

BACKGROUND**1.1 INTRODUCTION**

The presence of small amounts of nitrogen in alloy steels has a beneficial or a deleterious influence on the properties of the material, depending on its concentration, the thermal processing of the alloy, and the presence of alloying elements. In mild steel, low alloy steel and ferritic stainless steel, nitrogen is generally considered an undesirable impurity, causing porosity and the formation of brittle nitrides¹. In austenitic and duplex austenitic-ferritic stainless steels, however, nitrogen is often a valued alloying element. In part, this has stemmed from the desire to use nitrogen as a substitute for nickel, thereby reducing alloying element costs. In addition to the fact that the consumption of an expensive strategic metal is reduced, nitrogen is considered to be as much as thirty times as powerful as nickel as an austenite-former^{2,3}.

Nitrogen also imparts a number of other beneficial properties to austenitic and austenitic-ferritic duplex stainless steels. It is an excellent solid solution strengthening element in stainless steel, increasing the yield strength at room temperature and at sub-zero temperatures^{4,5}, with no significant decrease in toughness or ductility^{5,6}. As a result, nitrogen-alloyed austenitic stainless steels offer a unique combination of strength and toughness. Nitrogen is also reported to improve the passivation characteristics of stainless steels. It increases resistance to localised corrosion^{7,8}, and reduces sensitisation effects during welding^{9,10}.

In order to realise the advantages associated with nitrogen alloying, the nitrogen has to be in solution in the metal matrix. Excess nitrogen tends to cause porosity or form brittle nitrides. Iron, mild steel and low alloy steel have low solubility limits for nitrogen (the equilibrium solubility of nitrogen in iron at its melting point is only approximately 0,044 per cent (by mass) at 1 atmosphere pressure¹¹). It is therefore important to limit nitrogen absorption in these steels. This poses a particular problem during welding, where nitrogen from the surrounding atmosphere can be absorbed by the weld metal in spite of the precautions normally taken to shield the arc and the weld pool from the surroundings by slag and/or shielding gas. Without the benefits of effective shielding, nitrogen contents as high as 0,2 per cent have been reported in steel welds after arc welding¹¹. These concentration levels are far greater than those in the base and filler metals and indicate the importance of the dissolution of nitrogen into the metal from the arc atmosphere during welding.

Austenitic stainless steels can accommodate significantly higher levels of nitrogen in solution. In nitrogen-alloyed austenitic stainless steels, the most important problem during welding is often not nitrogen absorption, but nitrogen desorption to the arc atmosphere, resulting in lower nitrogen levels in the weld metal. A decrease in nitrogen concentration in the region of the weld has a detrimental effect on the mechanical properties and corrosion resistance of the joint.

In order to control nitrogen absorption and evolution from the molten pool during welding, a fundamental knowledge of the absorption and desorption mechanisms is essential. Over the past years a number of studies has dealt with arc melting experiments under static conditions (stationary arc), others concerned experiments under more realistic welding conditions (travelling arc). The results of these studies show that nitrogen absorption and desorption are complex phenomena, influenced by a large number of factors. An important finding is that the amount of nitrogen absorbed in arc melts is generally significantly higher than the amount absorbed in non-arc melts under equilibrium conditions. Furthermore, it appears that the nitrogen level of the weld metal depends on the welding parameters and also on the presence of surface-active elements, notably oxygen and sulphur. Each of these factors are considered in more detail below.

1.2 NITROGEN DISSOLUTION IN LIQUID IRON UNDER EQUILIBRIUM CONDITIONS

The solubility of nitrogen in liquid iron under equilibrium conditions is primarily determined by the nitrogen partial pressure above the melt, the melt temperature and the presence of alloying elements. These three factors are considered in the following sections.

1.2.1 The influence of nitrogen partial pressure on the solubility of nitrogen in liquid iron under equilibrium conditions

Since nitrogen gas generally assumes the form of a diatomic molecule (N_2), the solution of nitrogen in liquid iron can be written as:



where: \underline{N} (wt%) refers to nitrogen in solution in the liquid metal (percentage by mass), and N_2 (g) refers to diatomic nitrogen gas.

At constant temperature, the equilibrium solubility of nitrogen in liquid iron is governed by Sievert's law, which states that the nitrogen concentration in liquid iron is proportional to the square root of the partial pressure of diatomic nitrogen above the melt, as demonstrated by equation (1.2)¹²:

$$\underline{N}_{eq} (wt\%) = K_{eq} \sqrt{P_{N_2}} = \sqrt{P_{N_2}} \cdot \exp\left(-\frac{\Delta G_1^0}{RT}\right) \quad \dots(1.2)$$

where: \underline{N}_{eq} (wt%) is the nitrogen concentration in liquid iron at equilibrium with diatomic nitrogen,

K_{eq} is the equilibrium constant for reaction (1.1),

P_{N_2} is the partial pressure of N_2 in the atmosphere (atm),

ΔG_1^0 is the standard free energy for reaction (1.1),

R is the gas constant, and

T is the temperature of the liquid iron melt (K).

Sievert's law stipulates that a linear relationship exists between the solubility of nitrogen in liquid iron and the square root of the partial pressure of nitrogen in contact with the liquid metal, and implies that the nitrogen solubility limit in iron alloys can be raised by increasing the partial pressure of the diatomic gas

above the melt. This approach has been proposed for reducing nitrogen losses and for avoiding nitrogen-induced porosity during the welding of nitrogen-containing austenitic stainless steels. If Sievert's law applies under normal arc welding conditions, the addition of nitrogen to the shielding gas during welding should increase the nitrogen solubility in the weld pool and limit nitrogen losses. The validity of this approach is considered in §1.3.

1.2.2 The influence of temperature on the solubility of nitrogen in iron under equilibrium conditions

The influence of temperature on the nitrogen solubility limit in pure iron is illustrated in Figure 1.1, which indicates that the solubility of nitrogen in iron decreases slightly with decreasing temperature in the molten state, and decreases significantly on solidification. Mundra and DebRoy¹³ calculated the equilibrium nitrogen concentration in austenite as a function of partial pressure and temperature, based on Sievert's law estimations. Their results, shown in Figure 1.2, indicate that at a given partial pressure of diatomic nitrogen, the equilibrium nitrogen concentration decreases slightly with increasing temperature. This is consistent with Figure 1.1 for temperatures corresponding to the austenite phase field and suggests that the solubility of diatomic nitrogen in iron is not a strong function of temperature. At a given temperature, the equilibrium concentration increases linearly with the square root of the partial pressure of diatomic nitrogen.

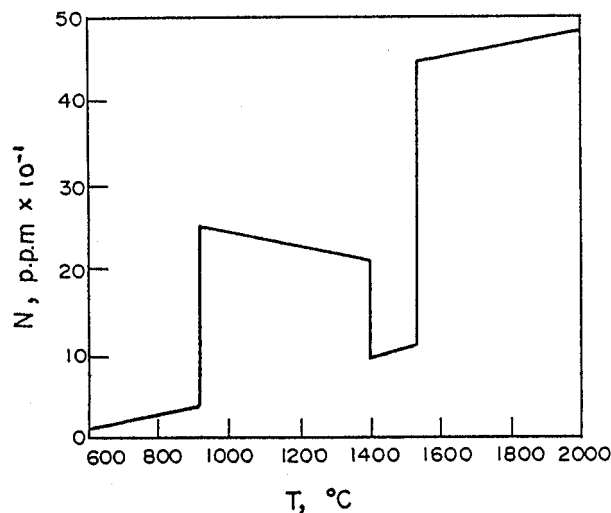


Figure 1.1 The solubility of nitrogen in pure iron¹².

1.2.3 The influence of alloy composition on the solubility of nitrogen in iron under equilibrium conditions

The presence of various alloying elements in iron has a significant influence on the solubility of nitrogen. As shown in Figure 1.3, the majority of the alloying elements commonly found in iron alloys increases the nitrogen solubility¹⁴. In this respect chromium and manganese play particularly important roles in increasing the nitrogen solubility limit in austenitic stainless steels. Nickel, another important alloying element commonly found in austenitic stainless steels, reduces the nitrogen solubility (as do tungsten,

copper, tin, silicon and cobalt). Alloying elements which increase the activity coefficient of nitrogen generally decrease the solubility. Solutes having greater affinity for nitrogen than iron will decrease the activity coefficient and increase the nitrogen solubility. The influence of various alloying elements on the nitrogen solubility in iron alloys was quantified by Wada and Pehlke¹⁵ using the approach described below.

