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Nitrogen Control in Chromium Steels

R.J. FRUEHAN

Department of Metallurgical Engineering and Materials Science, Carnegie Mellon University, Pittsburgh, USA

It is often necessary to reduce, or precisely control, the nitrogen content of Fe–Cr alloys. This paper reviews the thermodynamics and kinetics of nitrogen reactions with gases and slags. Some recent work on the kinetics of the dissociation, or formation, of the nitrogen molecule on Fe–Cr alloys using a unique isotope-exchange technique are given. It was found that chromium increases the rate, while sulphur retards it. Sulphur is surface active, and blocks the possible reaction sites on the surface.

A process model for nitrogen pick-up or removal in the AOD when N_2–O_2 or Ar–O_2 gas mixtures are used is presented. The model includes mass transfer and chemical kinetics at the surface. The rates depend on the sulphur and chromium contents, as well as on process parameters such as gas flowrate and bath depth. The model can be used to accurately predict the switch point from N_2 to Ar for the optimum processes. The model also predicts the rate of nitrogen pick-up when N_2 is used at the end of the blow.

It is often necessary to reduce the nitrogen content in the ladle. Vacuum degassing is possible, and a model was developed to explore this possibility. It was found that the rate depends on the chromium and sulphur contents and the degree of mixing. The results indicate that over 50 per cent of the nitrogen can be removed from 18-8 stainless steel and ferrochromium. Another possibility is the use of a special CaO–BaO–$A1_2O_3$–TiO_2 flux. It is predicted that 20 kg of this flux can remove over 50 per cent of the nitrogen from an 18-8 stainless steel containing 0,02 per cent aluminium.

Introduction

It is necessary to control the nitrogen content of Fe–Cr alloys within certain limits. In the AOD process, the cost can be reduced by optimizing the use of nitrogen in place of argon. This can be done through better control of the AOD, or through the removal of nitrogen from the metal after the process by some means other than argon flushing. This paper reviews the basic thermodynamics and kinetics of gas–metal and slag–metal reactions for nitrogen, and then gives recent research results for these reactions. Models are presented for optimization of nitrogen in the AOD and for vacuum degassing of Fe–Cr alloys. In addition, the possibility of removing nitrogen by a slag treatment is examined.

Thermodynamic Considerations

The nitrogen reaction with iron alloys can be written as

$$\frac{1}{2}N_2 = N \qquad [1]$$

$$K = \frac{f_N[\%N]}{P_{N_2}^{1/2}}. \qquad [2]$$

The value of K at 1600°C is 0,045, and the values of the activity coefficient of nitrogen for 1 wt per cent standard state (f_N) is given in Figure 1[1]. For Fe–Cr–Ni–C alloys, f_N can be calculated by use of equation [3]:

$$\log f_N = -0{,}047[\%Cr] + 0{,}0004[\%Cr]^2 + 0{,}13[\%C] + 0{,}0009[\%Ni] \qquad [3]$$

The net result is that the solubility of nitrogen is significantly higher in Fe–Cr alloys than in normal steels. For example, for one atmosphere of nitrogen, the solubility of nitrogen at 1600°C is 450 p.p.m. for iron and over 2000 p.p.m. for 18-8 stainless steel.

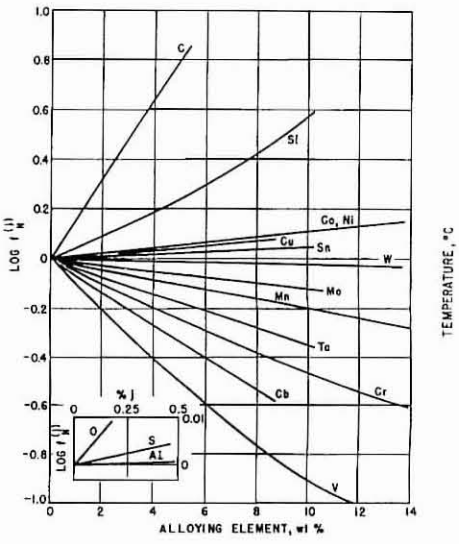

FIGURE 1. Solubility of nitrogen in iron alloys at 1600°C

Nitrogen can also react with slags, and the conventional method of expressing the ability of a slag to absorb nitrogen is the nitride capacity ($C_{N^{-3}}$), which is analogous to the sulphide capacity:

$$C_{N^{-3}} = (\%N) \frac{p_{O_2}^{3/4}}{p_{N_2}^{1/2}}, \qquad [4]$$

where (%N) is the nitrogen in the slag as nitride. Nitrogen can also be present as cyanide but, for the application to Fe–Cr alloys, nitride predominates.

