Thermodynamic analysis of nitrogen removal in EAF by DRI fines injection

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Electric arc furnace (EAF) steel typically contains about 70–120 ppm nitrogen, yet for some bar and flat rolled products, the maximum limit of nitrogen is 30 ppm. Nitrogen removal from steel is very difficult through vacuum degassing or inert gas purging, because of its low diffusivity, hence nitrogen removal is one of the major challenges to EAF operators. In the present study, direct reduced iron (DRI) fines have been injected into the steel bath which generates fine CO gas bubbles deep in the bath which help to remove dissolved nitrogen. Experimentation has been carried out in an indirect EAF on a 15 kg scale. Nitrogen removal has been found to be a very good in high carbon steel.

Introduction

Nitrogen is a harmful impurity in plain carbon steel, because it reduces mechanical properties (toughness, intergranular fracture in cast steel, stretcher strain formation in deep drawing operations, etc.), corrosion resistance and weldability. Arc furnace steel contains about 70–120 ppm nitrogen, whereas the tolerable limit of nitrogen in good quality flat products is <30 ppm. To meet this low nitrogen requirement, it is imperative to control the pick-up of nitrogen during operations and to remove nitrogen after melting or refining. Control of pick-up alone is not sufficient to produce such a low nitrogen containing steel. Therefore, special attention is needed to remove nitrogen.

Nitrogen increases during melting and refining. The solubility of nitrogen in low carbon steel is 448 ppm at 1873 K,[1] whereas its diffusivity in steel is very low[2] ($\sim 5 \times 10^{-8}$ m^2 s^{-1}), hence its removal is very difficult. Existing process such as vacuum degassing[3–5] can remove only up to 20% of nitrogen present in steel and the rate is very slow and cannot be accomplished within the short ladle refining time.

Several investigators have tried to remove nitrogen by inert gas purging (Ar) or CO$_2$/CO injection.[6,7] They have also observed 10–20 ppm nitrogen removal. However, during CO$_2$/CO injection, there may be a chance of O and C pick-up in the bath.

Carbon boiling is possible by direct reduced iron (DRI) charging, oxygen blowing or injection of oxide fines from the top. DRI charging is not so effective in removal of nitrogen, as DRI lumps float on the top of the bath and remove CO gas on the upper portion of the bath only.[8] Oxygen blowing is beneficial for removal of nitrogen when bath carbon is high (>0·8%).[9] Iron ore powder injection is very effective for the removal of nitrogen from steel.[10] However, it has not been commercialised owing to some operational problems.

All the above processes are removal of nitrogen through the gas phase. Several investigators[11–15] have tried a nitrogen removal through a slag phase also. They have used fluxes (BaO, TiO$_2$ and CaF$_2$) which have a high affinity for nitrogen. In the presence of these fluxes, slag containing other components such as CaO, MgO and SiO$_2$ can absorb nitrogen from liquid steel in the form of various nitrides. Here the fluxes are very costly and some alloying elements may be picked up from the added fluxes. Therefore, it may be applicable only for some specific alloy steel, not for mild steel.

In the present work, DRI fines have been injected into the bath. The DRI fines contain 20–25% FeO and 0·2–0·8% carbon. FeO and C in the fines and in the bath react to form CO bubbles as per the reaction below

$$FeO + C = Fe + CO \text{ (g)} \tag{1}$$

If DRI fines are injected with the help of Ar as a carrier gas, the fines are dispersed throughout the bath and each particle may form a separate nucleus of a CO bubble and hence large numbers of fine CO bubbles are formed. The produced CO bubbles are very fine and have a highly active surface area to accumulate/scavenge nitrogen dissolved in the metal bath, and come to the bath surface when their volume is increased. Therefore, these CO bubbles can purge out nitrogen while escaping the bath.

