NITROGEN DISSOLUTION IN CARBON-SATURATED IRON DURING PLASMA PROCESSING

L.J. Heaslip*, W.J. Maddever**, R.M. Nicolic*, A. McLean*
* Department of Metallurgy and Materials Science,
University of Toronto, Toronto, Canada
** Union Carbide Corporation, Tarrytown, New York

ABSTRACT

The behaviour of nitrogen in a single phase direct arc furnace equipped with a drilled graphite electrode has been investigated. With the technique of electrode gas injection, a stable arc column of controlled composition was produced above a bath of carbon saturated iron held in an induction furnace. The influence of plasma composition on melt nitrogen content was determined. An ammonia jet was used to model these effects.

1. INTRODUCTION

The behaviour of nitrogen during plasma processing and the possibility of producing high nitrogen iron-based alloys by a plasma technique has been extensively studied in Germany[1], Japan[2,3] and Russia[4-6]. In each of these studies, plasmas were produced using conventional, water-cooled torch technology. In the present study, a simpler system, which is well suited to the requirements of industry, whereby plasma is generated by the injection of gas through a consummable graphite electrode, is utilized. This particular technique was first reported by Nicolic[7] where an indirect arc melting technique is described. Application of this technology to the smelting of ores and waste oxides has been reported by Nicolic et al[8], and Pickles and co-workers [9,10]. Maddever et al [11,12] have studied the influence of electrode gas injection on conventional arc furnace steelmaking operations.

2. EXPERIMENTAL

The behaviour of nitrogen in iron-carbon alloys during plasma treatment was examined in two ways. In the first set of experiments, the nitrogen content of carbon saturated iron contained in an induction furnace and exposed to a plasma was closely monitored. In the second set of experiments, a jet of cool ammonia was directed against the surface of the metal bath.

The NH_3 molecule is very unstable at the temperatures associated with molten carbon-saturated iron. For the reaction

$$NH_3 \rightarrow \tfrac{1}{2}N_2 + \tfrac{3}{2}H_2$$

the equilibrium constant may be estimated (using data extracted from the JANAF thermochemical tables[13]) as:

$$K = 2.1 \times 10^4 \text{ at } 1673 \text{ K}$$

This instability can promote remarkably high levels of the elements hydrogen and nitrogen in iron. For the dissolution of ammonia in liquid iron, according to the reaction

$$NH_3(g) \rightarrow \underline{N} + 3\underline{H}$$

(where the underline indicates the dissolved state in liquid iron)

the equilibrium constant can be estimated as:

$$K = 8 \times 10^{-6}$$

With this equilibrium, iron containing 25 ppm of hydrogen (corresponding to a partial pressure of H_2 gas of 1 atm at 1873 K) can contain an unlimited quantity of nitrogen. Thus, it is considered that the behaviour of nitrogen in iron exposed to an impinging jet of ammonia can serve as a model for the behaviour of nitrogen in iron exposed to a jet of nitrogenous plasma. In each case, the apparent solubility of nitrogen will be controlled by a dynamic equilibrium between two opposing reactions; the absorption of nascent nitrogen atoms over a small area beneath the impinging jet and the desorption of nitrogen molecules in the form of bubbles within the melt and over the remaining surface.

2.1 EXTENDED ARC PLASMA/INDUCTION FURNACE

Figure 1 is a schematic drawing of the plasma/induction furnace. In this furnace, power is coupled to the melt in two ways; by means of an induction coil which surrounds the hearth and by means of a single graphite electrode mounted vertically through the roof. The graphite electrode is mounted on a sliding track attached to the steel shell of the roof. A water-cooled stainless steel pin placed in the refractory at the bottom of the crucible completes the electrical circuit so that the arc may be struck on the solid charge or liquid metal. Roof and hearth refractory are divided by a sand seal in order that the roof may be easily removed for charging or tapping. The refractory lining of the crucible was formed from 98% MgO ramming compound. The roof refractory was composed of MgO-Cr_2O_3 ramming mixture. Inductively coupled power was supplied by a 25 Kw solid state inverter. Maximum power output of the plasma arc was 15 Kw. Therefore, total power to the furnace was a maximum of 40 Kw. This allowed for a melt size of 10 Kg.

2.2 AMMONIA INJECTION EQUIPMENT

Ammonia injection trials were carried out using an arrangement similar to that shown in Figure 1, with two important differences. The graphite electrode was replaced in these experiments by a water-cooled stainless steel lance. A thermocouple encased in a mullite sheath was inserted into the furnace volume through the taphole.

