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Denitrogenization from Liquid Steel by Fluxes Treatment

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Abstract: By measuring the solubility of nitrogen in BaO – contained and TiO_2 – contained fluxes at 1623K, the nitride capacity and nitrogen distribution ratio were calculated. Both fluxes had high nitride capacity and nitrogen distribution ratio. The results indicated that Both fluxes treatment were available for denitrogenizing steel. The kinetic studies about denitrogenization showed that nitrogen transfer in liquid steel is the controlled step of denitrogenization reaction, so to improve the mass transfer condition in liquid steel could accelerate the rate of denitrogenization. Under proper test conditions, it was proved to be possible to remove nitrogen over 70 percent from steel with TiO_2 contained fluxes.

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

In order to produce high quality steel, considerable efforts have been done to remove various elements from liquid steel. As a results, it is now possible to reduce the concentration of many kinds of impurities in steel below the desired level. For example, oxygen and sulphur can be controlled below 2×10^{-5}. Nitrogen level must also be controlled because the pick-up of nitrogen of liquid steel in many steelmaking processes is very serious, however, there is no proper refining technique available to remove nitrogen effectively. Vacuum degassing can only remove small amounts of nitrogen. The need of low nitrogen content steel is in more and more urgent, for example, the limit of total content of carbon and nitrogen in IF steel is below 6×10^{-5}. So it is necessary to develop a new technique to reduce nitrogen in liquid steel.

There have been several investigations on the nitrogen solubility and nitride capacity of various fluxes systems[1~3] in order to confirm the possibility of removing nitrogen from steel with flux treatment. However the research work in this aspect can not be practical yet: (1) the nitrogen solubility was only measured for fewer flux systems; (2) in recent studies, the results were generally obtained by means of gas-flux equilibration technique, so there is a shortage of the available data of nitrogen distribution ratio between flux and steel.

In this study, the nitride capacity and the nitrogen distribution ratio for BaO – contained and TiO_2 – contained fluxes[4] were measured over a relatively wide composition range by flux-iron equilibration technique. The kinetic behaviour of nitrogen transfer to TiO_2 – contained fluxes was also studied.

1 Thermodynamics of Nitrogen in $BaO\text{-}B_2O_3\text{-}SiO_2$ and $TiO_2\text{-}B_2O_3\text{-}SiO_2$ Fluxes

1.1 Thermodynamic considerations for nitrogen removal

The reaction of nitrogen between fluxes and metal is given as following

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

For reaction (1), it is assured that nitrogen dissolves in fluxes as a nitride ion. Similar reaction can also be written if nitrogen in the fluxes is incorporated into a network. The equilibrium constant for reaction (1) is

$$K_1 = \frac{f_{(N^{3-})}\cdot(\%N^{3-})\cdot a_{[O]}^{3/2}}{f_{[N]}\cdot[\%N]\cdot a_{(O^{2-})}^{3/2}} \qquad (2)$$

In the previous studies, the nitride capacity of fluxes, $C_{(N^{3-})}$ has been determined from gas-flux equilibrium measurements according to the following reaction

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

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

The nitride capacity indicated by reaction (1) is

$$C_{(N^{3-})} = \frac{K_1\cdot a_{(O^{2-})}^{3/2}}{f_{(N^{3-})}} = \frac{(\%N^{3-})\cdot a_{[O]}^{3/2}}{f_{[N]}\cdot[\%N]} \qquad (5)$$

The nitrogen distribution ratio, L_N, between flux and metal is

$$L_N = \frac{(\%N^{3-})}{[\%N]} = C_{(N^{3-})} \cdot \frac{f_{[N]}}{\alpha_{[O]}^{3/2}} \qquad (6)$$

A high value of the nitrogen distribution ratio is desired for nitrogen removal. From equation (6), we know that in order to obtain a high value of the nitrogen distribution ratio, it is required that the fluxes have a high nitride capacity and the metal a low oxygen activity.

1.2 Experiments

The experiments were carried out in graphite crucible, in which the fluxes and carbon-saturated iron were melted and equilibrated at 1 623 K. Fig. 1 shows a schematic diagram of a SiC electric furnace and a mullite reaction tube. Temperature was controlled within ± 1 K. The gas nozzle was placed 1cm above the melts, and the mixture gases of $CO - N_2 - Ar$ were blown onto the surface of the fluxes at a flow rate of 200 ml/min. Under these conditions, the oxygen potential pressure was given by the equilibrium between C and CO, according to the reaction (7)

$$C(s) + (1/2)O_2(g) = CO(g) \qquad (7)$$

$$\Delta G^{\ominus} = -114440 - 85.77T \ (J/mol)^{[5]} \qquad (8)$$

After reaching equilibration, the flux was quenched and prepared for chemical analysis. Nitrogen in the fluxes was analysed by the "Kjedalhl Method", the fluxes composition were also analysed by different chemical methods.