DRI fines injection is considered to be more active than conventional oxygen blowing,[9] because during oxygen blowing, oxygen molecules are not finely dispersed in the bath, therefore, fewer large CO bubbles are generated. The majority of the oxygen reacts with Fe (as Fe is the bulk phase) and increases slag volume. K. Shinme et al.[10] has observed from his experiments that the removal of N from steel in the vacuum oxygen decarburisation (VOD) with iron oxide powder blowing is twice that via oxygen blowing.

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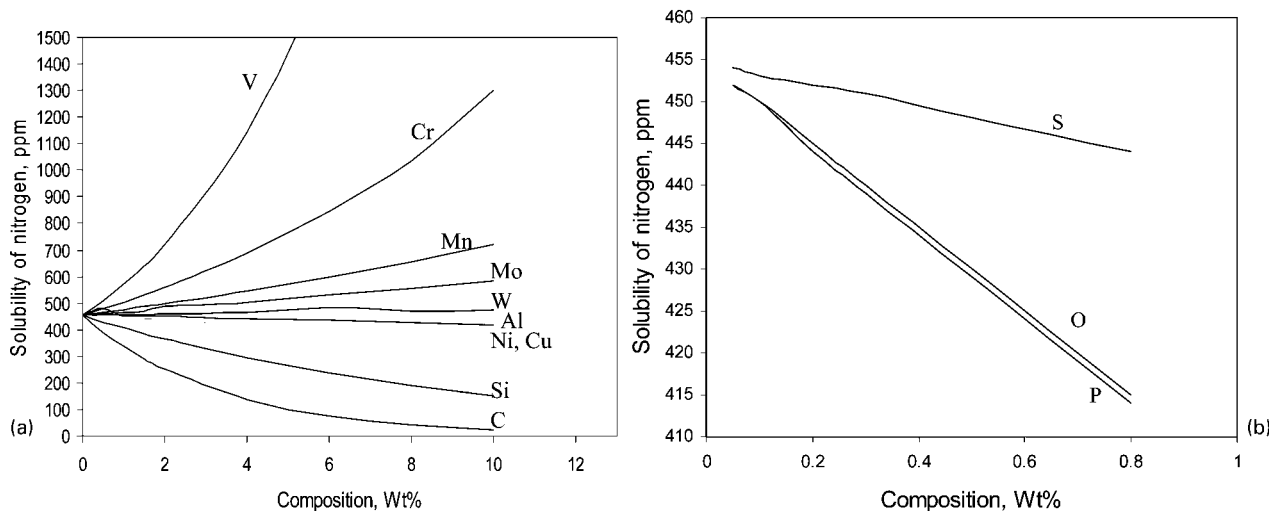
1 Effect of different alloying elements on solubility of nitrogen in iron melt at 1600°C

DRI fines and iron ore fines both contribute iron oxide to produce CO bubbles deep in the melt. Apparently both are same; however, in this work, attention is given on the injection of DRI fines owing to some advantages, namely, it has some carbon (0·2–1·5%) which takes part in reaction (1), high metallic Fe content which increases the yield of the melt, and good flowability and less moisture content enhance its suitability for injection. Moreover, DRI fines are denser and absorbed by the melt more easily than iron oxide fines, hence, ejection loss of fines with the off gas is expected to be lower.

Thermodynamic principles

Reaction of nitrogen in steel can be expressed by

$$\frac{1}{2}N_2 \text{ (g)} = [\%N] \qquad (2)$$

and the free energy ΔG_0 for the reaction is given by[16]

$$\Delta G_0 = 3598 + 23 \cdot 89T \text{ (J mol}^{-1}\text{)}$$
$$= 860 \cdot 7 + 5 \cdot 72T \text{ (cal mol}^{-1}\text{)} \qquad (3)$$

where T is the temperature in kelvin

$$\Delta G_0 = -RT \ln K_1 \qquad (4)$$

where equilibrium constant K_1 is given by

$$K_1 = \frac{a_N}{P_{N_2}^{1/2}} = \frac{f_N[\%N]}{P_{N_2}^{1/2}} \qquad (5)$$

where a_N is the activity of nitrogen in steel, P_{N2} is the equilibrium partial pressure of nitrogen in steel, f_N is the activity coefficient of nitrogen in steel and %N is the dissolved nitrogen in steel.

