THE EFFECT OF PERCENTAGE OF NITROGEN IN PLASMA GAS ON NITROGEN SOLUTION FROM AN ARC PLASMA INTO LIQUID IRON

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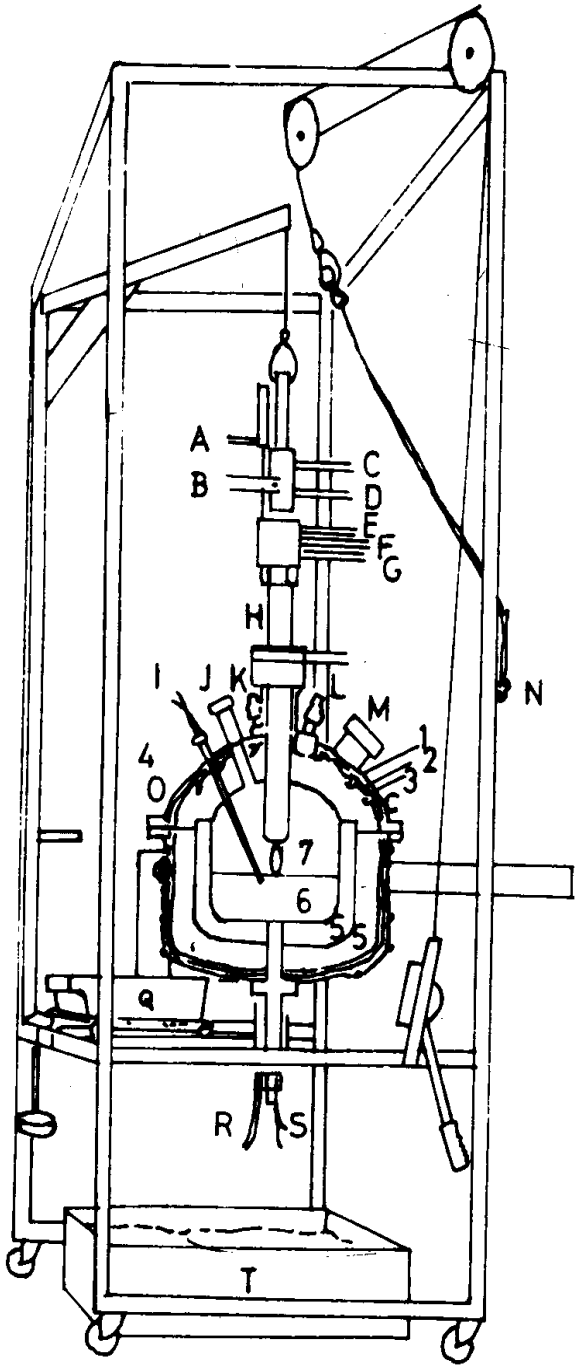
ABSTRACT
The effect of percentage of nitrogen in plasma gas on nitrogen solution from an arc plasma into liquid iron has been investigated by melting iron in an atmosphere of nitrogen and argon using an arc plasma. Results show that both the rate of nitrogen absorption and the steady-state (plateau) solubility are increased as the percentage of nitrogen in the plasma gas increased from 2% to 35%. Both effects are seen to become less pronounced as the percentage nitrogen *in* the plasma gas approaches 35%. Increase in nitrogen percent in the plasma gas results *in* increased content of dissociated nitrogen and molecular nitrogen possessing excess vibrational energy and therefore the increased solution of nitrogen in the liquid *iron.* It would appear that above 35% nitrogen in the plasma gas, frequency of collisions of species *in* the plasma gas create conditions for recombinations of species into molecular nitrogen, thus decreasing the effect of percent nitrogen *in* plasma gas on nitrogen absorption and plateau solubility.

