6). But it surely gets some differences from that relation supposed by Sommerville. The variation of $C_{N^{3-}}$ against temperature is shown in Fig.5. And it is deduced as

$$\lg C_{N^{3-}} = -11.51\lg\Lambda - \frac{22135}{T} - 2.04 \tag{8}$$

3.3. The $\gamma_{Si_{0.75}N}$ and γ_{AlN} in nitrogen bearing lime-alumina and lime-silica binary slags

The dissolving reaction of nitrogen in lime-silica slag is supposed as

$$\frac{1}{2}N_2 + \frac{3}{4}SiO_2 = Si_{0.75}N + \frac{3}{4}O_2 \tag{9}$$

Hence the activity coefficient of this nitride is

$$\gamma_{Si_{0.75}N} = \frac{114MK_{(9)}(a_{SiO_2})^{3/4}}{C_{N^{3-}}} \tag{10}$$

Here M denotes the sum mole amount of components in 100g slag. K is the equilibrium constant.

$$\lg K_{(9)} = -\frac{21926}{T} + 0.737 \tag{11}$$

The dissolving reaction of nitrogen in lime-alumina slag is supposed as

$$AlO_{1.5} + \frac{1}{2}N_2 = AlN + \frac{3}{4}O_2 \tag{12}$$

Thus

$$\gamma_{AlN} = \frac{14MK_{(12)}(a_{AlO_{1.5}})}{C_{N^{3-}}} \tag{13}$$

And,

$$\lg K_{(12)} = -\frac{27014}{T} + 2.505 \tag{14}$$

the variation of γ calculated according to equation (10) and (13) vs. slag composition is shown in Fig.6. The value of (a_{SiO_2}) and $(a_{AlO_{1.5}})$ are quoted from Rein et al[10]. This result is in good agreement with that of Ito et al[1]. The constant γ_{AlN} in lime-alumina system lahich mightbe resulted from the cell structure between Al^{3+} cations and N^{3-} anions in this slag does not to be

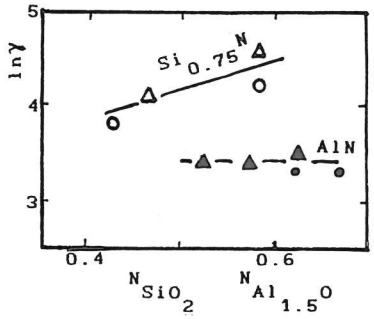

Fig.6. The relation of nitride activity coefficients vs composition

changeable. On the contrary, in lime-silica slag, changing $\%SiO_2$ might possibly cause the formation of double bond between Si^{4+} sations and N^{3-} anions, and this in turn to vary $\gamma_{Si_{0.75}N}$

4. Conclusion

The dissolving reaction of nitrogen from gaseous phase to molten slag is the process in which nitrogen replace the bridging oxygen anion.

$$\frac{3}{2}O_{br} + \frac{1}{2}N_2 = N_{br} + \frac{3}{4}O_2$$

The corresponding nitrogen capacity should be

$$C_{N^{3-}} = \%N^{3-}\frac{P_{O_2}^{3/4}}{P_{N_2}^{1/2}} = \frac{K_{(9)}(B_{O_{br}}Y_{O_{br}})^{3/2}}{\gamma_{N^{3-}}}$$

Here, $(B_{O_{br}}Y_{O_{br}})$ is the bonding basicity or an activity index of bridging oxygen anion.

The variation of $\gamma_{Si_{0.75}N}$ in lime-silica and that of γ_{AlN} in lime-alumina vs. slag composition are in good agreement with that of Ito et al. The reason of these variation is considered as to be possible whether the relevant cell structure is changeable or not.

Acknowledgement

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