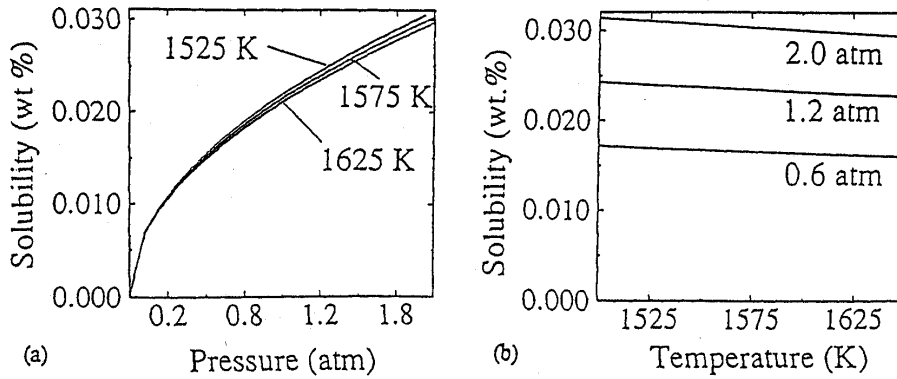


Figure 1.2 Computed equilibrium solubility of nitrogen in austenite exposed to diatomic nitrogen: (a) as a function of partial pressure of diatomic nitrogen at three temperatures, and (b) as a function of temperature at three partial pressures¹³.

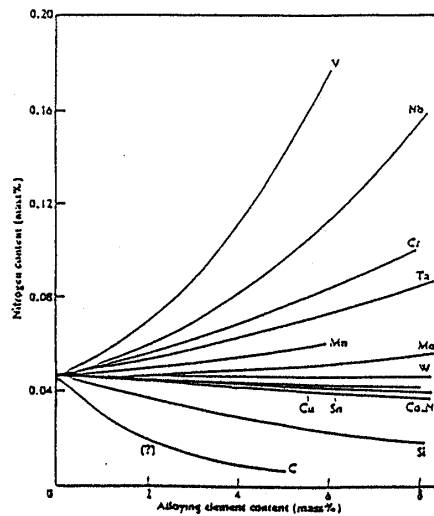


Figure 1.3 The solubility of nitrogen in binary iron alloys under equilibrium conditions at 1600°C and 1 atmosphere nitrogen pressure¹⁴.

The equilibrium constant, K_{eq} , in equation (1.2) is described by the following relationship:

$$K_{eq} = a_N \sqrt{P_{N_2}} = f_N (\%N_{eq}) \sqrt{P_{N_2}} \quad \dots(1.3)$$

where: a_N is the Henrian activity of nitrogen in the liquid alloy, and f_N is the activity coefficient of nitrogen in the liquid alloy.

Based on equation (1.3) for the equilibrium constant, Wada and Pehlke¹⁵ developed an equation that describes the equilibrium solubility of nitrogen in liquid Fe-Cr-Ni alloys containing manganese and molybdenum as a function of the activity coefficient of nitrogen, f_N , temperature, T , and the alloying element content. This relationship is shown in equation (1.4). The value of the activity coefficient of nitrogen, f_N , as a function of the alloying element content can be calculated using equation (1.5). In addition to chromium, nickel, molybdenum and manganese, the influence of a number of other elements (C, Si, P, S, Al, Ti, V, W and O) on the activity coefficient is also included in equation (1.5)¹⁴.

$$\log(N_{eq}) = -\frac{247}{T} - 1,22 - \left(\frac{4780}{T} - 1,51\right) \log f_{N,1873} - \left(\frac{1760}{T} - 0,91\right) (\log f_{N,1873})^2 \quad \dots(1.4)$$

$$\begin{aligned} \log f_N = \{ & -164[\%Cr] + 8,33[\%Ni] - 33,2[\%Mo] - 134[\%Mn] + 1,68[\%Cr]^2 - 1,83[\%Ni]^2 \\ & - 2,78[\%Mo]^2 + 8,82[\%Mn]^2 + (1,6[\%Ni] + 1,2[\%Mo] + 2,16[\%Mn]).[\%Cr] + \\ & (-0,26[\%Mo] + 0,09[\%Mn]).[\%Ni]\}/T + \{0,0415[\%Cr] + 0,0019[\%Ni] + \\ & 0,0064[\%Mo] + 0,035[\%Mn] - 0,0006[\%Cr]^2 + 0,001[\%Ni]^2 + 0,0013[\%Mo]^2 - \\ & 0,0056[\%Mn]^2 + (-0,0009[\%Ni] - 0,0005[\%Mo] - 0,0005[\%Mn]).[\%Cr] + \\ & (0,0003[\%Mo] + 0,0007[\%Mn]).[\%Ni]\} + 0,13[\%C] + 0,06[\%Si] + 0,046[\%P] \\ & + 0,007[\%S] + 0,01[\%Al] - 0,9[\%Ti] - 0,1[\%V] - 0,003[\%W] - 0,12[\%O] \end{aligned} \quad \dots(1.5)$$

where: $f_{N,1873}$ is the activity coefficient f_N at 1873 K, and
 $[\%M]$ is the alloying element content in wt%.

Equations (1.4) and (1.5) can be used to calculate the equilibrium nitrogen solubility in molten iron-based alloys at any temperature. In order to determine whether Sievert's law and Wada and Pehlke's approach are appropriate for calculating the nitrogen content of welds, the next section describes some of the available literature on the influence of welding on the nitrogen solubility limit in iron alloys.

1.3 NITROGEN ABSORPTION AND DESORPTION DURING ARC MELTING AND WELDING

During the majority of fusion welding processes, including arc, laser and electron beam welding, a plasma phase resides above the weld pool. This plasma is composed of ionised gas consisting of electrons, ions, excited atoms and molecules, and can collectively be both electrically neutral and conductive¹⁶. It has become clear in recent years that the behaviour of a plasma-metal system is significantly different from that of the corresponding gas-metal system¹⁷. When a diatomic gas such as nitrogen is transformed into a plasma phase, it may dissociate, ionise, or become electrically or vibrationally excited. Each of these individual species has a different equilibrium with the liquid weld metal. As a result, Sievert's law cannot be applied to describe the dissolution of diatomic gas species into liquid metal in the presence of a plasma.

In a paper published in 1969, Lakomskii and Torkhov¹⁸ described the results of arc melting experiments performed on iron samples in a number of argon-nitrogen shielding gas atmospheres. The authors reported that the nitrogen contents of iron samples exposed to low nitrogen partial pressures were

proportional to the square root of the nitrogen partial pressure in the plasma, as shown in Figure 1.4, however, the nitrogen concentrations measured were an order of magnitude higher than the concentrations predicted from equilibrium Sievert's law calculations. At higher nitrogen partial pressures (more than approximately 0,005 MPa), the nitrogen content of the weld metal reached a saturation level, and remained constant regardless of P_{N_2} . Kuwana and Kokawa¹⁹ studied the addition of nitrogen to argon shielding gas during the gas tungsten arc welding of pure iron and, as shown in Figure 1.5, obtained results similar to those reported by Lakomskii and Torkhov. Kuwana and Kokawa reported that nitrogen absorption in iron weld metal does not obey Sievert's law and is dependent on the welding conditions. As shown in Figure 1.5, the weld metal nitrogen content increases with an increase in P_{N_2} at low partial pressures, exceeding the equilibrium concentrations predicted by Sievert's law.

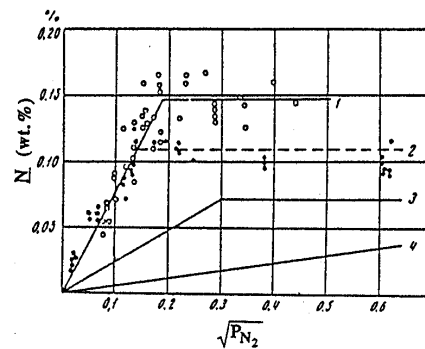


Figure 1.4 Isotherms of the reaction between nitrogen and liquid iron: (1) heating by an indirect-action plasmatron, (2) heating by a direct-action plasmatron, (3) heating by a free arc, and (4) induction heating¹⁸.

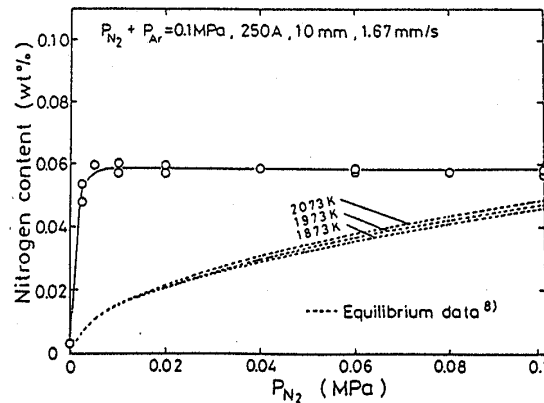
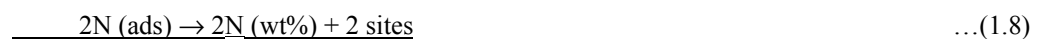


Figure 1.5 The relationship between the weld metal nitrogen content and the nitrogen partial pressure (P_{N_2}) in nitrogen-argon shielding gas mixtures during gas tungsten arc welding, compared to the equilibrium nitrogen solubilities at 1873 K, 1973 K and 2073 K¹⁹.