1. INTRODUCTION

The importance of absorption of nitrogen by iron and its alloys during melting and refining operations has been recognized for a long time. The last two decades have seen intensive investigations on the nitrogen absorption by liquid iron and its alloys. It is now widely accepted that nitrogen, under pressure of one atmosphere, behaves as a soluble gas and obeys Sievert's law [1]. However under the conditions of arc plasma, as in welding and plasma-arc remelting, it has also been established that nitrogen solubility in liquid iron is much higher than would be expected from Sievert's square root relationship [2-6]. This enhanced solubility has been attributed to the solution of atomic nitrogen in the plasma impingement area and desorpti0n of molecular nitrogen outside the plasma impingement area [4]. But the effects of operating variable of nitrogen gas in the plasma, on rate of nitrogen absorption and steady-state solubility have not been studied for large melts. Previous studies had been with charges oup to 300 gms. In this study charges varied from 4000gms to 7000gms.

2. APPARATUS

The experimental apparatus [7] consists of four major parts - the plasma torch, the water-cooled refractory-lined furnace, the plasma gas supply system, the power supply. The torch, which has a power rating of 30kva, consists of a brass and copper, water-cooled anode shell and a tungsten-tipped brass and copper, water- cooled central cathode. The cathode is mounted in insulated sleeve and can be moved relative to the anode to change the annular aperture from which the arc issues. An air cylinder and return spring serve to move the cathode and short it against the anode shell to produce a pilot arc which transfers to the charge which then acts as a grounded anode. The pilot arc current is limited by a dropping resistor to ground. The pilot arc current is limited by a dropping resistor to ground. The torch and furnace assembly are shown in Figure 1. The furnace, is of 10,000g. capacity and consists of a water-cooled stell shell and a separate, water-cooled steel roof containing valued ports for sampling, an immersion thermocouple port, and a glass inspection port 6.25cm (2.5") in diameter. A tap-hole in the crucible also serves as the outlet for the plasma gas. The refractory lining of the furnace is in four parts. The roof and crucible area are first packed



1 TOP LID
2 STEEL
3 FIBERFRAX
4 NAIL
5 RECASTABLE ALUMINA
6 CHARGE
7 PLASMA

A ACTUATING GAS
B POWER CABLE
C COOLING WATER
D COOLING WATER
E GAS
F COOLING WATER
G COOLING WATER
H TORCH
I THERMOCOUPLE
J OPTICAL PYROMETER PORT
K SAMPLING PORT
L SAMPLING PORT
M VIEW PORT
N LIFTING CABLES
O REACTION CHAMBER
P POURING PORT
Q MOLD
R POWER CABLE
S BOTTOM ELECTRODE THERMOCOUPLE
T SAND VESSEL

Fig 1 melting apparatus with sectioned view of furnace

with Fiberfrax 0.625cm (0.25") ±in thickness. The remainder of the roof consists of slipcast alumina; the crucible is also alumina, slipcast in a wooden form and fired at 1200 C. The space between crucible and lining is packed with unfired alumina. The bottom electrode is the same material as the charge (Armco iron) and is inserted into position in the crucible through. a swagelock fitting.

There are three separate water cooling circuits on the furnace one for the roof area, one for the body and one for the bottom electrode. The torch cooling water is on a separate system and contains a flow switch to shut the power off in case of water failure. The gas supply to the plasma torch can be adjusted to mix argon with hydrogen or nitrogen. The flow is monitored by two Rotameters, one for the argon supply, the other for the nitrogen or hydrogen. A pressure switch on the gas line insures shutdown of the power in case of gas line failure. Switching from pure argon to various chosen combinations of argon and nitrogen is accomplished through electrically operated solenoid valves. The gas mixture is deoxidized by a copper furnace before passing to the torch. The electrical circuit may be broken by a remotely located switch (the kill switch) in case of serious failure of the torch leading, for example, to introduction of water into the molten metal.

The furnace is mounted on trunnions and be tilted for pouring. The cast iron mold which is used to receive the metal after an experiment is mounted on a travelling table which is automatically positioned under the pouring spout by a linkage to the furnace tilting mechanism.

In operation the plasma torch is supported by a counter-weight so that it cannot fall into the molten metal in event of a failure of the seal. The furnace roof is bolted, through flanges, to the body using a silicone seal to insure gas tightness. The roof can be raised by a hoist for charging and inspection.