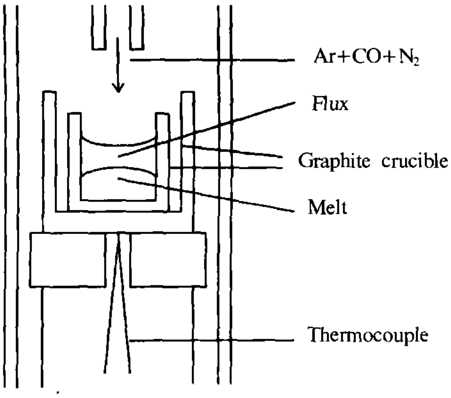

Fig.1 Schematic diagram of apparatus

1.3 Experimental results

Table 1 and table 2 are experimental results of BaO – contained and TiO_2 – contained fluxes. Both flux systems have high nitride capacity and nitrogen distribution ratio. In $BaO - B_2O_3 - SiO_2$ fluxes system, the nitrogen distribution ratio can reach 19.75. In $TiO_2 - B_2O_3 - SiO_2$ flux system, when the content of TiO_2 is 5%~ 15%, SiO_2 is 45%~ 55%, the fluxes have high nitride capacity and nitrogen distribution ratio. The results indicate that from thermodynamic point both BaO— contained and TiO_2 – contained fluxes can be used for the denitrogenization from liquid steel.

Table 1 Experimental results for $BaO-B_2O_3-SiO_2$ system
T=1623K, P_{N_2}=1.01×10⁴Pa P_{CO}=1.01×10⁴ Pa

No.	$w(BaO)/\%$	$w(B_2O_3)/\%$	$w(SiO_2)/\%$	$(\%N^{3-})$	$[\%N]$	$C_{(N^{3-})}/\times10^{-13}$	L_N
1	78.25	9.95	11.80	0.147	0.023	4.12	6.39
2	70.68	17.20	12.12	0.158	0.008	12.69	19.75
3	54.47	35.72	9.81	0.183	0.023	5.11	7.96
4	44.07	38.27	17.66	0.235	0.013	11.61	18.08
5	72.65	5.88	21.47	0.084	0.024	2.25	3.50
6	57.71	17.03	25.26	0.140	0.014	6.42	10.00
7	44.08	32.83	23.08	0.204	0.015	8.78	13.60
8	19.10	61.40	19.50	0.258	0.014	11.84	18.43
9	41.24	26.46	32.30	0.170	0.020	5.46	8.50
10	41.87	20.41	37.72	0.215	0.015	9.21	14.33
11	19.22	50.00	30.78	0.207	0.069	1.93	3.00
12	9.79	53.77	6.44	0.239	0.026	5.19	9.19
13	42.73	8.63	48.64	0.156	0.015	6.68	10.40

Table 2 Experimental results for $TiO_2-B_2O_3-SiO_2$ system

T = 1 623 K, P_{N_2}=1.01×10^4 Pa, P_{CO}=1.01×10^4 Pa

No.	$w(TiO_2)$/%	$w(B_2O_3)$/%	$w(SiO_2)$/%	$(\%N^{3-})$	[%N]	$C_{(N^{3-})}$ /×10^{-13}	L_N
1	22.48	23.69	53.82	0.172	0.065	1.70	2.65
2	^{2}9.81	16.62	53.57	0.115	0.041	1.80	2.81
3	9.58	36.70	53.73	0.238	0.022	3.74	5.82
4	16.54	22.38	61.08	0.118	0.064	1.18	1.84
5	12.58	38.60	50.84	0.182	0.013	8.99	14.00
6	40.61	13.12	46.28	0.500	0.141	2.29	3.55
7	24.16	26.50	49.36	0.170	0.032	3.41	5.31
8	18.72	43.83	38.45	0.136	0.019	4.60	7.16
9	9.22	35.87	54.19	0.153	0.016	6.14	9.56
10	25.69	20.62	33.69	0.172	0.020	5.53	8.60
11	9.97	40.08	50.00	0.237	0.014	10.38	16.93
12	39.31	33.37	27.32	0.120	0.022	3.50	5.46
13	31.32	44.28	24.60	0.129	0.064	1.29	2.02
14	18.48	53.72	27.80	0.152	0.032	4.25	6.61
15	10.24	62.74	27.02	0.245	0.082	1.92	3.00

2 Kinetics of Denitrogenization by Fluxes Treatment

2.1 Kinetic consideration for denitrogenization

While B_2O_3 – contained flux is used for nitrogen removel, the denitrogenization reaction can be described as following

$$(1/2)(B_2O_3) + [N] = (BN) + (3/2)[O] \qquad (9)$$

On the basis of "dual film theory",the whole processes include: mass transfer in fluxes, interface chemical reaction and mass transfer in liquid steel, the rate of the reaction is controlled by the slowest one of these three processes. At high temperature, it is considered that the chemical reaction proceeds rapidly, and therefore, can not be the controlled step. If the reaction is limited by nitrogen transfer in steel, then the rate of nitrogen transfer from liquid steel to flux is given by Equation (10)

$$J_N = m_N(C_{[N]_b} - C_{[N]_i}) \ (g/(cm^2 \cdot s)) \qquad (10)$$

Where m_N is the mass transfer coefficient of nitrogen (cm/s), $C_{[N]_b}$ and $C_{[N]_i}$ are the concentrations of nitrogen in bulk phase and flux-metal interface.