The nitride capacity varies with the slag basicity in a complex manner[2,3]. It can enter the slag as a free nitride ion and is, therefore, favoured by high basicity or oxygen ion activity, as indicated by the following reaction:

$$\underline{N} + \left(\tfrac{3}{2} O^{-2}\right) = N^{-3} + \tfrac{3}{4} O_2. \qquad [5]$$

The nitride capacity of common slags is shown in Figure 2. Nitrogen can also enter the silica network and decrease with decreasing SiO_2 content. In general, C_N^{-3} would vary with the concentration of the basic component (*XO*), e.g., CaO, BaO as shown in Figure 3.

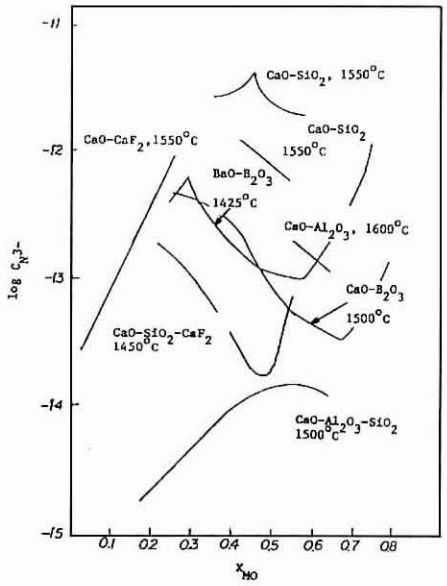

FIGURE 2. Nitride capacities of common slags

If one knows the nitride capacity and the prevailing oxygen potential, one can calculate the nitrogen partition ratio, L_N, between slag and metal:

$$L_N = \frac{C_{N^{-3}} f_N}{K_N p_{O_2}^{3/4}} \qquad [6]$$

$$L_N = \frac{(\%N)_{(slag)}}{[\%N]_{[metal]}} \qquad [7]$$

Kinetics of Reaction

The nitrogen gas reaction with Fe–Cr alloys is controlled by the dissociation of the N_2 molecule on the surface:

$$N_2 = 2N \ (surface). \qquad [8]$$

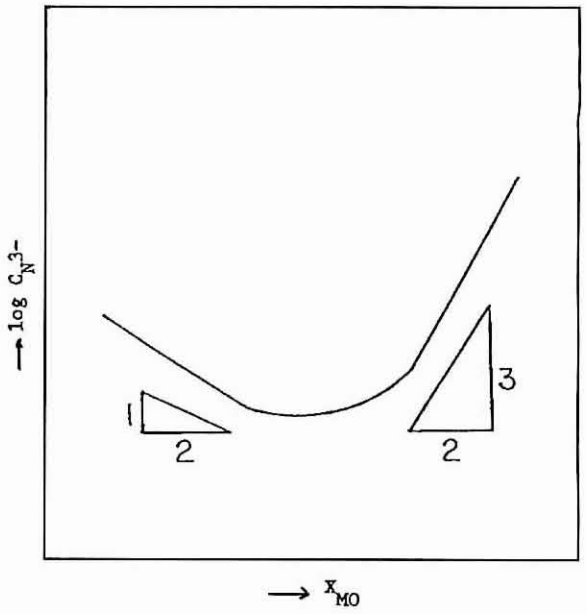

FIGURE 3. Variation of the nitride capacity with the activity of the basic component

The rate for Fe–Cr alloys has been measured by conventional[4] techniques, but these measurements were influenced by liquid-phase mass transfer. Recent work[5] using an isotope-exchange technique overcomes the problem associated with liquid-phase mass transfer since the reaction is made at equilibrium. With the isotope $N^{30}{}_2$, the following reactions occur at equilibrium:

$$N^{30}{}_2 = 2N^{15}(surface) \qquad [9]$$

$$N^{15} + N^{14} = N^{29}{}_2. \qquad [10]$$

When the change in the concentration of $N^{30}{}_2$ or $N^{29}{}_2$ is measured, the rate of dissociation of nitrogen can be determined.