3. EXPERIMENTAL PROCEDURE

To start a run, the furnace roof is raised and the crucible charged with about 7kg of pre-cleaned Armco iron sheets. The roof is then lowered and bolted down the torch inserted and adjusted so that it is approximately one inch from the solid charge, and the cooling water and argon gas to the torch turned on. The pilot arc is struck, the plasma transferred to the charge and the torch is then raised to an appropriate height for meltdown. Meltdown takes approximately 45 minutes and, during this time, hydrogen is added to argon to prevent oxidation of the charge. The power supply is controlled manually.

A typical run consists of melting down under argon and switching to the appropriate nitrogen-argon mixture. Sampling begins immediately and samples are taken at one minute intervals gradually lengthening to about five minutes for a period of about 45 minutes. At this point the plateau solubility has been reached. After switching back to pure argon gas, samples are taken during desorption. During each run the area of the melt surface covered by slag is visually estimated.

3.1 Chemical Analysis for Nitrogen Content

Analysis of the samples for nitrogen is done with a Leco inert gas fusion apparatus. The apparatus used a small graphite crucible heated by induction. For an analysis the empty crucible is first heated in helium for degassing. Then a sample is dropped into the crucible and heated again in a helium atmosphere. Evolved gases are entrained in the helium carrier gas. The evolved gas is mainly nitrogen but there may be small amount of carbon dioxide and hydrogen. These are oxidized in a copper oxide train and the carbon dioxide and water removed in a separator containing anhydrone, ascarite and activated charcoal. Ascarite absorbs carbon dioxide, anhydrone absorbs water and activated charcoal takes out any tramp gases. We now have a nitrogen and helium mixture which is led through a previously balanced thermal conductivity cell with two thermistors. Through one thermistor passes pure helium and through the other thermistor the nitrogen-helium mixture which results in an unbalanced cell due to the amount of nitrogen in the sample. An electronic circuit incorporated in the apparatus gives a digital readout, in ppm, of the nitrogen in the sample.

4. RESULT

4.1 Percentage of Nitrogen in the Plasma Gas.

The effect of PN_2 in the plasma gas was studied by varying the nitrogen content of the plasma gas from 2% to 50%. The effect of varying the percentage of nitrogen in the plasma gas is shown in Figure 2. Both the rate of nitrogen absorbption and the steady-state solubility are increased as the percentage of nitrogen in the plasma gas is increased from 2% to 35%. Both effects are seen to become less pronounced as the percent nitrogen in the plasma gas approaches 35%. The finding is not in agreement with the findings of Grigorenko, Dvoryakin and Torkhov [6] who, in their experiment, varied PN_2 in the plasma gas from 25% to 100%. They found the rate of absorption to decrease and the steady-state solubility to increase as PN_2 was increased.

In Figure 3, the steady-state solubilities for different nitroger contents of the plasma gas are plotted as a function of PN_2 for three differed runs. These same results are also plotted in Figure 4 as a function of PN2. Although the number of points for individual runs is small, the form of the plots in figure 3 is essentially that observed by Lakomsky and Torkov [3], and Grigorenko et. al [6] and Figure 4 is an equally good fit. Both suggest the existence of a plateau solubility at sufficiently high nitrogen pressures in the plasma gas. However in the present study, the initial slope of the lines varies considerably from one run to another and the plateau solubility is higher the higher the slope.