The activity coefficient of nitrogen in steel f_N as a function of other constituents in steel is expressed by

$$\log f_N = \log f_N^0 + e_N^i(\%i) + e_N^j(\%j) + \dots \qquad (6)$$

where e_N^i and e_N^j are interaction parameters of i and j components respectively.

Because f_N^0, which is f_N at infinite dilution in binary alloy, is always 1, by definition $\log f_N^0 = 0$
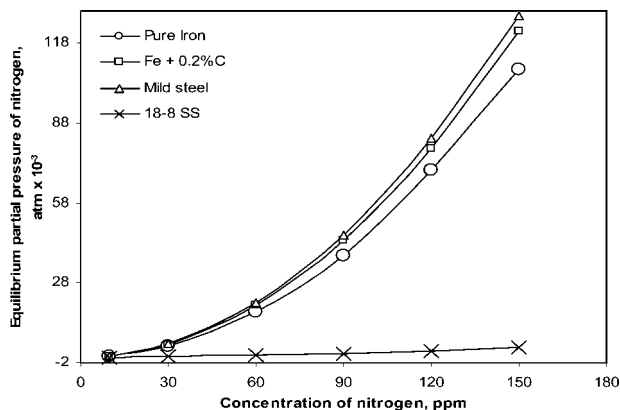
Hence

$$\log f_N = e_N^i(\%i) + e_N^j(\%j) + \dots \qquad (7)$$

The values of K_1 at different temperatures can be calculated from equations (3) and (4). It is 0·0455 at 1600°C. In equation (5), %N is the nitrogen content of steel, i.e. solubility of nitrogen at any value of partial pressure P_{N2}. Therefore, solubility of nitrogen can be calculated from the known value of activity coefficient f_N and P_{N2}. The effect of different alloying elements on the solubility of nitrogen in the liquid iron at 1600°C is shown in Fig. 1. The value of f_N for each composition were calculated from equation (7) using interaction coefficient values given in Table 1.[17]

It is observed from Fig. 1*a* that solubility of nitrogen in pure iron is 455 ppm at 1600°C. Vasudeva *et al.*[1] have reported 450 ppm at the same temperature. Moreover, the solubility of nitrogen decreases as the carbon percentage increases. Therefore, the denitrogenation of high carbon steel is easier than that of low carbon steel. Similarly, Si, Ni and Cu decrease the solubility of nitrogen in steel. On the other hand, V, Cr, Mn, Mo and W increase the solubility on nitrogen in steel. Vanadium has a significant effect on solubility, whereas effect of W is negligible. Figure 1*b* shows the decrease in solubility of nitrogen in steel for O, S and P. Although

Table 1 Interaction coefficient $e_i^j \times 10^2$ for elements dissolved in liquid iron at 1600°C

Dissolved element	Added elements												
N	C	Si	S	P	Mn	Cr	Al	V	Ni	Mo	W	Cu	O
–	13	4·7	1·3	5·1	−2·0	−4·5	0·3	−10	1·0	−1·1	−0·2	0·9	5

2 Equilibrium partial pressure of N$_2$ at 1600°C in iron melt of different compositions

1: Ar gas cylinder; 2: rotameter; 3: Ar gas inlet; 4: chamber of fluidised bed injector; 5: nozzle for dust outlet; 6: outlet pipe of injector; 7: graphite lance; 8: EAF shell; 9: graphite electrodes, X valves

3 Experimental set-up

thermodynamically, oxygen and sulphur are beneficial in denitrogenation, in practice, it is not so because these are surface active elements.