2.3 PROCEDURE

Experiments were conducted using a structural steel alloy of the following

composition as the base material:

	C	Mn	Si	S	N
wt.pct.	0.20	1.13	0.20	0.033	0.015

Once melted, the liquid metal was saturated with carbon by the addition of graphite. This addition caused a vigorous CO boil immediately after meltdown. The flushing action of this boil, which ceased once carburization and deoxidation were complete, caused a lowering in the nitrogen content from approximately 150 ppm in the base metal to a 30-40 ppm level, which is somewhat lower than that expected for equilibrium with air at 1673 K.

Samples were taken a various time intervals with a pyrex tube and a suction bulb. The metal pin samples produced were analyzed for nitrogen, oxygen, carbon, and sulphur. Nitrogen and oxygen were determined with an inert gas fusion technique. Samples for carbon or sulphur analysis were combusted in oxygen and the gases produced were analyzed either gravimetrically or by titration.

3. RESULTS AND DISCUSSION

3.1 ARC CHARACTERISTICS

A short flaring arc was typically observed during operation of the direct arc furnace without gas injection. With an arc voltage of approximately 40 Volts, the arc length was 5 mm at a bath temperature of 1773 K. Bath temperature was an important parameter since both the emissivity of liquid iron and the heat content of the gas in the furnace increase as melt temperature increases. Therefore, longer arcs are possible at higher bath temperatures. However, very long arcs could only be achieved when an arc stabilizing gas was injected through the electrode. A 3 cm long arc was easily achieved with argon injection at the same bath temperature and lower arc voltage mentioned previously.

Increased arc stability with gas injection also manifests itself in smoother electrical operation. Figure 2 presents oscillograms of the arc voltage and current for different modes of furnace operation. Operation of the furnace without gas injection produced voltage and current waveforms which are characteristic of a carbon arc in air. An air arc displays a roughly square voltage waveform which has an initation peak at the beginning of each half-cycle. This peak is coincident with the beginning of current flow. The plateau which follows the initation peak has some harmonic distortion. Arcs with argon injection have nearly sinusoidal voltage and current waveforms while the waveforms associated with nitrogen injection are intermediate between those associated with air and argon arcs. The current waveforms of all three arcs are very similar, the major difference being that the air arc shows an increased time when no current flows (i.e. when the arc produces no power). Evident in all three pairs of waveforms is an asymmetry between the positive and negative portions of the oscillograms. This asymmetry is due to the different electron emission characteristics of graphite and the iron-carbon melt.

3.2 BEHAVIOUR OF NITROGEN UNDER AN EXTENDED ARC

Final nitrogen contents for several heats made under air, argon or nitrogen arcs are shown in Figure 3. In each case the gas injection rate through the electrode was maintained at between 85 and 140 litres per hour. Starting temperatures ranged between 1623 and 1673 K. When arcing was complete, bath temperatures were typically 1773 to 1823 K. Although temperature control was difficult, at no time did the bath temperature exceed 1873 K. Metal samples were analyzed for carbon, sulphur, oxygen, and nitrogen. Carbon contents varied between 4.80 and 5.01 wt.pct. while sulphur was in the range 0.026 to 0.031 wt.pct. Oxygen content never exceeded 0.0005 wt.pct.

Each heat of Figure 3 was exposed to the arc for 30 minutes and the influence of the particular arc treatment on the final nitrogen content is shown as the height of the bars on the diagram. The number of trials with each treatment is written within each bar. The hatched area on a bar expresses the variability between the maximum and minimum nitrogen contents within that group of experiments. Also marked on the diagram are the nitrogen contents expected for thermodynamic equilibrium between nitrogen gas at 1 atm pressure and liquid iron containing 4.7% carbon at 1823 and 1873 K.

It can be seen from Figure 3 that an argon plasma maintains the nitrogen content at a level lower than that expected for equilibrium with nitrogen gas while melts held under an air or nitrogen arc exceed the equilibrium levels. It is interesting to note that further treatment has no appreciable effects on the nitrogen levels shown in Figure 3. Doubling the treatment time to one hour produced no further change in the nitrogen content. It is not suggested, however, that chemical equilibrium was attained. It is suggested that the levels in Figure 3 represent the steady state values or apparent solubilities achieved as a result of the dynamic equilibrium between the gas and metal phases beneath the arc and that between metal and gas over the remaining surface area of the melt.

3.3 TREATMENT WITH AN AMMONIA JET

In these experiments the behaviour of nitrogen in carbon saturated iron at 1673 K during the injection of ammonia through a 2 mm inside diameter water-cooled lance positioned 8-10 mm above the surface of the bath was investigated. A typical set of results of one such experiment at an NH_3 flowrate of 1.75 litres per minute is shown in Figure 4. The initial nitrogen level was 37 ppm. The steady state nitrogen content during ammonia jetting was reached in approx. 25 minutes. A weak boiling action of the bath commenced a few moments after the ammonia treatment was begun. This boil is attributed to the desorption of hydrogen and nitrogen gas from the bulk of the liquid. The solubility of hydrogen at 1723 K in carbon-saturated iron under 1 atm of H_2 is approximately 7 ppm. This hydrogen content must be rapidly achieved during ammonia treatment since dissociation of the ammonia molecule supplies three times more hydrogen than nitrogen to the bath.