5. DISCUSSION

The effect of percentage of nitrogen gas in the plasma gas, on the absorption

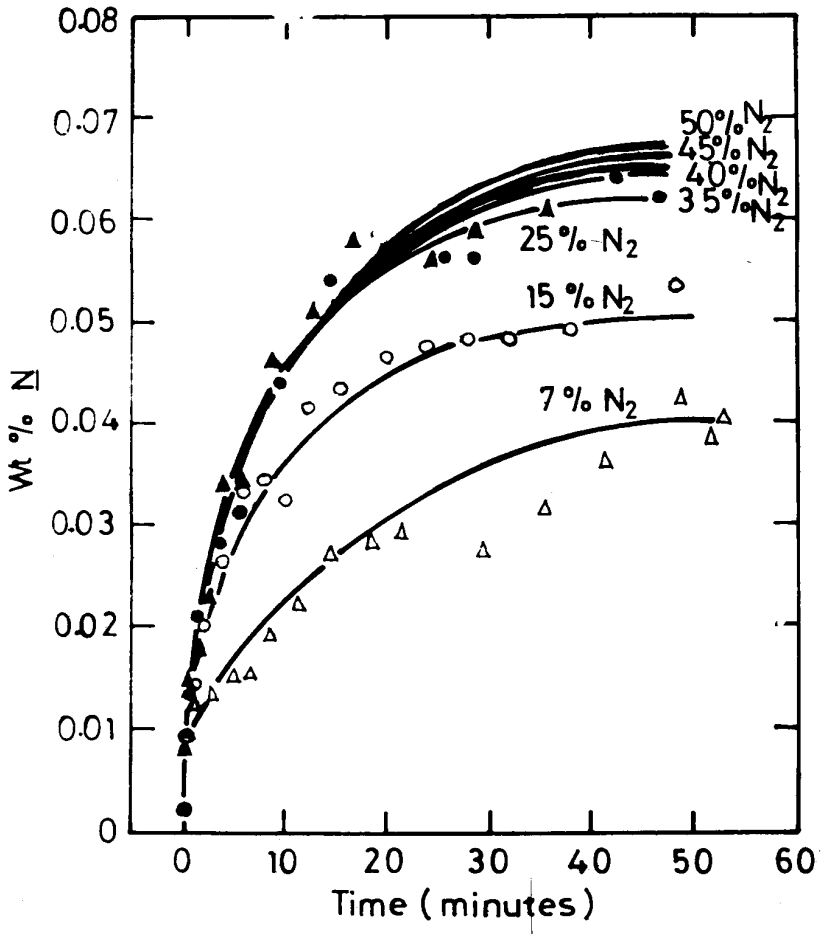


Figure 2. Effect of partial pressure of nitrogen in plasma gas on steady state solubility and rate of solution in liquid iron