Blake and Jordan²⁰ studied nitrogen absorption and desorption in iron during arc melting in argon and argon-nitrogen atmospheres as a function of time and welding variables. They reported that nitrogen is absorbed from argon-nitrogen shielding gas atmospheres, with the rate of absorption increasing with current and nitrogen partial pressure. After a certain time a saturation value is reached, characterised by

bubble formation in the molten metal. The final nitrogen concentrations in the iron samples were well above the values expected from the reaction of molecular nitrogen with molten iron. The molten iron appears to absorb nitrogen rapidly from the arc until it reaches saturation, followed by nucleation of molecular nitrogen bubbles in the melt. At this point a dynamic equilibrium is created whereby the rate of absorption at the melt surface is balanced by bubble formation in the melt. Blake and Jordan found that the steady-state nitrogen content is in excess of that required to provide an internal pressure of one atmosphere at the assumed temperature of the molten iron button, and concluded that some degree of supersaturation occurs.

Based on the linear relationship between the nitrogen solubility and the square root of the nitrogen partial pressure observed by Lakomskii and Torkhov¹⁸ at low partial pressures (as shown in Figure 1.4), these authors concluded that the weld metal reacts with molecular nitrogen, and attributed the enhanced solubility of nitrogen at low partial pressures to the presence of excited nitrogen molecules, N_2^* , in the arc plasma. The proposed nitrogen absorption reactions are shown in equations (1.6) to (1.9). The excited nitrogen molecules possess high internal energy acquired through the interaction between electrons and neutral particles in the arc. The authors reasoned that the retention of sufficient vibrational energy in the nitrogen molecules plays a significant role in breaking the interatomic bond at the moment when nitrogen adsorbs onto the surface of the liquid iron before going into solution. The excitation energy lowers the energy required for dissociation of the nitrogen molecules on the metal surface before adsorption, thereby increasing the equilibrium constant, K^* , and the equilibrium concentration of nitrogen in solution. As shown in Figure 1.4, the nitrogen concentration in the weld metal becomes independent of the nitrogen partial pressure in the arc atmosphere at higher nitrogen partial pressures, reaching a constant steady-state concentration. In this region the metal is oversaturated with nitrogen, so the latter escapes from the metal in the form of gas bubbles.



where: N_2^* represents nitrogen molecules with excess vibrational energy provided by the electric field, and

the postscript (ads) refers to an adsorbed species on the metal surface.

In response to Lakomskii and Torkhov's conclusions, Katz and King²¹ argued that once an excited diatomic molecule is adsorbed onto a metal surface, its vibration is significantly dampened. Therefore, it cannot play a significant role in enhancing solubility. These authors postulated that the increased solubility in the presence of a plasma results from the existence of monatomic nitrogen, N , in the arc. The nitrogen atoms form as the gas is heated in the arc plasma and individual molecules acquire more energy. At low temperatures, this energy is mainly translational, i.e. the energy associated with the velocity of motion. At higher temperatures diatomic molecules such as nitrogen absorb energy firstly by rotation and secondly by vibration - an in-and-out movement of the two atoms relative to each other.

When the vibrational energy reaches a sufficiently high level, it may rupture the valence bonds holding the two atoms together, causing them to dissociate into the monatomic state¹⁶.

Den Ouden and Griebing²² studied the absorption of nitrogen in pure iron samples during arc melting in controlled gas atmospheres. They measured the amount of nitrogen in the samples as a function of various experimental conditions, including time, gas composition, arc current, and arc length. As shown in Figure 1.6, their experimental results confirm that the nitrogen concentrations in the metal samples are considerably higher than expected from equilibrium considerations. Figure 1.6 also shows that the weld metal becomes oversaturated at higher partial pressures, resulting in bubble formation and porosity. Like Katz and King²¹, Den Ouden and Griebing attributed the enhanced solubility of nitrogen to monatomic nitrogen atoms formed in the arc by the dissociation of nitrogen molecules. The degree of dissociation depends on the arc temperature and the nitrogen content of the arc. The individual reactions describing the dissolution process are shown in equations (1.10) to (1.12). The authors proposed that monatomic nitrogen is absorbed by the weld pool directly under the arc and is then desorbed at the weld periphery. The amount of nitrogen leaving the liquid metal will increase with increasing nitrogen concentration, and a steady-state condition is reached when the amount of nitrogen entering the weld pool per unit time equals the amount of nitrogen leaving the weld pool per unit time.

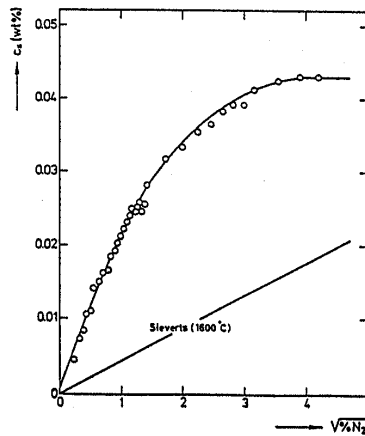


Figure 1.6 Nitrogen concentration in an iron sample as a function of the square root of the nitrogen partial pressure in the shielding gas²².

Bandopadhyay *et al*¹⁷ also attributed the enhanced nitrogen solubility in iron to the existence of neutral atoms (N) in the plasma, and confirmed this hypothesis by analysing isothermal helium-nitrogen plasmas using optical emission spectroscopy methods. They identified neutral atoms (N), excited atoms (N*), excited molecules (N₂*), and ions (N⁻, N⁺ and N₂⁺) in the arc plasma. The authors reasoned that it is extremely improbable for nitrogen ions to contribute to the observed enhanced solubility since the flux of highly mobile electrons to the liquid surface in a plasma is far greater than the flux of heavier ion species.

As a result, an electrically insulating metal surface becomes negatively charged when exposed to a plasma and the adsorption of negatively charged species, such as N^- , is highly improbable. Furthermore, positively charged ions such as N^+ and N_2^+ are attracted towards the metal surface, where they absorb electrons near the surface and are converted to N and N_2 . Excited molecules cannot contribute towards enhanced solubility because they lose their excess vibrational energy when adsorbed onto metal surfaces. Thus, the increased solubility most likely results from the presence of monatomic nitrogen in the plasma.

Gedeon and Eager²³ developed a model for the absorption of hydrogen (also a diatomic gas molecule) in iron weld metal and showed that Sievert's law cannot be applied since the assumption of a one-step absorption process which neglects the effects of dissociation, solute rejection upon solidification and diffusion of hydrogen away from the weld region, is too simplistic to provide realistic values. The authors attributed the enhanced hydrogen concentration in the weld metal to the presence of monatomic hydrogen in the plasma. They suggested a two-step absorption process in which hydrogen dissociates in the high temperature regions of the arc, followed by absorption of both diatomic and monatomic hydrogen into the weld pool at the temperature of the weld pool surface. Their results showed that appropriate hydrogen absorption values can be obtained if the dissociation temperature is approximately 10 to 20 per cent higher than the absorption temperature.

Although the enhanced dissolution process appears to be consistent with the presence of monatomic nitrogen in the arc plasma, a general model is needed to calculate the extent of enhancement for a given condition. In this respect determination of the nature of the plasma and the concentration of various species within the plasma phase is an important first step. Three issues are of special interest in welding: the extent of dissociation of a diatomic gas in the welding environment, the effect of temperature on the species concentration in the weld metal for different gases, and the concentration of dissolved species in the weld pool retained by the weld metal after cooling. The alloying element content of the weld metal, including the prior nitrogen content and the concentration of surface active elements, also plays a significant role. No unified theory for the quantitative understanding of the extent of enhanced dissolution in stainless steels has emerged up to this point.

An investigation into nitrogen dissolution in stainless steel weld metal has to start with an understanding of the solubility of nitrogen in pure iron welds. General rules of behaviour established for iron can then be extended to those for stainless steel weld metal, taking into account the influence of alloying elements as well as the nonequilibrium conditions that prevail during welding. In the following section two existing thermodynamic models for nitrogen dissolution in iron and stainless steel are discussed. The influence of the alloying element content of the weld metal on nitrogen absorption is also considered.

1.4 THERMODYNAMIC MODELS FOR NITROGEN DISSOLUTION IN WELD METAL

1.4.1 The two-temperature model

In 1987 Gedeon and Eager^{23,24} developed a thermodynamic model describing the dissolution of hydrogen in steel welds. This model was subsequently modified by Mundra and DebRoy¹³ and Palmer and

DebRoy²⁵ to describe the dissolution of nitrogen in weld metal. In accordance with available literature, the authors based their model on the assumption that monatomic nitrogen is responsible for the enhanced nitrogen solubility observed at low nitrogen partial pressures in molten iron exposed to plasma. The appropriate nitrogen dissolution reaction is represented by equation (1.12), and equation (1.13) displays the free energy relationship for this reaction.

$$\underline{N}(\text{wt}\%) = P_N \exp\left(-\frac{\Delta G_{12}^0}{RT}\right) \quad \dots(1.13)$$

where: P_N is the partial pressure of monatomic nitrogen in the arc plasma (atm), and ΔG_{12}^0 is the standard free energy for reaction (1.12).