The equilibrium partial pressure of nitrogen for iron of different compositions has been calculated from equation (5) as shown in Table 2 and plotted in Fig. 2. From the figure, it is clear that denitrogenation of mild steel is easier than pure iron and stainless steel (SS). The equilibrium partial pressure of nitrogen in SS is too low to remove nitrogen by gas/metal interaction. The equilibrium partial pressure of nitrogen can be reduced either by generation of vacuum or using flushing gas. Thermodynamically, both are equivalent.
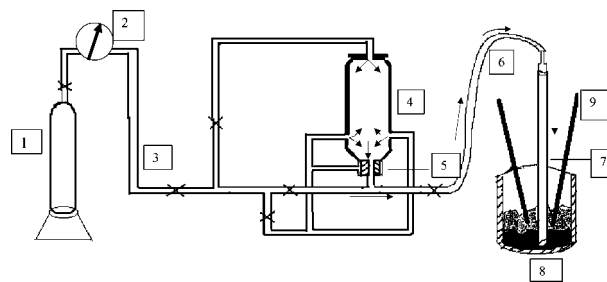
Experimental

Experimentation was carried out in a 30 kg capacity, 50 kVA indirect electric arc furnace (EAF) (Fig. 3). In each experiment, 15 kg of steel scrap has been melted. After melting, the temperature was raised to ~1600°C [measured by infrared (IR) pyrometer, 'ULTIMAX' and range: 900–3500°C]. Samples were taken by a 4 mm diameter quartz tube for N, O, S and C analysis. Injection of DRI fines (−60 mesh) was carried out for 10 min using fluidised bed type injector where argon gas was used as the carrier gas. Here argon flow was 12 L min^{-1}. DRI fines injection rate was ~250 g min^{-1}. The amount of fines injected was measured by taking the initial and final weight present in the injection chamber. Initial, final and intermediate samples were taken by a quartz tube. The carbon content of the bath was increased either by coke powder addition or by pig iron addition, because the steel scrap

contained very low carbon. Intermediate metal samples were analysed for nitrogen and oxygen by LECO apparatus. Final metal samples were analysed for N, O, C and S [N by thermal conductivity detector (TCD) technique; O, C and S by IR technique]. Chemical analyses of final metal samples were carried out for Si, Mn and P.

Results and discussion

The chemical analysis of scrap and sponge iron fines is shown in Table 3. After melting, the nitrogen content of the melt was observed to be very high at around 150–200 ppm and sometimes even up to 300 ppm, whereas the nitrogen content in scrap was 60 ppm. This high pick-up was due to the smaller size of furnace and wide exposed surface with respect to volume. The extent of nitrogen removal depends upon bath depth, carbon content of bath, addition level, etc. When bath depth was 3 cm for the 15 kg heat, nitrogen removal was observed to be very poor, however, with an 8 cm bath depth, a remarkable improvement in nitrogen removal was found for the same size of heat, i.e. the nitrogen removal is favorable at a higher bath depth. This is because the higher the bath depth, the lower the loss of fines with flue gas. Therefore, all other experiments were carried out at a 15 kg scale keeping bath depth of 8 cm, the possible maximum bath depth in the same set-up.

Carbon content of bath

Experimentation was carried out in the steel bath containing varying carbon contents from 0·66 to 1·3 wt-%, keeping all other parameters the same. The initial nitrogen content after melting was ~170 ppm. The result is plotted in Fig. 4. From this figure, it is understood that in the case of high carbon containing baths, nitrogen removal is better than lower carbon baths for injection of the same amount of DRI fines in 10 min. When the carbon content was increased to 1·3 wt-%, the nitrogen content of the steel was reduced

Table 2 Equilibrium partial pressure $P_{N2} \times 10^3$ of nitrogen at 1600°C in iron melt*

Nitrogen content, ppm	Equilibrium partial pressure, atm $\times 10^3$			
	1	2	3	4
10	0·483	0·544	0·57	0·0175
30	4·3	4·9	5·13	0·158
60	17·3	19·6	20·5	0·632
90	38·3	44·0	46·2	1·422
120	69·55	78·45	82·0	2·529
150	108	122·57	128·0	3·952

*1: pure Fe; 2: Fe+0·2%C; 3: Fe+0·2%C+0·02%S+0·03%P+ 0·3%Si+0·3%Mn (mild steel); 4: 18-8 stainless steel. All values given are in wt-%.