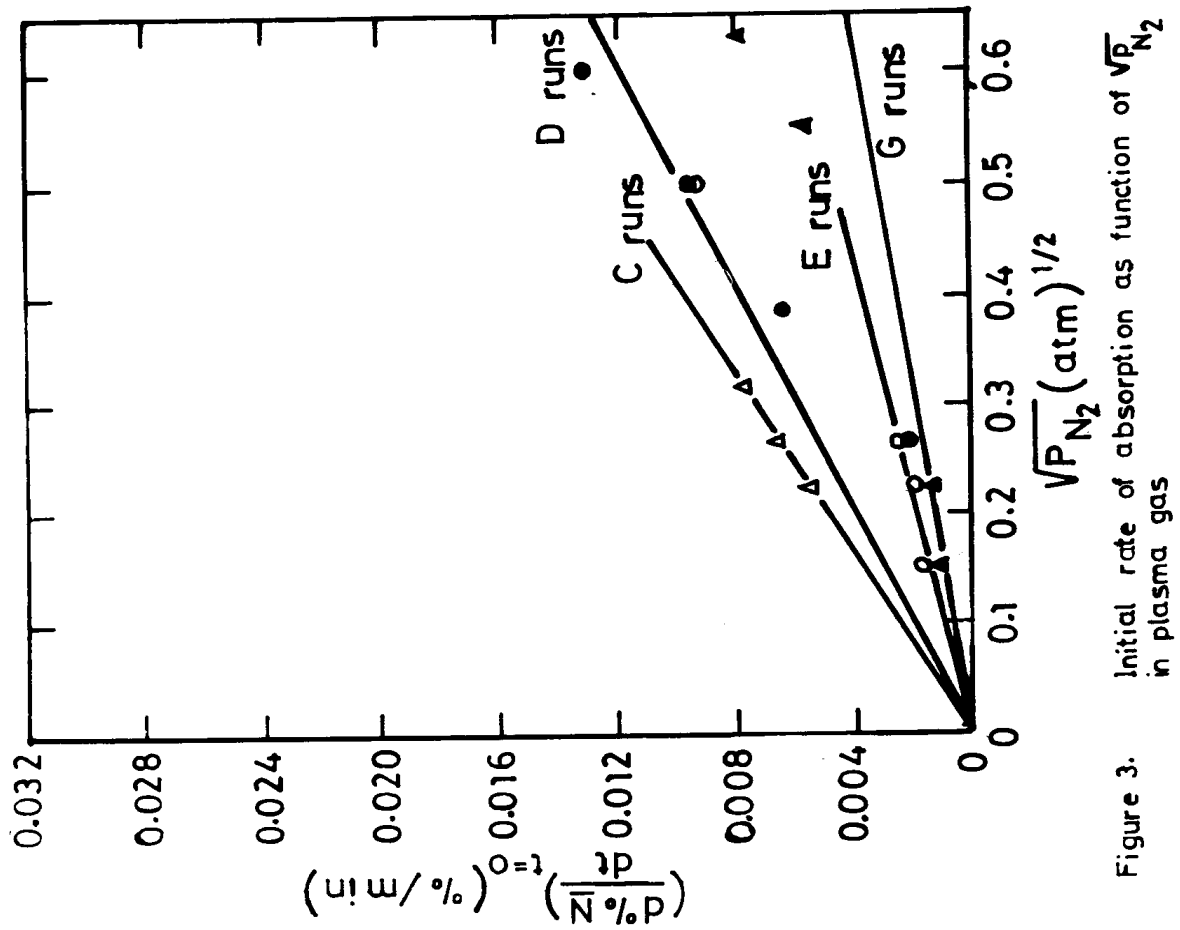


Figure 3. Initial rate of absorption as function of $\sqrt{P_{N_2}}$ in plasma gas