Mundra and DebRoy¹³ calculated the equilibrium solubility of monatomic nitrogen in iron using equation (1.13) and the applicable free energy data for reaction (1.12). Their results are shown in Figure 1.7 as a function of partial pressure and temperature. In contrast to the behaviour of the iron-diatomic nitrogen system shown in Figure 1.2, the equilibrium solubility of nitrogen in austenite exposed to monatomic nitrogen increases in a linear manner with increasing monatomic nitrogen partial pressure, and shows a significant decrease in a nonlinear manner with temperature. Since the monatomic nitrogen solubility increases sharply with decreasing temperature below approximately 1575 K, small changes in temperature can cause large changes in the ensuing equilibrium nitrogen concentration. Variation in temperature plays a much greater role than pressure in determining the extent of nitrogen dissolution in iron exposed to monatomic nitrogen.

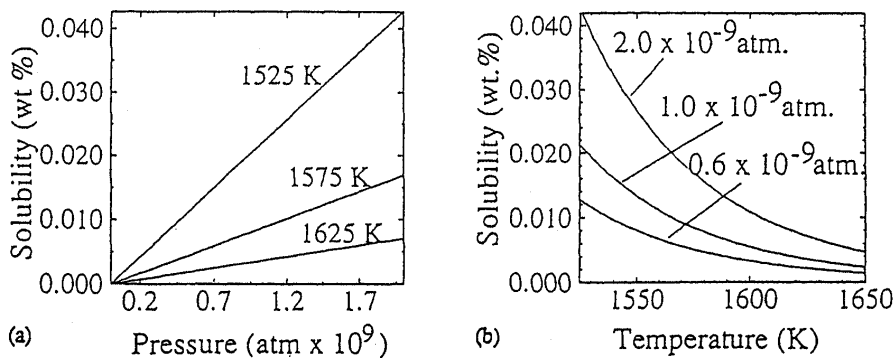


Figure 1.7 Computed equilibrium solubility of nitrogen in austenite exposed to monatomic nitrogen: (a) as a function of the partial pressure of monatomic nitrogen at three temperatures, and (b) as a function of temperature at three partial pressures¹³.

The two-temperature model is based on the premise that the concentration of monatomic nitrogen formed in an arc plasma due to the dissociation of nitrogen molecules is higher than what would be obtained solely from consideration of thermal equilibrium between the two species at the system temperature and pressure. If the actual concentration of atomic nitrogen in the arc plasma is known, its concentration in iron can be estimated by considering equilibrium between the monatomic nitrogen and the metal. In a plasma, the extent of dissociation of diatomic nitrogen depends on factors such as the nature of the power

source, the energy dissipated, the overall system geometry, and the nature of the diatomic gas. The authors^{13,23,24,25} defined a hypothetical dissociation temperature, T_d , at which the equilibrium thermal dissociation of diatomic nitrogen would produce the actual partial pressure of monatomic nitrogen present in the plasma. The monatomic nitrogen in the arc plasma then dissolves in the weld metal at the surface temperature of the molten pool, T_s . This model is schematically illustrated in Figure 1.8. It is fair to assume that, after dissociation of diatomic nitrogen at T_d , no significant change in the partial pressures of diatomic and monatomic nitrogen occurs during the transport of these species towards the metal surface. Unlike the dissociation of diatomic molecules, the recombination of the product atoms in the gas phase is difficult. First, because the extent of dissociation in the arc is small, the probability of collision between two nitrogen atoms is much smaller than that between N and N₂, or between N and inert gas atoms in the shielding gas. Second, because the recombination reaction is highly exothermic, exothermic heat has to be removed from the recombined molecule, as in a three-body collision. From a statistical consideration, the probability of a three-body collision is very small²⁵.

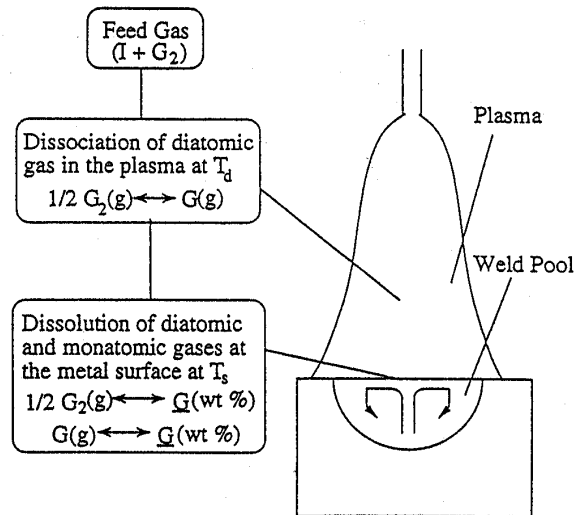


Figure 1.8 A schematic diagram showing the dissolution of a gas, G, from the plasma phase into a weld pool¹³.

The nitrogen dissociation reaction in the arc is represented by equation (1.14) and the partial pressure of monatomic nitrogen in the plasma by equation (1.15):



$$P_N = \sqrt{P_{N_2}} \exp\left(-\frac{\Delta G_{14,T_d}^0}{RT_d}\right) \quad \dots(1.15)$$

where: $\Delta G_{14,T_d}^0$ is the standard free energy for reaction (1.14) at T_d .

The extent of dissociation of diatomic nitrogen at T_d can be calculated from equation (1.15). Since the extent of dissociation of diatomic nitrogen is low under typical welding conditions, P_N can be assumed to be equal to the partial pressure of N₂ in the inlet gas, $P_{N_2}^{in}$. Combining equations (1.13) and (1.15), and

bearing in mind that the dissociation of N_2 is considered at T_d and the dissolution of N at T_s , the equilibrium nitrogen concentration in iron is given by equation (1.16):

$$\underline{N}(\text{wt}\%) = \sqrt{P_{N_2}^{\text{in}}} \exp \left(-\frac{1}{R} \left(\frac{\Delta G_{14}^0}{T_d} + \frac{\Delta G_{12}^0}{T_s} \right) \right) \quad \dots(1.16)$$

Equation (1.16) represents the solubility of nitrogen in iron exposed to a plasma environment with the metal at temperature T_s . The hypothetical dissociation temperature, T_d , is higher than the temperature of the sample, T_s , and is a measure of the partial pressure of the atomic nitrogen in the plasma.

In analysing the validity of the model, Mundra and DebRoy¹³ used nitrogen solubility data from the available literature, substituting the data into equation (1.16), and calculating the effective dissociation temperatures which explain the enhanced solubility. The calculated dissociation temperatures fell within a range of 100 to 300 K above the sample temperature for all the systems analysed. Figure 1.9 illustrates the relationship between the percentage dissociation of diatomic nitrogen and T_d , based on the experimental work of Bandopadhyay *et al*¹⁷, and shows that the dissociation of diatomic nitrogen increases with increasing temperature. Palmer and DebRoy²⁵ performed similar calculations and, as shown in Figure 1.10, reported effective dissociation temperatures approximately 100 to 215 K higher than the sample temperature. The authors concluded that, if experimental data are not available, a rough estimate of the nitrogen concentration can be obtained by assuming a hypothetical dissociation temperature about 100 to 200 K higher than the sample temperature.

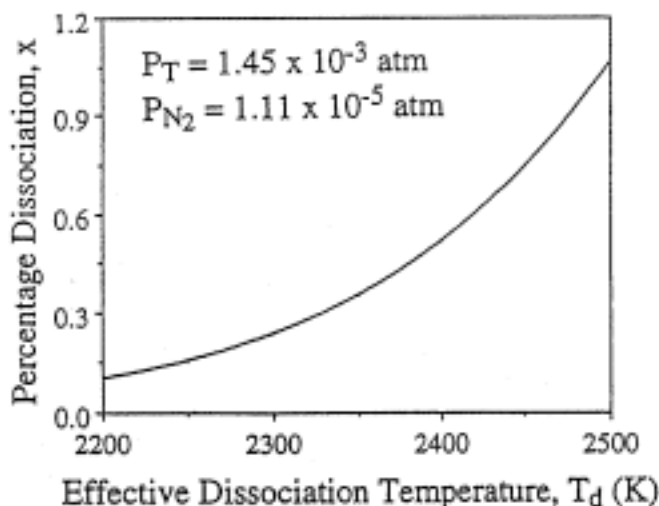


Figure 1.9 The percentage nitrogen dissociated as a function of the effective dissociation temperature¹³.

Mundra and DebRoy¹³ and Palmer and DebRoy²⁵ developed the two-temperature model based on the results of isothermal experiments performed in glow discharge plasmas. Unlike these experiments, the temperature of the weld pool surface during welding shows significant spatial variation. If the partial pressure of diatomic nitrogen was the main factor determining the nitrogen concentration in the weld metal, the consequences of the spatial variation in the weld pool surface temperature would be fairly

insignificant (as demonstrated in Figure 1.2). In contrast, for monatomic nitrogen species, a slight variation in temperature can lead to a significant variation in the equilibrium solubility of nitrogen (as shown in Figure 1.7). By making a few simplifying assumptions, Palmer and DebRoy²⁵ extended the application of the two-temperature model to actual welding experiments. The authors used published results obtained by Kuwana and Kokawa¹⁹ during the gas tungsten arc welding of a low alloy steel in controlled nitrogen atmospheres.