The rate equation is expressed by

$$R = k_p A\,(1-\theta)\,(P_{N_2} - p^s_{N_2}), \qquad [11]$$

where k_p is the rate on a pure metal surface, A is the surface area, θ is the fraction of sites occupied by surface-active elements, and $p^s_{N_2}$ is the equilibrium nitrogen pressure for the amount of nitrogen in the metal as calculated from [2]. For example, sulphur and oxygen are surface elements and retard reaction rates on metal surfaces. At moderate sulphur levels ($1-\theta$) is inversely proportional to the sulphur activity.

It was found that the rate increases with the chromium content and decreases with the sulphur activity, as shown in Figures 4 and 5. It should be noted that the sulphur-activity coefficient (f_s) depends on the chromium content; f_s decreases with increasing chromium content:

$$\log f_s = -0{,}011[\%Cr]. \qquad [12]$$

The N_2 reaction on Fe–Cr–Ni alloys was also studied, and it was found that nickel had only a small effect on the rate[6].

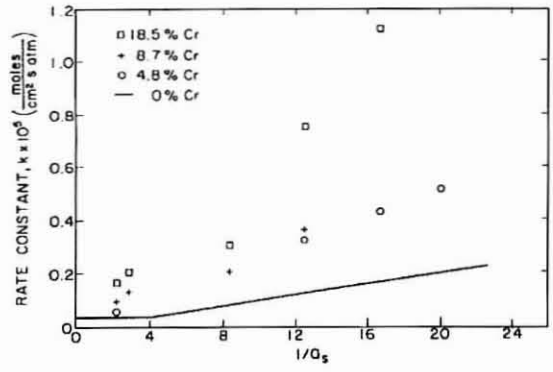

FIGURE 4. Effect of sulphur on the N_2 reaction of Fe–Cr alloys at 1600°C

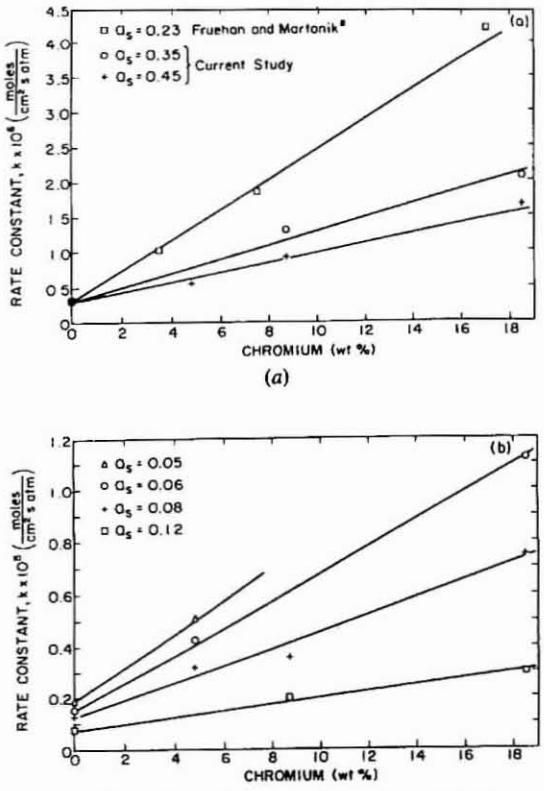

FIGURE 5. Effect of chromium on the N_2 reaction of Fe–Cr alloys at 1600°C

In actual operations, the rate of nitrogen reaction can be influenced, or controlled, by liquid-phase mass transfer. The flux of nitrogen in the metal is given by

$$J_N = \frac{mA\rho}{100}\,[\%N^S - \%N], \qquad [13]$$

where m is the liquid-phase mass-transfer coefficient, ρ is the density of the alloy, and $\%N^S$ and $\%N$ are the surface and bulk concentrations respectively. If the rate is completely controlled by mass transfer, $\%N^S$ is equal to the concentration in equilibrium with the gas, and

$$\frac{d\%N}{dt} = \frac{A\rho m}{W}\,[\%N^e - \%N], \qquad [14]$$

where W is the weight of the metal.