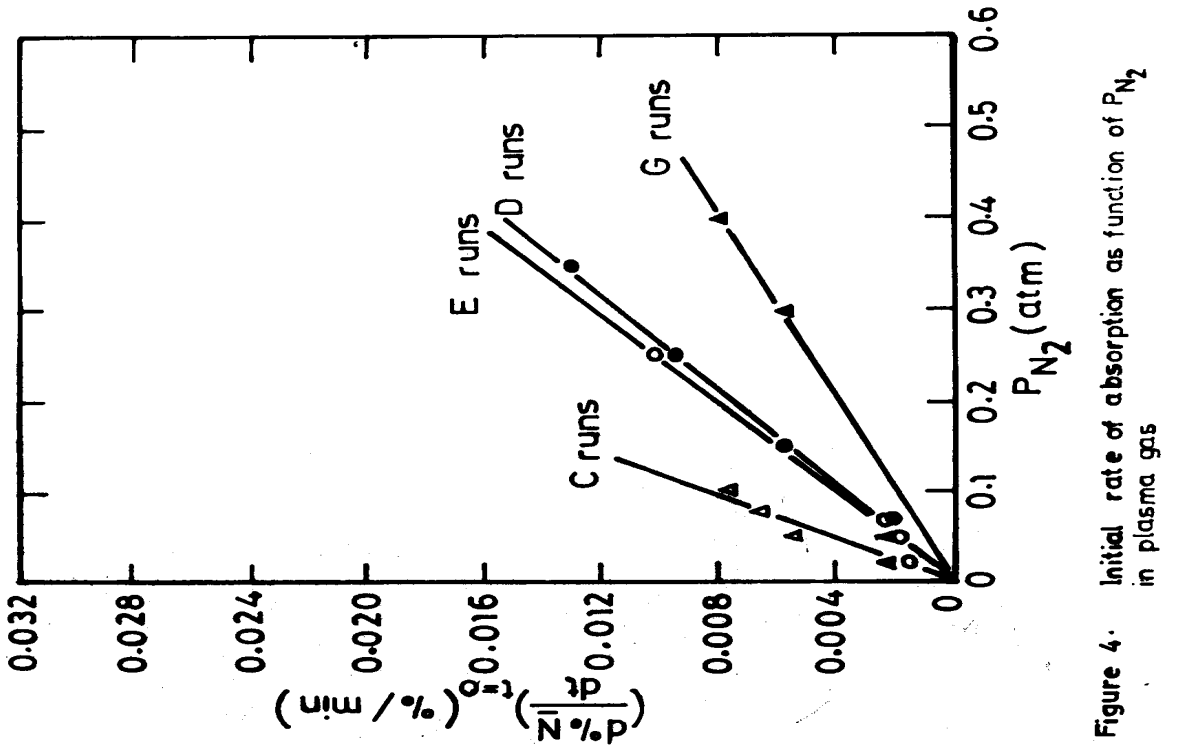


Figure 4. Initial rate of absorption as function of P_{N_2} in plasma gas

rate and the steady-state solubility lead to the hypothesis that the overall process involves absorption in the plasma impingement area and desorption from the surrounding area of the melt surface [8]. Desorption, which starts almost immediately after absorption in most runs, is much slower initially and increases in intensity to a maximum at the time the steady-state solubility is reached. In the absence of desorption, the fast solution in the plasma impingement zone would lead to very high dissolved nitrogen contents. But with desorption occuring, there comes a time when the rate of absorption of nitrogen by the melt within the impingement area equals the rate of desorption from the area outside. This establishes a dynamic equilibrium, shown by a plateau or steady-state solubility. It is well known that diatomic gases, dissolve in metals atomically and for diatomic gasses, such as nitrogen, the overall solution process is:

N_2 (g) = 2N (1)

$\%\underline{N} = K P_{N2}$ (2)

At around 160^0C the solubility of nitrogen in liquid iron from molecular nitrogen is 0.045% for nitrogen pressure of one atmosphere. Thus in equation 2, K = .045. The temperature coefficient of nitrogen solubility$_{-6}$ in liquid iron at 1600^0c - 800^0cis 8 x 1 % per °c as reported by Gomersall et al [9] and Pelhke and Elliot [1]. On the basis of the results obtained for molecular nitrogen, the equilibrium value of nitrogen solubility obtained in run C-5 would have been

$\%\underline{N}$ = 0.45 0.05 = 0.01%

for a nitrogen partial pressure of 0.05 atmosphere. Instead, the value obtained for plasma melting is seven times as high as the solubility from induction melting. This enhanced solubility has been reported in other plasma arc remelting studies [3,5,6] and in arc welding [2] for melts with temperatures ranging from 1600^0C to 2000^0C as shown in Table 1.

The reason for the enhanced solubility would seem to be in the composition of the nitrogen gas in the torch nozzle area, the nitrogen gas plasma becomes appreciably dissociated [10] (see Table 2 into atomic nitrogen and ions [11] and electrons which maintain current flow between the cathode and anode. Lower down the plasma column towards the cooler melt surface, some nitrogen atoms recombine to produce nitrogen molecules. However, as recombination progresses, there now exist ions, atoms and molecules of nitrogen and ions, and atoms of argon. There could be three-body collisions [12] involving these species. Given the temperature gradient in the boundary layer, the vibrational energy-translational energy exchange may be incomplete making it possible for some nitrogen molecules produced during recombination to possess excess vibrational energy [13). In the plasma impingement area, the gas boundary layer above the melt surface is therefore likely to contain ions, nitrogen atoms, nitrogen molecules. However, the presence in appreciatible amount of nitrogen molecules possessing excess vibrational energy in the plasma impingement area is very doubtful in view of the works of Takeda and Nakamura (14) and Byron [15]. According to their reported work (14) the time for gases to pass the boundary layer in nitrogen-argon plasma jets impinging on liquid iron surface is about one millisecond while the relaxation time for recombination reaction of nitrogen atoms in the plasma impingement area is found (15) to be 50 - 100 miliseconds. Furthermore the frequency of collion of nitrogen atoms in the gas boundary layer above the liquid iron is very low and gets even lower for lower nitrogen partial pressure in the plasma gas. On would therefore expect that in the plasma impingement area, time will be too short for recombination reaction to start for nitrogen molecules with excess vibrational energy to be present and contribute to the enhanced solubilities observed. The enhanced solubility obtained with the plasma arc would therefore suggest that absorption under the arc involves the reaction of iron with dissociated nitrogen in the research on tungsten-argon arc melting, Blake and Jordan (16) have attributed the increased solubility they observed to reaction of iron with dissociated nitrogen. The same conclusion has been reached by Uda and Wada (17), and Uda and Ohno [18]. O'Brien and Jordan [19], who have observed high nitrogen conents of 0.07% $\underline{N}$ in arc welding with only 10% nitrogen in their N_2 - $C0_2$ welding gas, also attribute the high nitrogen absorption to the reaction of the weld pool with dissociated nitrogen.