After 35 minutes of treatment, the ammonia was shut off. It can be seen from Figure 4 that the nitrogen level of the melt declined once ammonia blowing was discontinued. This denitrogenization continued at a decreasing rate as the equilibrium nitrogen content under air was approached.

4. SUMMARY

The injection of argon through a small axial hole in the graphite electrode of a single phase direct arc furnace promotes the formation of an electrically stable plasma column above the bath.

These experiments demonstrated the effectiveness of the electrode gas injection technique to produce a plasma which can either promote low or high nitrogen contents depending on the gas phase composition within the plasma zone.

The ability of an ammonia injection technique to promote and sustain nitrogen levels which exceed the solubility value as determined by thermodynamic equilibrium with gaseous N_2 has been shown.

The nitrogen level achieved during treatment with ammonia or plasma containing dissociated nitrogen may be determined by a dynamic equilibrium between two opposing reactions. The rapid dissolution over a small area, of nitrogen produced by the dissociation of either ammonia or nitrogen gas, supplies nitrogen to the bath. Nitrogen removal occurs by the slow desorption of nitrogen molecules over the remaining surface area of the melt and into any bubbles rising from within the liquid pool.

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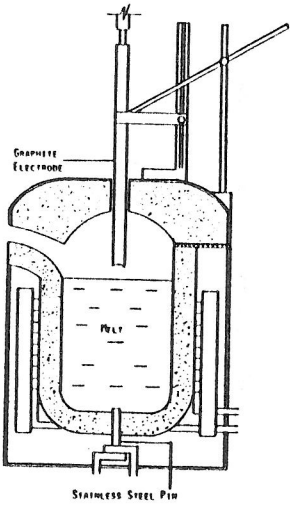

Fig. 1 Extended arc plasma/ induction furnace

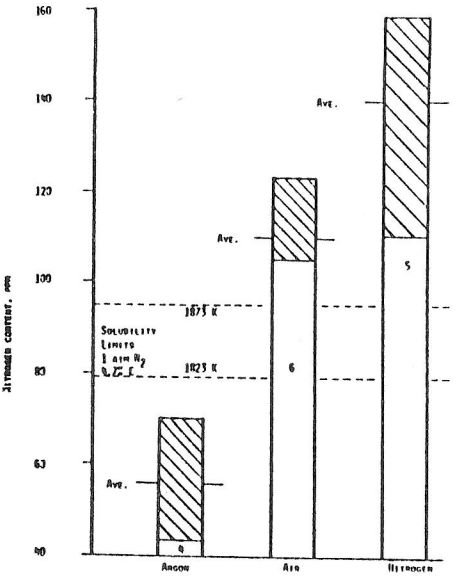

Fig. 3 Final nitrogen contents of carbon saturated iron melts exposed to argon, air and nitrogen arcs

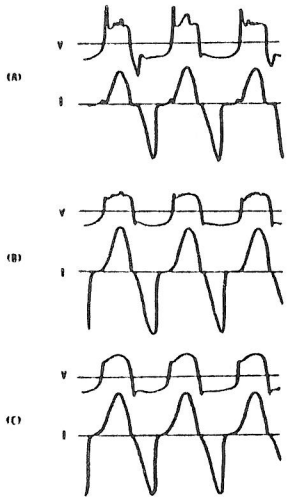

Fig. 2 Oscillograms of voltage (above) and current (below) for arcs in (a) air and with (b) nitrogen and (c) argon injection.

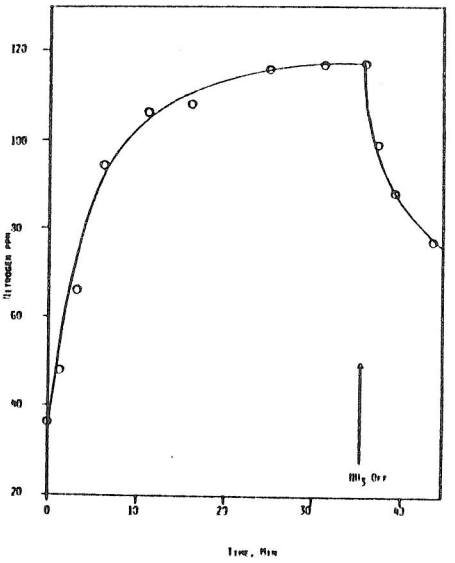

Fig. 4 Nitrogen absorption by a carbon saturated melt from an ammonia jet.