In the case where nitrogen is reacting with a liquid slag, the rate is normally controlled by mass transfer in the metal, and the rate is given by [14]. In that case, $\%N^e$ is in equilibrium with the slag, and m is the liquid-phase mass-transfer coefficient. The area term includes that associated with any slag–metal emulsion that may exist.

Nitrogen Reaction in the AOD

During stainless steelmaking in the AOD, O_2–N_2 gas mixtures are normally used in the blow, resulting in nitrogen pick-up, and O_2–Ar mixtures are used later, resulting in nitrogen removal. Also, nitrogen blowing at the end is used to add nitrogen to the steel if necessary. A complex reaction model has been developed to describe these reactions. The model considers chemical kinetics, liquid-phase mass transfer, and decarburization; details are given elsewhere[7].

In the model, the flux of nitrogen to, or from, the surface given by equation [13] is equated to the rate of the chemical reaction given by equation [11]. When O_2–N_2 mixtures are used and nitrogen is picked up, the pressure of N_2 in the rising bubble depends on the rate of decarburization. The calculated p_{N_2} is shown in Figure 6 for a 75 t AOD.

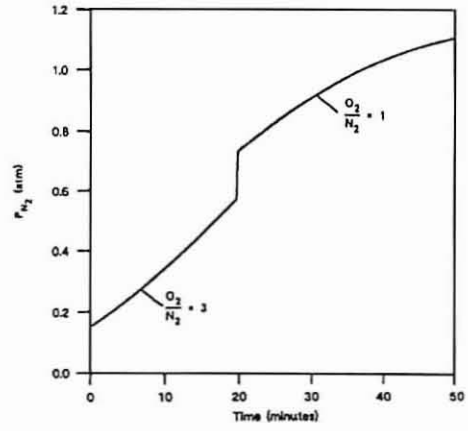

FIGURE 6. Pressure of nitrogen during the decarburization of 18-8 stainless steel for $O_2/N_2 = 3$ and $O_2/N_2 = 1$

When the flux of nitrogen to the surface by mass transfer, equation [13], is equated to the rate of the chemical reaction on the surface, [11] gives

$$\frac{Ak}{K}\,[\%N_S]^2 + \frac{Am\rho}{100}\,[\%N_S] + k\,p_{N_2}A + \frac{m\rho A}{100}\,[\%N]. \qquad [15]$$

Equations [13] and [15] are solved simultaneously. The surface area of the bubbles is calculated from the velocity of the rising bubble (v), the bath height (H), the bubble radius (r), and the total gas flowrate of the N_2 and CO (V):

$$A = \frac{3VH}{v\,r}. \qquad [16]$$

The mass-transfer coefficient from the rising bubbles is given by

$$m = 1{,}28\,\left(\frac{Dv}{2r}\right)^{\frac{1}{2}}, \qquad [17]$$

where D is the diffusivity of nitrogen in the metal. Similar equations can be developed for the removal of nitrogen.

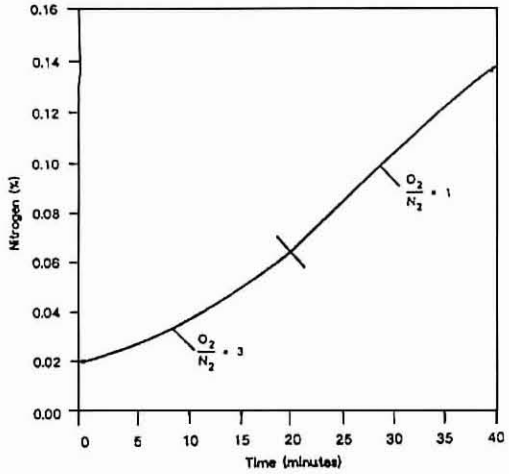

FIGURE 7. Nitrogen pick-up in 75 t of 18-8 stainless steel containing 0,03 per cent sulphur, using gas mixtures $O_2/N_2 = 3$ and $O_2/N_2 = 1$ and with a total flow of 0,85 m³ per second at 1600°C