Table1. Nitrogen Solubilities Obtained from Plasma Melting and Induction Melting

Study	Temp(^{o}C)	Method	%N	%O	%N_2 used
This study	1760	Plasma Melting	0.085	129	7%
	1680		0.069	0.084	5%
	1600		0.094	0.087	10%
Pehlke and Elliot [1]	1606	Induction Melting	0.045	0.074	100%
Commersall et al [12]	1600^{0}C	Induction	0.0436	0.075	100%
	8	Melting			
Uda and Wada [10]	1800^{0}C	Plasma Melting	0.065	-	6%
Lakomsky et al [3]	1600	Plasma Melting	0.070	-	25%

Table 2. Degree of Dissociation for N_2[10] at a total pressure of 1 atm for various temperatures for nitrogen dissociation energy of 9.76 electron volts.

Temperature, OK	Degree of Dissociation, %
5000	1.63
7000	43.39
10000	99.0

Lakcmsky and Torknov [3] have suggested that enhanced nitrogen solubility be attributed to the reaction of iron with nitrogen molecules possessing excess vibrational energy.

The rate of the surface reaction of nitrogen atoms may be faster than that of nitrogen molecules possessing excess vibrational energy which in turn is expected to be faster than that or normal molecular nitrogen. These processes are considered as follows [7]:

N (g) = N (ads) (3a)

N (ads) $\underline{N}$ (3b)

$\boldsymbol{N_2^*\ (g) = N_2^*\ (ads)}$ (4a)

$\boldsymbol{N_2^*\ (ads)\ 0\ 2N\ (ads)}$ (4b)

2N (ads) 0 $2\underline{N}$ (4c)

N_2 (g) 0 N_2 (ads) (5a)

N_2 (ads) 0 2N (ads) (5b)

2N (ads) = $2\underline{N}$ (5c)

According to equation 3, nitrogen atoms adsorb on the melt surface and then dissolve in the liquid. According to equations 4 and 5 however, nitrogen molecules possessing excess vibrational energy or normal molecules adsorb first, then there is the surface reaction of dissociation before dissolution in the liquid. The surface reaction for both the

normal molecular nitrogen and nitrogen molecules possessing excess vibrational energy involves two adsorbed species and so steps 4b and 5b are expected to be slow [20]. The surface reaction for nitrogen molecules possessing excess vibrational energy should be faster than that for normal nitrogen molecules as they are in higher energy state.

When higher percentages of nitrogen gas are introduced into the plasma arc, and all other variables are held constant, the plasma gas would be expected to contain a larger fraction of dissociated nitrogen and molecular nitrogen possessing excess vibrational energy. This would give rise to higher nitrogen absorption rates, as actually observed. But as the nitrogen percent in the plasma gas is increased the plasma gas contains increasing amount of species - atomic nitrogen, molecular nitrogen molecular nitrogen possessing excess vibrational energy and of course ionized nitrogen atoms. It would then appear that as the percent nitrogen gets to 35% and above the number of species present in the plasma gets to a level when appreciable recombination to molecular nitrogen occurs. The recombination seeds to reduce the amount of species to the level prevalent when percent nitrogen is 35%. This reasoning is borne out by Fig.2. All the results obtained using nitrogen percent of 2% - 50% in plasma gas have shown the pattern in fig. 2.

6 CONCLUSION

The effects of experimental variable on nitrogen solution from an arc-plasma into liquid iron have been studied. Iron was melted under an atmosphere of nitrogen and argon using arc-plasma. Samples were taken at intervals and quenched in water, measuring the nitrogen content of the solidified samples by chemical analysis. The experimental variable changed was percentage of nitrogen in plasma gas. Results showed that both the steady-state solubility and rate of nitrogen absorption are seen increase with higher percentage of nitrogen in plasma gas, up to 35% nitrogen the plasma gas. Thereafter the effect of higher nitrogen percent becomes less pronounced on the absorption rate and plateau solubility. It would appear that these nitrogen percentages above 35% appreciable recombination of atomic nitrogen into molecular nitrogen take place. The recombination seems to reduce the concentration of species in the plasma gas to the levels when nitrogen percent is around 35%.

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