Table 3 Chemical analysis of sponge iron fines and steel scrap used, wt-%

Sponge iron fines		Steel scrap	
Fe (total)	88·2	C	0·29
FeO	25·26	Si	0·30
C	0·85	Mn	0·40
Al$_2$O$_3$	2·12	N	0·0060
S	0·011	O	0·0131
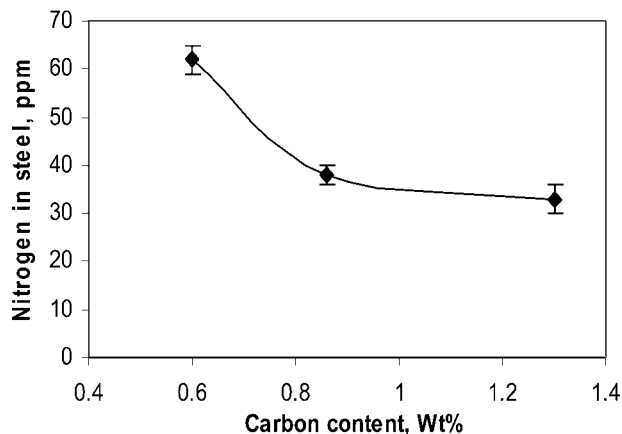
4 Carbon content *v.* nitrogen present in steel after 2·5 kg DRI fines injection

to 33 ppm, compared with around 60–70 ppm with a 0·6% carbon bath. The removal of nitrogen at higher carbon contents is favourable because the activity coefficient of nitrogen in steel increases with increasing carbon content. Figure 5 shows the solubility of nitrogen in steel at 1600°C for varying carbon contents. The curve is plotted on the basis of theoretical calculation from basic thermodynamic relations as mentioned earlier. The solubility of nitrogen in steel indicates residual nitrogen in steel, therefore, the trend of the actual curve in Fig. 4 looks similar to the curve in Fig. 5.
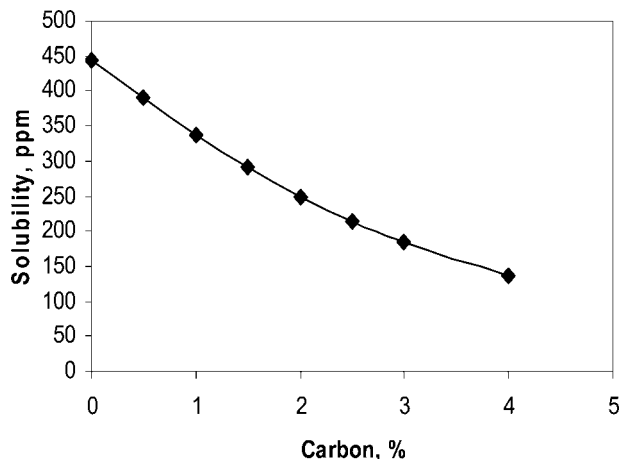
It is clear that this process is favourable for high and medium carbon steel. Scrap charged in EAFs generally contains ~0·2% or lower carbon, however, in most of the mini steel plants in India, mini blast furnaces (mainly KORF's MBF) are available. They use hot metal of ~4%C from MBFs (40–60%) as charge materials with DRI or scrap. Therefore, as the average carbon content of charge materials is very high, this process is expected to be useful in EAFs of Indian mini steel plants with MBFs.