By changing unit to mass fraction, equation (10) can be deduced to

$$\frac{d[\%N]}{dt} = \frac{A \cdot m_N \cdot \rho}{W}([\%N]_b - [\%N]_i) \qquad (11)$$

Where A is the flux-metal interface area, cm^2, ρ is the density of the steel, g/cm^3, W is the mass of steel, g, $[\%N]_b$ and $[\%N]_i$ are mass fraction of nitrogen in steel and flux-metal interface. According to reaction (9), from mass balance, the equation (11) can be deduced to

$$F([\%N]) = \int_{[\%N]_{t=0}}^{[\%N]_{t=t}} G([\%N])dt = -\frac{Am_N \cdot \rho}{W} \cdot t \quad (12)$$

It is clear that the plot of the left hand side of equation (12) versus time should give a straight line if the rate of nitrogen removal is controlled by nitrogen transfer in liquid steel.

2.2 Experiments and results

A frequency induction furnace was used for the experi-- ments. Alumina crucibles were used to contain the

Table 3 Nitrogen content during denitrogenization process ×10^{-6}

No.	Experimental condition	0	30″	1′	1′30″	2′	2′30″	3′	3′30″	4′
1	A, 0.05l/m, 1813 K	116	107	98	87	76	66	51	45	40
2	A, 0.1l/m, 1 813 K	118	105	90	81	69	50	42	37	32
3	A, 0.2l/m, 1 813 K	108	97	82	70	59	42	37	33	34
4	B, 0.2l/m, 1813K	112	105	93	80	72	65	52	40	35
5	C, 0.2l/m, 1813K	121	108	96	83	75	64	53	42	37
6	A, 0.2l/m, 1 813 K	112	102	85	72	52	41	33	35	32
7	A, 0.2l/m, 1 943 K	107	96	81	72	55	38	32	32	30
8	A, 0.2l/m, 1 813 K	140	121	107	89	68	55	47	34	32
9	A, 0.2l/m, 1 813 K	70	62	55	49	45	40	37	35	33

Note: A: middle argon blowing, B: shallow argon blowing, C:deep argon blowing.

metal and flux. Experimental metal compositions(mass fraction) are C: 0.03%, Si: 0.009%, S: 0.017%, P: 0.01%. Experimental salg composition(mass fraction) are TiO_2: 13.21%, B_2O_3: 45.37%, SiO_2: 40.60%. Argon was blown during the experiments. For each experiment, 1 kg of steel and 20 g of premelted flux were used. Various argon blowing conditions, temperatures, initial content of nitrogen in steel were chosen. The steel was melted under nitrogen atmosphere. When the desired temperature was reached and stabilized, the fluxes was added and argon was bubbled. The samples were taken by quartz tube every half a minute. The experimental results were shown in table 3.

2.3 Discussion

The results in table 3 show that at 1 813 K, with proper argon-blowing condition, it only takes four minutes that the nitrogen content in liquid steel can be reduced to 3×10^{-5} from initial 1×10^{-4}. Using the results of various experimental conditions and plotting the left-hand side of equation (12) versus time, the line is straight as shown in Fig. 2. This result indicates that the nitrogen transfer in liquid steel is the determination step of denitrogenization process.

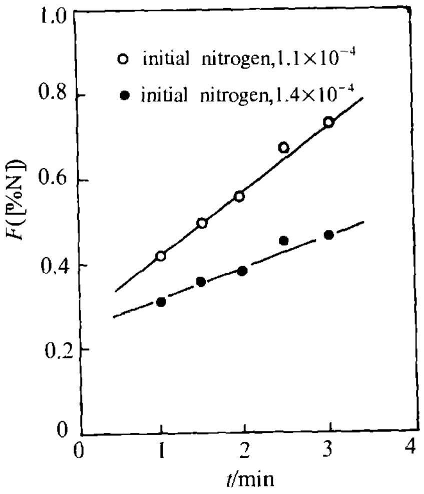

Fig.2 The relationship between left-hand side of equation (12) and time

3 Conclusions

(1) Under experimental conditions, $BaO\text{-}B_2O_3\text{-}SiO_2$ and $TiO_2\text{-}B_2O_3\text{-}SiO_2$ fluxes have high nitride capacity and nitrogen distribution ratio. Both fluxes are indicated to be practical to used for denitrogenization.

(2) Nitrogen transfer in liquid steel is the determination step of reaction. Improving mass transfer condition in liquid steel can accelerate the denitrogenization rate.

(3) Under the proper experimental conditions, it only takes four minutes that the nitrogen in liquid steel can be reduced to 3×10^{-5} from initial 1×10^{-4}, the nitrogen removal can reach to 70 percent.

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