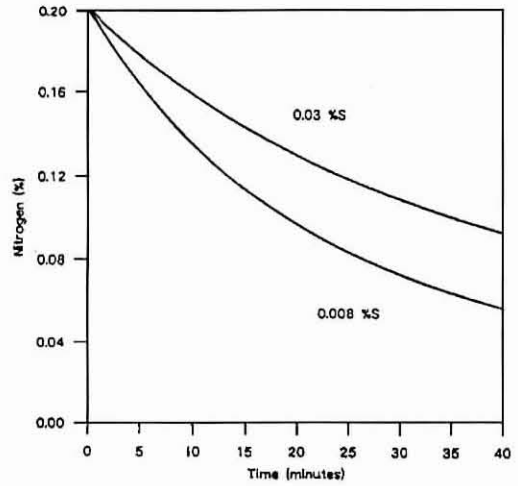

FIGURE 8. Rate of nitrogen removal from 75 t of 18-8 stainless steel containing 0,008 and 0,03 per cent sulphur, using 0,85 m³ of O_2 and Ar per second at 1600°C

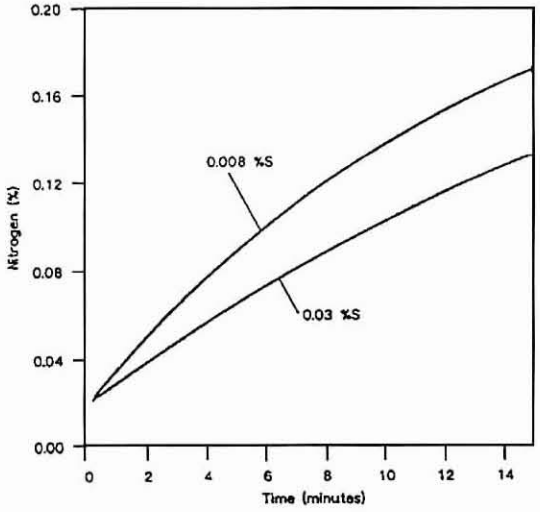

FIGURE 9. Nitrogen pick-up in 75 t of 18-8 stainless steel containing 0,008 and 0,030 per cent sulphur, using 0,85 m³ of N_2 per second at 1600°C

Typical results for a 75 t AOD using 0,85 m³ of gas per second and producing an 18-8 stainless steel are shown in Figure 7 for nitrogen pick-up during the O_2–N_2 period. The removal of nitrogen during the latter stage of the process when $O_2/Ar = 1$ depends on the sulphur content, as shown in Figure 8. Nitrogen can be alloyed by the use of N_2 at the end of the blow; again, the rate depends on sulphur, as shown in Figure 9.

The results briefly described above are for an assumed AOD, and are examples of how the nitrogen content can be computed. Such calculations will allow for a more precise control of the nitrogen content and minimize the use of argon.

Vacuum Treatment for Nitrogen

Nitrogen can be removed from Fe–Cr alloys by vacuum treatment. Such a process could decrease the cost of argon in the AOD, allow for the production of ultra-low nitrogen alloys, or be used in the production of ferrochromium. The feasibility of this was examined by use of a process model similar to the one for the AOD. The model is for a simple ladle or tank degasser. The flux of nitrogen to the surface was equated to the kinetics on the surface. In this case the chemical kinetics are given by

$$R = k'A\left[(\%N_S)^2 - (\%N_e)^2\right], \qquad [18]$$

where k' is the rate constant for the reverse reaction and is related to k through the equilibrium constant

$$k' = \frac{k f_N^2}{K^2}. \qquad [19]$$

The equilibrium nitrogen content $(\%N_e)^2$ is calculated from the nitrogen pressure in the vacuum tank by use of equation [2].

The rate will depend on the rate of mass transfer and of the chemical reaction, which depends on the sulphur and chromium contents. The mass-transfer coefficient can be estimated from the surface velocity and diffusivity. Estimates of m range from 0,02 to 0,06 cm/s. The rate constants are taken from the work of Glaws and Fruehan[6]; in some cases these results had to be extrapolated. For both the chemical reaction and the mass transfer, only the planar surface area was considered. If there is extensive splashing in which metal drops are exposed to the atmosphere, the rates would be significantly faster.