Addition level

Metal samples at different time intervals during the injection were analysed. Examples for some experiments are given in Table 4. Multiplication of rate of injection and injection time indicates the quantity of DRI fines injected into the bath at a particular time. The plots for a high carbon steel (0·86%) and for a medium carbon steel (0·6%) are shown in Fig. 6a. The trend of nitrogen removal is similar in both the cases, but for high carbon steel, the requirement of DRI fines is less for all levels of nitrogen. Initially, the rate of removal is higher than that at a lower nitrogen level with a constant rate of DRI fines addition. Therefore, at a lower level of nitrogen, more DRI fines injection is needed for nitrogen removal. For medium carbon steel, removal rate at the initial stage is very high, because initial nitrogen content in steel is also very high.

5 Solubility of nitrogen in iron melt *v.* carbon content at 1600°C and 1 atm pressure

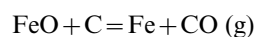The amount DRI fines required for denitrogenation can be calculated as follows

Assumed initial nitrogen content of steel $= N_i$(wt − %)

Final nitrogen content after removal $= N_f$(wt − %)

Weight of FeO required $= w$

Weight of steel $= W$

DRI fines react to form CO gas bubbles as per equation (1)

$$FeO + C = Fe + CO \text{ (g)}$$

Volume of CO gas generated $= 22 \cdot 4 \dfrac{w}{72}$

where it is assumed that 100%FeO in DRI fines is consumed.

The equilibrium partial pressure of nitrogen in steel P_{N2} is expressed as

$$P_{N_2} = \frac{\textit{volume of nitrogen removed from steel}}{\textit{volume of nitrogen removed from steel} + \textit{volume of CO gas generated}}$$
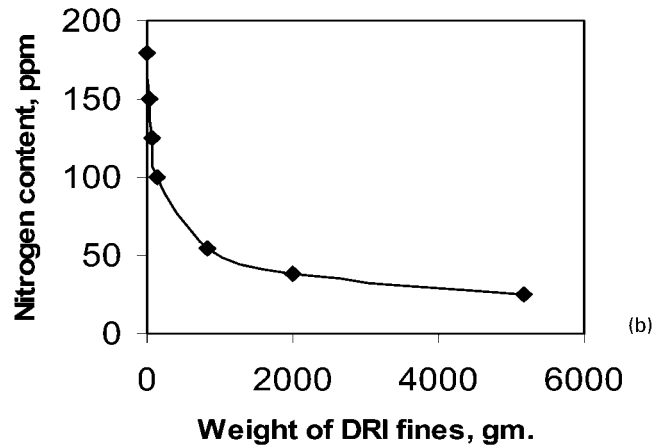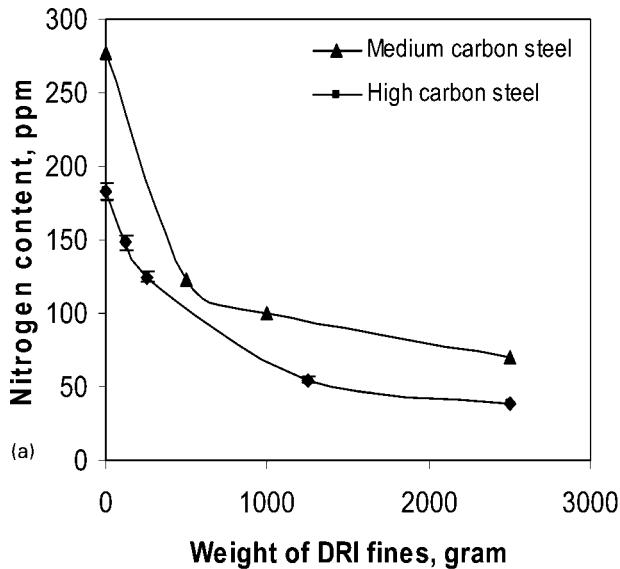
where volume of nitrogen removed from steel $= 22 \cdot 4(N_i - N_f)W/(28 \times 100)$, volume of CO gas generated can be calculated form equation (1) as mentioned above. Therefore, P_{N2} can be expressed as

$$P_{N_2} = \frac{\frac{22 \cdot 4(N_i - N_f)W}{28 \times 100}}{\frac{22 \cdot 4(N_i - N_f)W}{28 \times 100} + 22 \cdot 4 \frac{w}{72}} \tag{8}$$