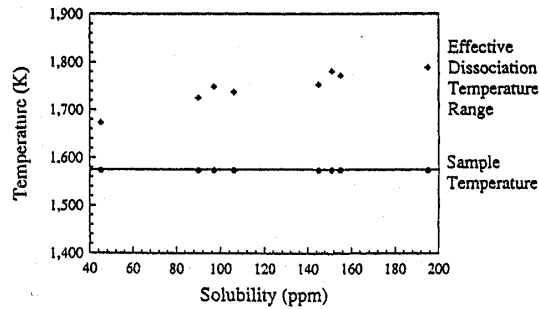


Figure 1.10 Comparison between the nitrogen solubility (wt%) and the effective dissociation temperature over the experimental pressure range¹³.

Palmer and DebRoy's²⁵ first assumption concerned the extent of coverage of the weld pool by the arc plasma, as determined by the welding parameters. The significance of the extent of coverage of the pool surface is demonstrated in Figure 1.11. Complete coverage of the weld pool by the plasma can be assumed if welding is performed at reasonably low currents and the weld pool is fairly narrow. In order to compare the experimental data with the calculated values, the authors also needed the temperature distribution at the surface of the weld pool. Khan²⁶ demonstrated that the temperature distribution at the surface of the weld pool is represented by equation (1.17).

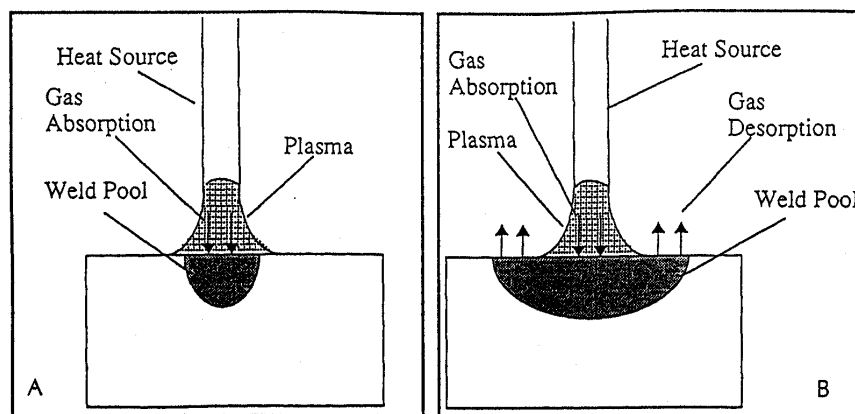


Figure 1.11 Schematic diagrams of a weld pool: (A) completely covered by plasma, and (B) incompletely covered by plasma²⁵.

$$T = T_{MAX} \exp(-ar^{*2}) \quad \dots(1.17)$$

where: T is the temperature at any location on the weld pool surface,
 T_{MAX} is the weld pool surface temperature at the axis of the arc,
 a is a constant,
 r^* is a dimensionless distance from the axis of the arc given by the ratio r/r_0 ,
 r is the radial distance from the centre of the molten pool or the arc axis, and
 r_0 is the radius of the molten pool.

Since the temperature at the fusion line, i.e. at $r = r_0$, is known (the temperature at the solid/liquid interface is equal to the liquidus temperature of the base metal), the value of the variable a can be calculated if T_{MAX} is known. Palmer and DebRoy²⁵ assumed values for T_{MAX} and calculated the temperature distribution on the surface of the weld pool for these values. The calculated temperature profiles for two values of T_{MAX} are shown in Figure 1.12(a) as a function of the dimensionless distance, r^* .

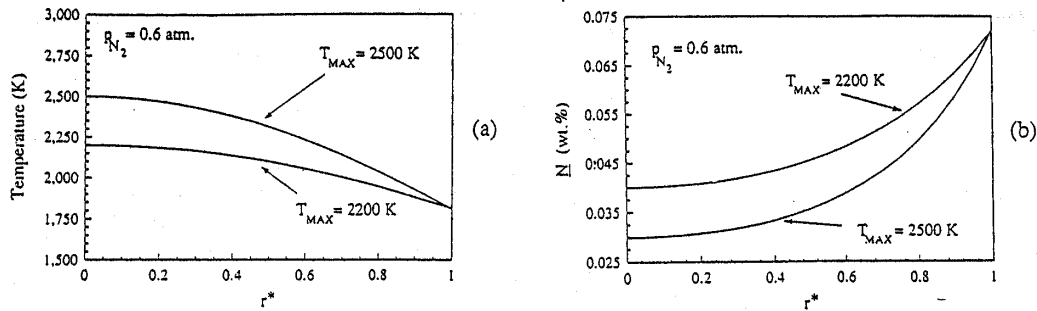


Figure 1.12 Computed values for: (a) temperature, and (b) nitrogen concentration, across the radius of the weld pool for T_{MAX} values of 2500 K and 2200 K and a diatomic nitrogen partial pressure of 0,6 atm²⁵.

In addition to the surface temperature distribution, the dissociation temperatures are necessary to calculate the nitrogen concentration distribution on the weld pool surface from equation (1.16). As shown earlier, Palmer and DebRoy²⁵ demonstrated that the value of the dissociation temperature, T_d , is approximately 100 to 200 K higher than the sample temperature. The exact difference between the surface temperature and the dissociation temperature depends on the concentration of monatomic gas in the plasma, which, in turn, depends on the properties of the plasma. The higher the partial pressure of monatomic nitrogen in the plasma, the higher the dissociation temperature. In view of the continuous movement of the arc with respect to the workpiece during welding, the plasma continually mixes with the surrounding gas, which tends to reduce the concentration of monatomic nitrogen in the plasma. As a result, a relatively small difference between the dissociation temperature and the surface temperature of the weld pool is appropriate. Palmer and DebRoy assumed a temperature difference of 125 K between the dissociation temperature and the surface temperature in the case of gas tungsten arc welding.

The equilibrium concentration of nitrogen at all locations on the surface of the weld pool can be computed from equation (1.17) once the dissociation temperature at each of these locations is known.

The computed nitrogen concentration values are shown as a function of the dimensionless distance in Figure 1.12(b). The nitrogen concentrations are higher at the outer edges of the weld pool since the monatomic nitrogen solubility increases sharply with decreasing temperature. In view of the fact that the weld metal undergoes vigorous recirculation, the nitrogen from the surface is readily transported to the interior of the weld pool.

Finally, Palmer and DebRoy²⁵ assumed that the overall nitrogen concentration in the weld metal, \underline{N}_{AV} (wt%), if nitrogen is not lost from the pool in any appreciable amount, is determined by an average concentration of nitrogen on the weld pool surface integrated over the entire surface:

$$\underline{N}_{AV} \text{ (wt\%)} = \frac{1}{\pi r_0^2} \int_0^{r_0} 2\pi r \underline{N} \text{ (wt\%)} dr = \int_0^1 2r^* \underline{N} \text{ (wt\%)} dr^* \quad \dots(1.18)$$

where: \underline{N} (wt%) is the local value of the nitrogen concentration at any location on the weld pool surface, and

r^* is the dimensionless radial distance from the axis of the heat source on the weld pool surface.

The computed overall nitrogen concentration in the weld pool for two values of T_{MAX} is shown in Figure 1.13 as a function of P_{N_2} in H_2-N_2 shielding gas mixtures from the experimental data of Kuwana and Kokawa¹⁹. This figure shows that fair agreement exists between the computed results and the experimental data. Improved agreement between the experimental and predicted values can be obtained by selecting a temperature difference of approximately 100 K between the surface temperatures and the dissociation temperatures.

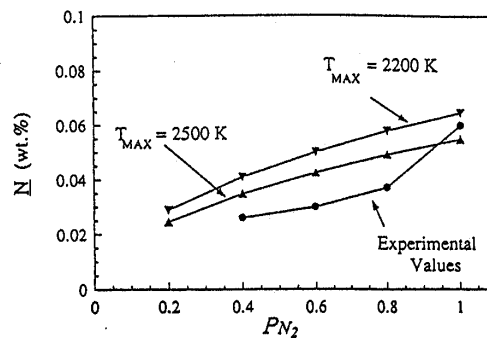


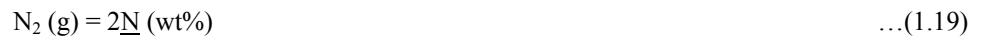
Figure 1.13 Comparison between the experimental solubility results of Kuwana and Kokawa¹⁹ and the computed nitrogen solubility predictions based on the two-temperature model²⁵.