Calculations were made for a 50 t tank or ladle degasser 3 m in diameter. The results for 18-8 stainless steels containing 0,04 per cent and 0,01 per cent sulphur are shown in Figures 10 and 11 respectively. The rate increases with stirring and decreasing sulphur content. Below 0,01 per cent sulphur, the rate is primarily controlled by mass transfer, and further lowering of the sulphur is of no benefit. The rate of removal of nitrogen from a high-carbon ferrochromium melt containing 0,03 per cent sulphur is shown in Figure 12. It should be stressed that these rates are theoretical; however, they do indicate that the removal of nitrogen by vacuum degassing is feasible and show which variables influence the rate.

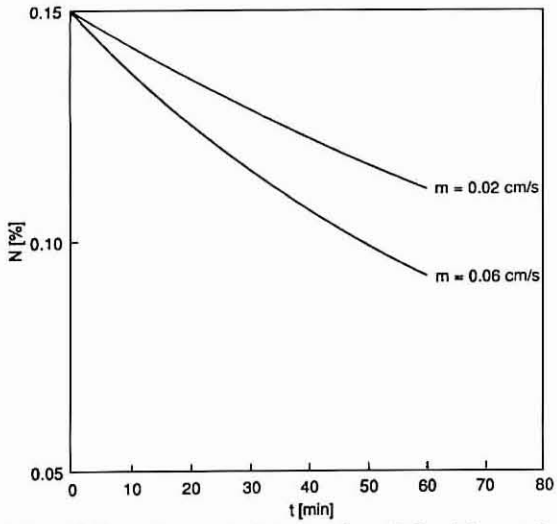

FIGURE 10. Rate of removal of nitrogen from 18-8 stainless steel with 0,04 per cent sulphur for a 50 t degasser of 3 m diameter

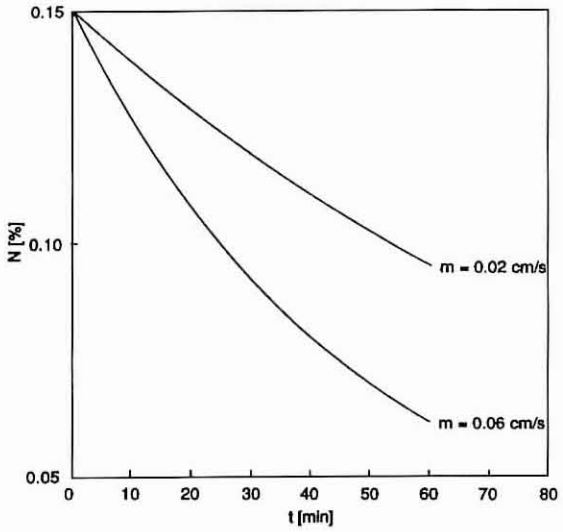

FIGURE 11. Rate of removal of nitrogen from 18-8 stainless steel containing 0,01 per cent sulphur for a 50 t degasser of 3 m diameter

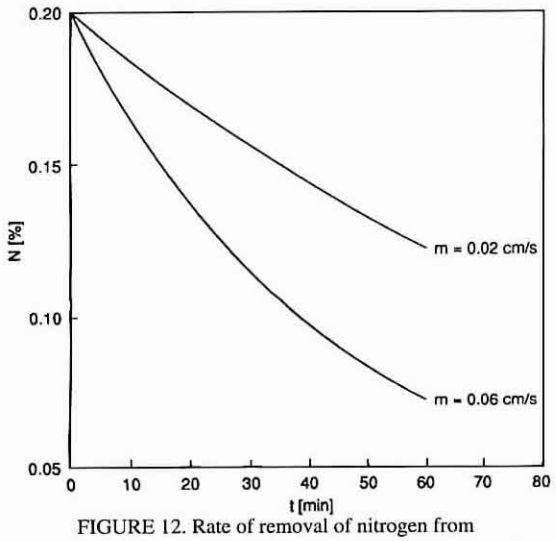

FIGURE 12. Rate of removal of nitrogen from 47%Cr–47%Fe–6%C–0,03%S melt for a 50 t degasser of 3 m diameter

Nitrogen Removal by Slags or Fluxes

For effective nitrogen removal by slags, the nitride capacity (C_N^{-3}) must be relatively large, and the prevailing oxygen potential or pressure low. The nitride capacities of normal steelmaking slags are too low to effectively remove nitrogen. Recent work[8] has indicated that special fluxes containing BaO and TiO_2 have high nitride capacities. BaO–TiO_2 slags have been shown to be effective in removing nitrogen from steel, as shown in Figure 13. However, these slags would be relatively expensive.