From equation (5), the following equation can be obtained

$$K_1 = \frac{f_N(\%N_f)}{P_{N_2}^{1/2}}$$

i.e. $P_{N_2} = \dfrac{f_N^2 [\%N_f]^2}{K_1^2}$ (9)

Table 4 Removal of nitrogen during DRI fines injection in 15 kg bath

Sample no.	Carbon content, wt-%	Rate of injection, kg min⁻¹	Nitrogen content, ppm							
			Initial	0·5 min	1·0 min	1·5 min	2·0 min	4·0 min	5·0 min	Final (10 min)
1	0·86		183	148	125	–	–	–	55	38
2	1·00		181	–	–	–	86	–	50	27
3	0·60		277	–	–	123	–	100	–	70
4	0·66	0·250	300	–	–	–	100	–	85	62

a actual; *b* calculated

6 Removal of nitrogen on injection of DRI fines

From equations (8) and (9), the following equation can be obtained

$$\frac{w}{W} = \frac{(N_i - N_f)(K_1^2 - f_N^2 N_f^2)}{38 \cdot 9 f_N^2 N_f^2} \qquad (10)$$

where w/W is the ratio of FeO/steel weight, which is a function of N_i, N_f, K_1 and f_N. f_N depends upon composition of steel and temperature, however, the temperature dependence of f_N can be neglected in the narrow range of steel making temperature[18] (1550–1650°C). K_1 is temperature dependent; however, temperature has a minor effect on K_1 as per equations (3) and (4). Hence w/W ratio does not severely depend upon temperature

$$Percentage\ of\ DRI\ fines\ required =$$

$$\frac{10{,}000w}{W \times Percentage\ of\ iron\ oxide\ in\ DRI} \qquad (11)$$

If the steel contains $0 \cdot 6\%C - 0 \cdot 5\%Si - 0 \cdot 4\%Mn - 0 \cdot 03\%P - 0 \cdot 02\%S$

$$\log f_N = 0 \cdot 13 \times 0 \cdot 6 + 0 \cdot 047 \times 0 \cdot 5 - 0 \cdot 02 \times 0 \cdot 4 + 0 \cdot 051 \times$$

$$0 \cdot 03 + 0 \cdot 013 \times 0 \cdot 02 = 0 \cdot 0953$$

where $f_N = 1 \cdot 24$.

From equation (2), $\Delta G_0 = 11288$ cal mol^{-1}.

From equation (3), $K_1 = 0 \cdot 0455$.

The weight of DRI fines is needed for 15 kg heat is calculated from equations (10) and (11) as shown in Table 5 for medium carbon steel. The calculated data is plotted in Fig. 6*b*. The trend of the actual curve (Fig. 6*a*)

and this theoretical curve (Fig. 6*b*) are similar for medium carbon steel. The amount of DRI fines needed in the tests is higher than that in theoretical case because of fines loss with a flue gas and unreacted FeO in DRI which enters the slag phase. Theoretically, Fig. 6*b* shows that large amounts of fines are needed for removal of nitrogen below 30 ppm. This high amount of DRI fines injection is not possible in practice. Practically, as there is a coherent effect of CO bubbles formed by DRI fines and injected Ar gas bubbles, the removal up to 25 ppm may be possible.