Although the two-temperature model developed by Gedeon and Eager^{23,24}, Mundra and DebRoy¹³ and Palmer and DebRoy²⁵ appears to provide fair agreement between the calculated and experimentally determined nitrogen solubility values in iron, the model has significant limitations which restrict its extension to the current investigation. The first limitation is that the model does not take into account the alloy composition, which has been shown to have a significant effect on the solubility of nitrogen in iron (refer to §1.2.3). Kuwana *et al*²⁷ addressed this issue in the form of a thermodynamic model, discussed in

§1.4.2, developed to predict the nitrogen solubility in stainless steel weld metal. The second limitation is that the two-temperature model does not consider the influence of the surface active element concentration of the weld metal, the prior nitrogen content of the base metal or the welding parameters on nitrogen absorption and desorption during welding. These issues are considered in more detail in §1.5 and §1.6.

1.4.2 The thermodynamic model developed by Kuwana *et al*²⁷ for predicting the nitrogen solubility of stainless steel welds

Kuwana *et al*²⁷ studied the dissolution of nitrogen in iron and stainless steel welds during autogenous gas tungsten arc welding with nitrogen containing shielding gas mixtures. They attributed the enhanced nitrogen solubility observed during welding to the presence of monatomic nitrogen in the arc, but in contrast to the two-temperature model considered in §1.4.1, Kuwana *et al* also assumed that undissociated diatomic nitrogen in the plasma can contribute towards nitrogen absorption. They suggested that three reactions, represented by equations (1.19) to (1.21), occur simultaneously during welding.



Equation (1.19) describes the absorption of diatomic nitrogen from the arc atmosphere, and equation (1.21) the absorption of monatomic nitrogen produced by dissociation, equation (1.20), in the arc. As shown in Figure 1.14, Kuwana *et al* proposed that dissociation of diatomic nitrogen according to equation (1.20) produces a thin nitrogen-rich surface region exposed to the arc, but that the greater part of nitrogen absorption is controlled by reaction (1.19) at the temperature of the central region of the molten pool due to active convection. The authors stated that the nitrogen content approaches the equilibrium solubility of nitrogen at the temperature of the central region of the molten pool. When the nitrogen content of the central region is lower than the equilibrium solubility, nitrogen is transferred from the nitrogen-rich surface region to the central region. When the nitrogen content of the central region is higher than the equilibrium solubility, the excess nitrogen is released to the atmosphere through the weld pool surface not covered by the arc.

After exposure to the arc the weld pool cools down to room temperature. During the cooling cycle, the equilibrium solubility of nitrogen changes with temperature. As shown in Figure 1.1, the weld metal loses a small amount of nitrogen during cooling in the molten state, and a significant amount during solidification due to the large solubility gap between the liquid and solid states. Nitrogen losses after solidification are negligible due to the lower diffusivity of nitrogen in the solid state.

Accordingly, the nitrogen content of a steel gas tungsten arc weld at room temperature, $(\%N)_w$, can be described by equation (1.22):

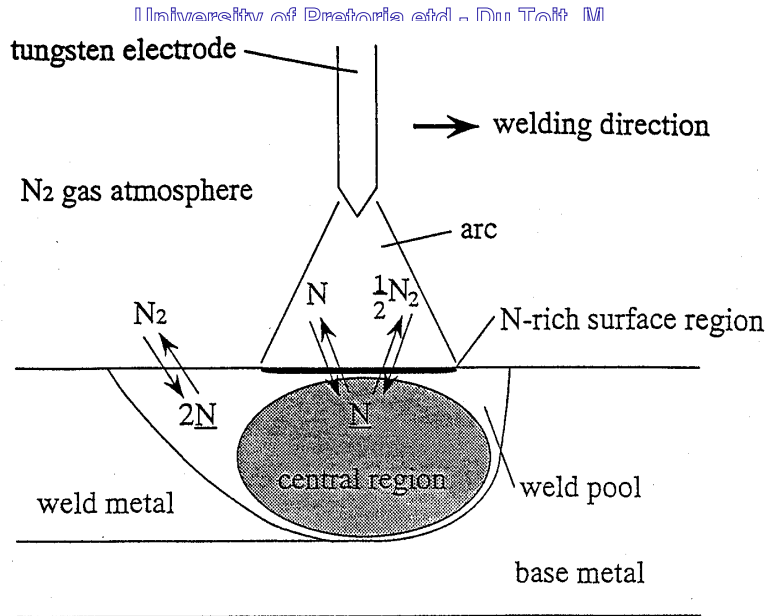


Figure 1.14 A schematic illustration of the behaviour of nitrogen during gas tungsten arc welding according to Kuwana *et al*²⁷.

$$(\%N)_w = (\%N)_{eq} + \Delta A + \Delta B + \Delta C \quad \dots(1.22)$$

where: $(\%N)_{eq}$ is the equilibrium solubility of nitrogen at the temperature of the central region of the molten weld pool,

$(\%N)_{eq} + \Delta A$ is the nitrogen content of the weld pool exposed to the arc,

ΔB is the change in the nitrogen content of the liquid weld pool during cooling to solidification, and

ΔC is the amount of nitrogen evolved on solidification.

Based on these assumptions, Kuwana *et al* investigated the influence of chromium and nickel on the nitrogen solubility of iron gas tungsten arc welds. The sum of the chromium and nickel contents of each alloy was limited to less than 30 weight per cent in all cases. The outline of the procedure followed by the authors in calculating $(\%N)_w$ is as follows: First, the temperature of the central region of the molten weld pool was determined as a function of the chemical composition of the alloy, and the equilibrium solubility of nitrogen, $(\%N)_{eq}$, was calculated at the weld pool temperature and 0,1 MPa nitrogen atmosphere. Next, $\Delta A + \Delta B + \Delta C$ was described as a function of alloy content using the difference between the experimental nitrogen content of the weld metal and $(\%N)_{eq}$. Following this, equations to predict the nitrogen content of gas tungsten arc welded iron alloys in 0,1 MPa nitrogen atmospheres were determined based on equation (1.22). The prediction was then extended to nitrogen partial pressures of 0 to 0,1 MPa in the arc atmosphere. Each of these steps are considered in more detail below.

- Weld pool temperature

The temperature of the central region of the molten weld pool is required in order to calculate the equilibrium solubility of nitrogen, $(\%N)_{eq}$, in the weld metal. Kuwana *et al*²⁷ measured the temperature of

the central region of the molten pool during gas tungsten arc welding using thermocouples, and derived an equation to describe the temperature of this region. Earlier work by the authors²⁸ established that the molten weld pool temperature during the gas tungsten arc welding of pure iron and type 304L austenitic stainless steel was approximately 100 K higher than the liquidus temperature of the weld metal, regardless of the welding current. Based on these results, the temperature of the weld pool during gas tungsten arc welding, T_{WP} , can be expressed in the form of equation (1.23) as a function of the liquidus temperature. The liquidus temperature of the weld metal can be calculated from the chemical composition of the melt^{29,30}.

$$T_{WP} = T_L + 100 \quad \dots(1.23)$$

where: T_L is the liquidus temperature of the weld metal.

- Equilibrium solubility of nitrogen

The equilibrium solubility of nitrogen, $(\%N)_{eq}$, at the temperature of the molten weld pool, T_{WP} , can be calculated using equations (1.4) and (1.5) considered earlier.

- Nitrogen absorption from nitrogen containing shielding gas atmospheres

If the experimental nitrogen content of gas tungsten arc welds, $(\%N)_w$, and the equilibrium solubility of nitrogen, $(\%N)_{eq}$, calculated using equations (1.4), (1.5) and (1.23) at 0,1 MPa nitrogen atmosphere, are represented as iso-nitrogen contour lines on an Fe-Cr-Ni ternary diagram (as shown in Figure 1.15), the difference between the calculated and experimental values is large in the high and low chromium regions. The nitrogen content appears to be strongly dependent on the chromium content and the iso-nitrogen contour lines are roughly parallel to the $[\%Cr]=0$ line. Figure 1.16 shows the calculated and experimental nitrogen contents on Fe-Cr and Fe-Ni binary cross sections. In the Fe-Ni system, the calculated nitrogen concentrations are slightly lower than the experimental values, but the difference is very small. In the Fe-Cr system, the calculated values are slightly lower than the experimental values in the low chromium region, but higher in the high chromium region. Chromium appears to influence nitrogen absorption by increasing the equilibrium nitrogen solubility and the period of time required to reach this equilibrium value.

Figure 1.17 demonstrates the influence of the weld metal chromium content on the difference, $\Delta(\%N)$, between the experimental nitrogen content of Fe-Cr welds, $(\%N)_w$, and the equilibrium solubility of nitrogen, $(\%N)_{eq}$, where $\Delta(\%N)=(\%N)_w-(\%N)_{eq}$. This figure indicates that in alloys containing less than about 7% chromium, $\Delta(\%N)$ increases slightly with chromium content, but at higher chromium levels, $\Delta(\%N)$ decreases with an increase in chromium content. The authors explained these results in terms of the time required to reach the equilibrium nitrogen solubility limit in these alloys. Due to the low solubility of nitrogen in low chromium alloys, the melting time during welding may be sufficient for nitrogen absorption to increase the weld metal nitrogen content to a level approaching the equilibrium value. In high chromium alloys with high solubility limits, enough time may not be available during welding for nitrogen absorption from the arc atmosphere to increase the weld metal nitrogen content to a

level approaching the equilibrium value. This results in an increasing difference between the measured and equilibrium nitrogen content, $\Delta(\%N)$, with increasing chromium content.