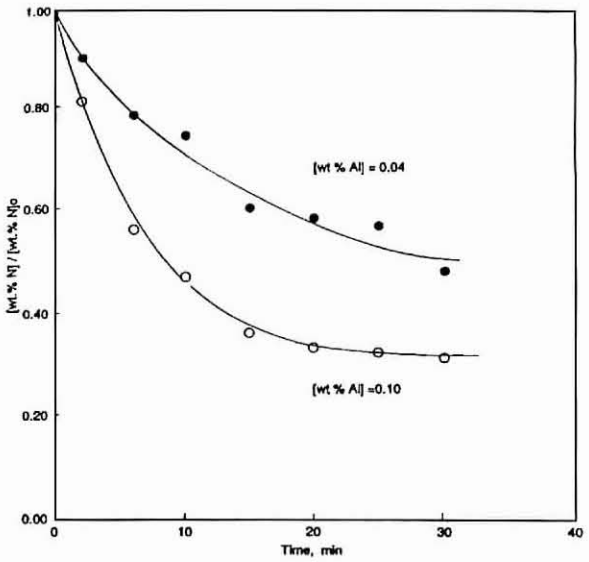

FIGURE 13. The nitrogen change in the metal as a function of time using a slag containing 45 wt per cent BaO, 45 wt per cent TiO_2, and 10 wt per cent Al_2O_3 at 1873 K

Of more practical interest are CaO–BaO–Al_2O_3–TiO_2 slags, which would remove nitrogen at a reasonable cost. The nitride capacity of these slags is shown in Figures 14 and 15. These slags can be used to remove nitrogen from stainless steel after reduction with aluminium.

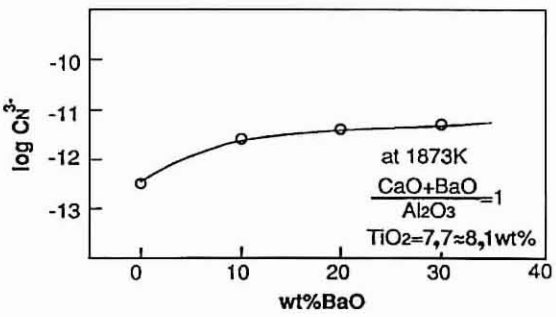

FIGURE 14. Variation of nitride capacity of CaO–BaO–Al_2O_3 slags as a function of BaO content[9]

Once the equilibrium oxygen potential for slag–metal reactions and nitride capacity is known, the nitrogen-distribution ratio (L_N) can be calculated from equation [6]. The oxygen potential is calculated on the assumption of Al–Al_2O_3 equilibrium. Liao and Fruehan[10] measured the activity coefficient of aluminium in an 18-8 stainless steel relative to 1wt per cent (f_{Al}) as 4,24. The calculated

nitrogen distribution between two possible slags as a function of the aluminium content in an 18-8 stainless steel is shown in Figure 16. From the distribution ratio (L_N), the effectiveness of a slag for nitrogen removal can be estimated. For example, for the metal containing 0,03 per cent aluminium, the distribution ratio for a 35 per cent CaO–10% BaO–35% Al_2O_3–10% TiO_2 slag is 132. When 20 kg of slag per tonne of metal is used, and the initial nitrogen content of the metal is 0,10 per cent, the final nitrogen content would be 0,027 per cent if only nitrogen comes from the metal. This, of course, is the theoretical maximum. Kinetic considerations and the pick-up of nitrogen into the slag and metal will reduce the degree of denitrogenization. However, it appears that such a slag treatment could reduce the nitrogen content by 50 per cent or more.