For establishing equation (10), it has been assumed that 100% iron oxide in DRI fines is consumed in the reaction; however, it is not possible practically owing to the fines loss through off gas and unreduced oxide in the slag phase. Moreover, there may be some effects of carrier gas (Ar) which helps denitrogenation. Assuming Ar gas cannot reach all the nucleation sites of fine CO bubbles, its effect is considered to be minor and therefore, it has not been counted in calculation.
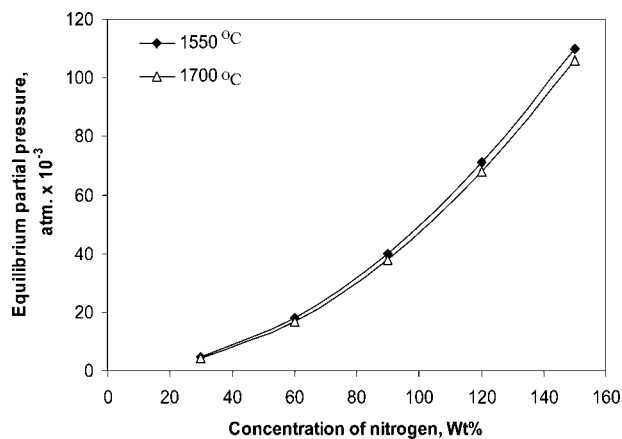
The author's laboratory scale study (15 kg) indicates that a very high percentage of DRI fines injection is necessary for denitrogenation. However, at a higher scale, it is expected that huge amounts of DRI fines (15–17% of melt) are not needed, because of a higher bath depth and hence lower fines loss with off gas.

Bath temperature

Bath temperature is another parameter on which nitrogen removal depends. Here bath temperature was

Table 5 Amount of DRI fines needed for nitrogen removal

Carbon content, %	Initial nitrogen, ppm	Final nitrogen, ppm	Percentage of DRI fines required, %	Weight of DRI fines for 15 kg heat, kg
0·6	180	150	0·153	0·023
		125	0·43	0·07
		100	1·025	0·15
		55	5·59	0·84
		38	13·46	2·02
		25	34·5	5·17
		20	55	8·25

7 Plot of equilibrium partial pressure of nitrogen in pure iron *v.* concentration

Table 6 Energy consumption for 15 kg heat

	Actual, kW h	Calculated, kW h
Melting	25	5·9
Injection	4	2·05

16% and at the same time, metallic yield is also increased by 14%.

Conclusions

1. Nitrogen removal is possible by DRI fines injection up to a very low level ($\sim$30 ppm) for high carbon steel only.

2. For low carbon steel, nitrogen removal up to very low level is difficult by this method.

3. Kinetics of nitrogen removal at the higher level of nitrogen is faster than that in a lower level.

Acknowledgements

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maintained at 1550–1650°C, however, removal of nitrogen at different temperatures was not studied owing to the following reasons:

(i) bath temperature was measured by a IR pyrometer. Although it is a very good pyrometer, still there is a little inaccuracy because of interference of smoke dust and gases. It was found that its accuracy was $\pm$15°C. Therefore, it was considered only as a close approximation

(ii) equilibrium partial pressure of nitrogen depends upon temperature but it is not so severe if the temperature range is close. Equilibrium partial pressures of nitrogen in iron at different concentrations of N at 1700°C and 1550°C were calculated from equation (5) and are shown in Fig. 7. The curve shows that there is no wide difference in equilibrium partial pressures of nitrogen at 1700 and 1550°C. Interaction coefficients are taken at a fixed temperature, 1600°C, although interaction coefficients are temperature dependent. However, as per A. Ghosh *et al.*[18], 'within a limited temperature range, interaction coefficient may be taken as independent of temperatures'.

Therefore, experimentation in different temperatures has been avoided as partial pressure of nitrogen is not severely dependent.

Heat balance

Power consumption at different stages was measured by kW h meter fixed in the panel. The power consumption was calculated theoretically as shown in Table 6. For melting, actual power consumption was much higher than the calculated power consumption, because the furnace was very small, hence there was a high heat loss for radiation and conduction. Actual power consumption for injection of DRI fines is 4 kW h, which is higher than calculated power owing to the heat loss. It has been observed that owing to the injection of DRI fines into the bath, total actual power consumption is increased by