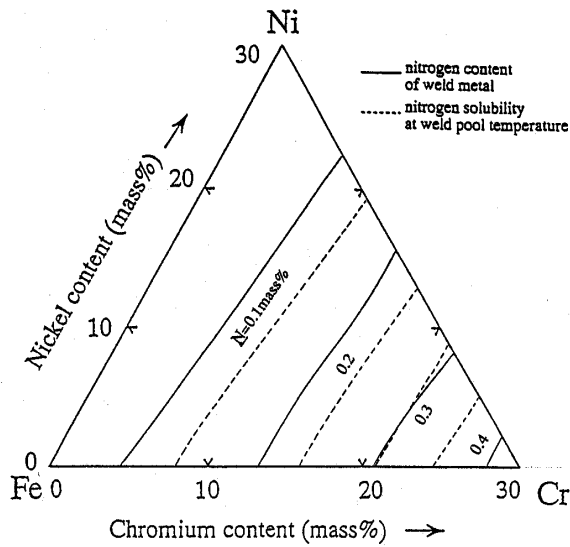


Figure 1.15 Iso-nitrogen contour lines on the Fe-Cr-Ni ternary phase diagram indicating the experimental nitrogen contents of gas tungsten arc welds and the equilibrium solubility values of nitrogen at the weld pool temperature²⁷.

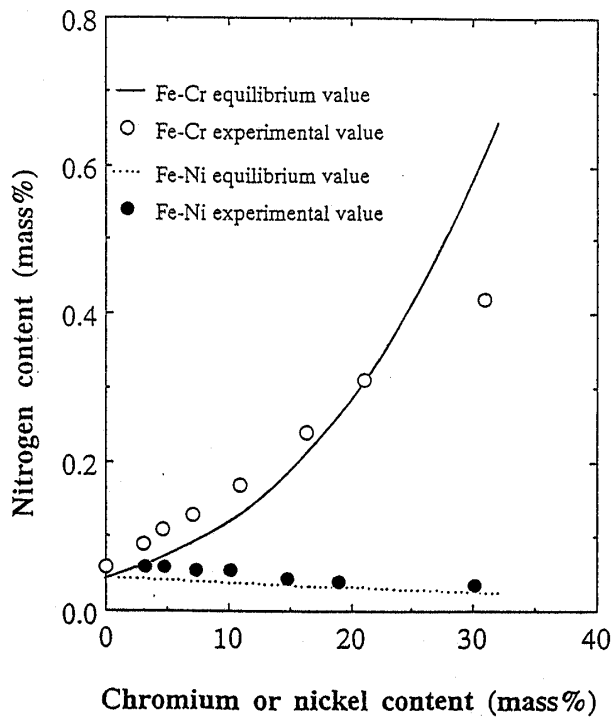


Figure 1.16 The influence of the chromium and nickel contents of binary Fe-Cr and Fe-Ni alloys on the nitrogen content of gas tungsten arc welds, compared to the equilibrium solubilities at the weld pool temperature²⁷.

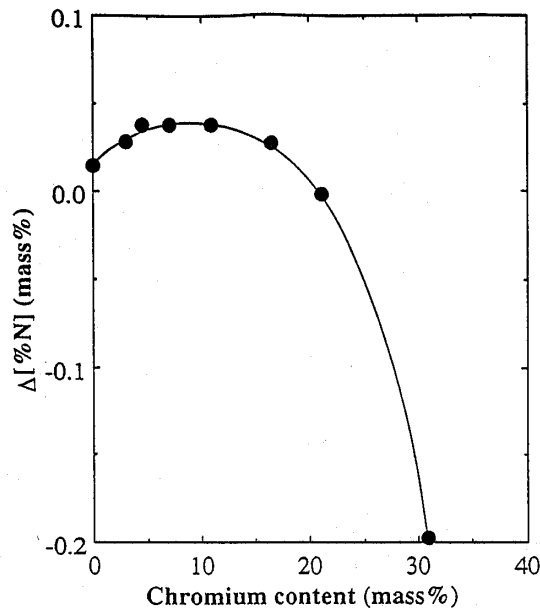


Figure 1.17 The influence of chromium on the difference between the weld metal nitrogen content, $(\%N)_w$, and the equilibrium nitrogen solubility, $(\%N)_{eq}$, in Fe-Cr welds²⁷.

Based on the results in Figure 1.17, Kuwana *et al* developed a relationship, shown in equation (1.24), for computing the calculated nitrogen content, $(\%N)_c$, of chromium containing weld metal as a function of the chromium content.

$$(\%N)_c = (\%N)_{eq} + (1,46 \times 10^{-2}) + (7,12 \times 10^{-3}) \cdot [\%Cr] - (7,25 \times 10^{-4}) \cdot [\%Cr]^2 + (3,38 \times 10^{-5}) \cdot [\%Cr]^3 - (8,08 \times 10^{-7}) \cdot [\%Cr]^4 \quad \dots(1.24)$$

As shown in Figure 1.18, good agreement was obtained between the calculated and experimental nitrogen contents of Fe-Cr welds. The nitrogen contents, $(\%N)_c$, of Fe-Cr-Ni welds were also calculated, using equations (1.4), (1.5), (1.23) and (1.24), and by assuming that the difference between the measured and equilibrium nitrogen contents is only a function of the chromium content, since the iso-nitrogen contour lines are roughly parallel to the $[\%Cr]=0$ line in Figure 1.15. As shown in Figure 1.19, good agreement between the calculated and experimental nitrogen contents was also obtained for Fe-Cr-Ni welds.

In order to examine the application of this model to a typical stainless steel, the nitrogen content of a type 304L austenitic stainless steel, welded using the gas tungsten arc process with similar welding parameters, was calculated using equations (1.4), (1.5), (1.23) and (1.24). Kuwana *et al* predicted a $(\%N)_c$ value of 0,24 wt% for this alloy, which is slightly lower than the measured value, $(\%N)_w$, of 0,26 wt%. The authors attributed this small difference to an incorrect calculation of the liquidus temperature of the alloy. Overestimation of the molten weld pool temperature leads to an underestimation of the nitrogen content of high chromium weld metal.

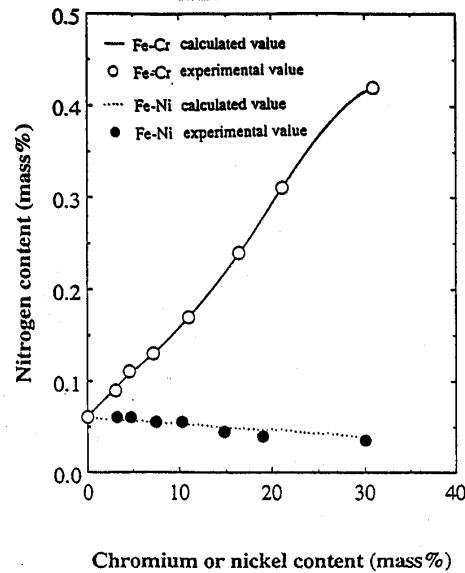


Figure 1.18 The influence of chromium or nickel on the experimental and calculated nitrogen contents of Fe-Cr and Fe-Ni welds²⁷.

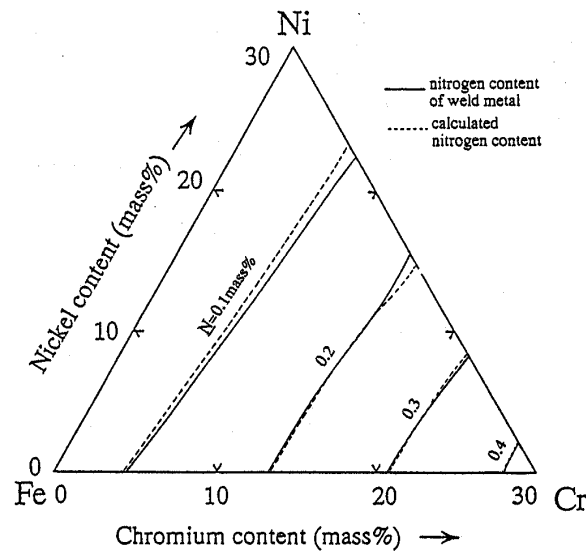


Figure 1.19 Iso-nitrogen contour lines showing the experimental and calculated nitrogen contents of Fe-Cr-Ni welds²⁷.

- Argon-nitrogen mixed shielding gas atmospheres

Kuwana *et al*²⁷ also extended the above calculations, which were performed for pure nitrogen shielding gas atmospheres (0,1 MPa nitrogen), to argon-nitrogen shielding gas mixtures with varying nitrogen partial pressures and a total pressure of 0,1 MPa.