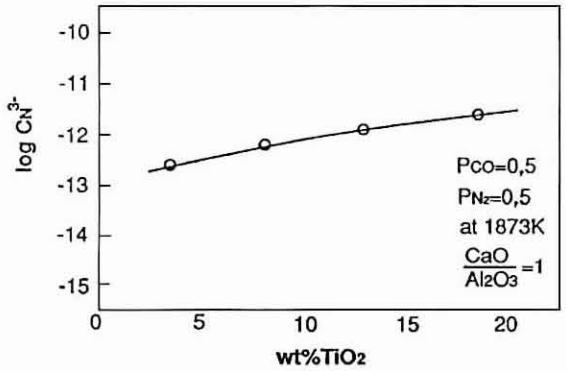

FIGURE 15. Variation of nitride capacity of CaO–Al_2O_3–TiO_2 as a function of TiO_2 content in slag[9]

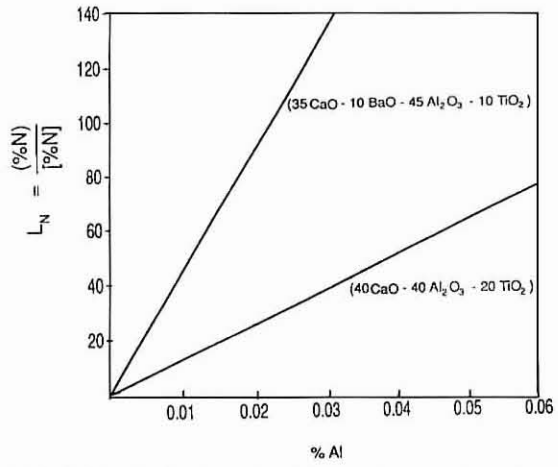

FIGURE 16. The distribution ratio of nitrogen between slag and metal for an 18-8 stainless steel at 1600°C as a function of aluminium content

Ito and Fruehan[11] examined the possible use of a highly reducing Ca–CaF_2 flux to remove nitrogen from Fe–Cr alloys. The reaction can be expressed as

$$\frac{3}{2}Ca + N = (Ca_{1,5}N) \qquad [20]$$

or

$$3\,Ca + 2\,N = (Ca_3N_2). \qquad [21]$$

Reaction [20] is more thermodynamically consistent because of the ionic nature of the flux. The activity coefficient of $(Ca_{1,5}N)$ in the flux was measured, from which the nitrogen-distribution ratio can be calculated as a function of chromium content, as shown in Figure 17. Owing to the vaporization of calcium, the highest activity that could be maintained is less than 0,2. Therefore, for an 18-8 stainless steel, the highest distribution ratio would be less than 10. In view of the cost and difficulties in the use of a Ca–CaF_2 flux, this does not appear to be an attractive process.

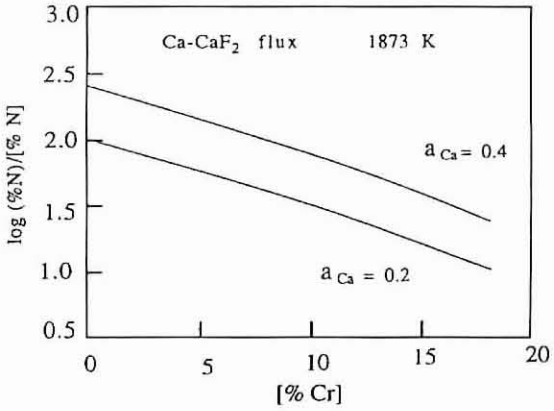

FIGURE 17. The distribution ratio of nitrogen between Ca–CaF_2 flux and Fe–Cr alloy as a function of chromium concentration at 1873 K

Summary and Conclusions

The solubility of nitrogen in liquid Fe–Cr alloys is relatively high compared with that of other common alloys. However, there are three possible methods for reducing the nitrogen content: flushing with inert gas, vacuum degassing, and use of a special slag. The rate of dissociation or formation of nitrogen (N_2) increases with increasing chromium content and decreases with increasing sulphur content.

A model for nitrogen control in the AOD process was presented. By use of this model the switch point from O_2–N_2 to O_2–Ar gas mixtures can be optimized, and nitrogen alloying by N_2 injection can be controlled. The model was extended to vacuum degassing for the removal of nitrogen using a ladle or tank degasser. The model included mass transfer and chemical kinetics, which depend on the sulphur content. Therefore, the rate depends on both the chromium and the sulphur contents. Considering only the reaction on the surface, it was estimated that about 50 per cent of the nitrogen can be removed by the optimum process.

The use of special fluxes containing CaO, BaO, Al_2O_3 and TiO_2 originally developed for steel can be used for stainless steel. The use of 20 kg of such a flux per tonne on an 18–8 stainless steel containing 0,02 per cent aluminium could remove 50 per cent or more of the nitrogen.

Acknowledgments

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