Figure 1.20 illustrates the influence of the nitrogen partial pressure in Ar-N₂ shielding gas atmospheres on the nitrogen content of gas tungsten arc welded steel and stainless steel, compared to the equilibrium

solubility of nitrogen in these alloys at the molten pool temperature. The results confirm that the nitrogen content of welds tends to increase with nitrogen partial pressure up to a saturation level. At higher partial pressures the weld metal nitrogen content assumes a constant value, regardless of the nitrogen partial pressure in the shielding gas. Figure 1.20 also confirms that the nitrogen solubility in welds is enhanced over that predicted from equilibrium considerations at all nitrogen partial pressures, with the exception of alloys containing more than approximately 20 wt% chromium at nitrogen partial pressures approaching 0,1 MPa. It is also evident that stainless steel welds dissolve significantly more nitrogen than lower chromium alloys, presumably because chromium increases the nitrogen solubility limit in these alloys. Based on these results, Kuwana *et al* concluded that the dissociation of diatomic nitrogen in the arc plasma, equation (1.20), and the subsequent dissolution of monatomic nitrogen, equation (1.21), have a marked influence on nitrogen absorption. Accordingly, the authors developed a thermodynamic model, described below, to account for the observed nitrogen dissolution behaviour.

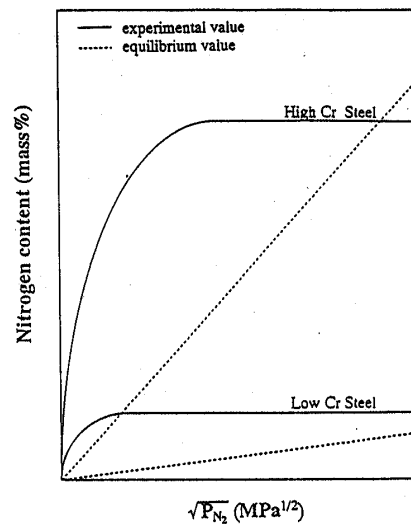


Figure 1.20 The influence of the nitrogen partial pressure in Ar-N₂ shielding gas mixtures on the nitrogen content of steel welds, and the equilibrium nitrogen solubility at the weld pool temperature²⁷.

Kuwana *et al*²⁷ assumed that the dissociation of molecular nitrogen gas into monatomic nitrogen in the arc plasma is represented by equation (1.20). The equilibrium constant, K , of this reaction is given by equation (1.25), and the relationship between K and the standard free energy for reaction (1.20), ΔG_{20}^0 , is represented by equation (1.26).

$$K = \frac{(P_N)^2}{P_{N_2}} \quad \dots(1.25)$$

where: P_N is the partial pressure of monatomic nitrogen (N) in atm, and
 P_{N_2} is the partial pressure of molecular nitrogen (N₂) in atm.

$$\ln K = -\frac{\Delta G_{20}^0}{RT} \quad \dots(1.26)$$

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where: ΔG_{20}^0 is the standard free energy for reaction (1.20), and
 R is the universal gas constant.

Equation (1.27) can be derived by combining equations (1.25) and (1.26):

$$\ln \left[\frac{(P_N)^2}{P_{N_2}} \right] = -\frac{\Delta G_{20}^0}{RT} \quad \dots(1.27)$$

The standard Gibbs free energy change, ΔG_{20}^0 , for the dissociation reaction is given by equation (1.28):

$$\Delta G_{20}^0 = \Delta H_{20}^0 - T\Delta S_{20}^0 \quad \dots(1.28)$$

where: ΔH_{20}^0 is the change in enthalpy for the dissociation of nitrogen (966,67 kJ/mol), and
 ΔS_{20}^0 is the change in entropy for the dissociation of nitrogen (136,44 J/K.mol).

Equations (1.27) and (1.28) provide a relationship between P_N (or P_{N_2}) and temperature at 0,1 MPa nitrogen pressure. Figure 1.21 shows the influence of the initial N_2 partial pressure in Ar- N_2 shielding gas mixtures on the degree of dissociation of diatomic gas at high temperatures, assuming that the total pressure remains at 0,1 MPa. This figure indicates that the degree of dissociation decreases with a decrease in temperature and an increase in the initial P_{N_2} . Even though a lower initial P_{N_2} in the shielding gas leads to a higher degree of dissociation, the partial pressure of monatomic nitrogen in the arc, P_N , does not increase because of the lower nitrogen concentration in the arc atmosphere. Figure 1.22 demonstrates the influence of the initial P_{N_2} in Ar- N_2 shielding gas mixtures on P_N at high temperatures, calculated using equations (1.27) and (1.28). It is evident that the partial pressure of monatomic nitrogen, P_N , decreases with a decrease in the initial P_{N_2} and rapidly approaches zero when the initial P_{N_2} approaches zero.

Based on these conclusions, Kuwana *et al* assumed that the weld metal nitrogen content increases with the nitrogen partial pressure up to a nitrogen partial pressure of P_{N_2}' , and assumes a value of $(\%N)_{0,1}$ at nitrogen partial pressures higher than P_{N_2}' , where $(\%N)_{0,1}$ is the nitrogen content of the weld metal calculated using equations (1.4), (1.5), (1.22), (1.23) and (1.24) at 0,1 MPa nitrogen partial pressure. The authors therefore assume that no supersaturation occurs in the weld metal. From the results of the Fe-Cr welds, and assuming that P_{N_2}' depends on the chromium content, the nitrogen content, $(\%N)_c$, of gas tungsten arc welded iron alloys in argon-nitrogen shielding gas mixtures can be calculated using equations (1.29) and (1.30):

$$\text{when: } 0 \leq P_{N_2} < P_{N_2}', \quad (\%N)_c = (0,0308.[\%Cr] + 0,271).(P_{N_2})^{1/4} \quad \dots(1.29)$$

$$\text{when: } P_{N_2}' \leq P_{N_2} \leq 0,1 \text{ MPa, } \quad (\%N)_c = (\%N)_{0,1} \quad \dots(1.30)$$

$$\text{where: } P_{N_2}' = \left\{ \frac{(\%N)_{0,1}}{(0,0308.[\%Cr] + 0,271)} \right\}^4$$

As shown in Figure 1.23, the calculated and experimental nitrogen contents, $(\%N)_c$ and $(\%N)_w$, display good agreement for the range of steels investigated. However, the model developed by Kuwana *et al* is simplified and has several shortcomings which would limit wider application. It was developed for a specific set of welding parameters (gas tungsten arc welding with electrode negative polarity, an arc length of 10 mm and a travel speed of 3,33 mm/s). The model would probably need adjustment for other sets of welding parameters since the reaction time between the molten weld pool and nitrogen in the arc atmosphere is likely to change. The reaction time appears to play a significant role, particularly in the case of high chromium alloys. The model also does not take into account the influence of the base metal nitrogen content or the presence of surface active elements. These factors are considered in §1.5 and §1.6.

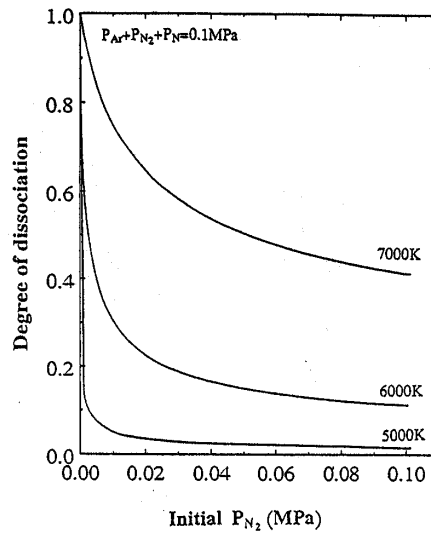


Figure 1.21 The influence of the initial N_2 partial pressure in mixed Ar- N_2 shielding gas atmospheres on the degree of dissociation at high temperatures²⁷.

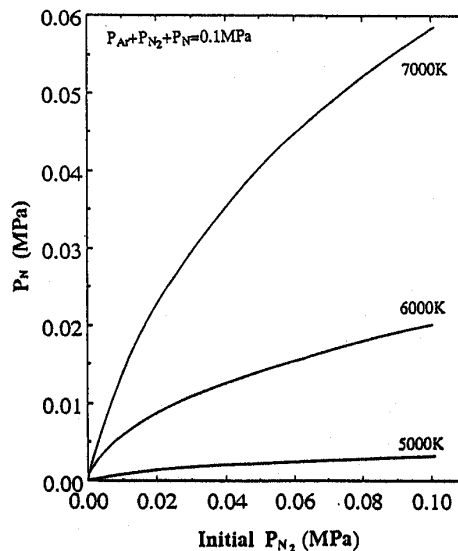


Figure 1.22 The influence of the initial N_2 partial pressure in Ar- N_2 shielding gas atmospheres on the partial pressure of monatomic nitrogen, P_N , at high temperatures²⁷.

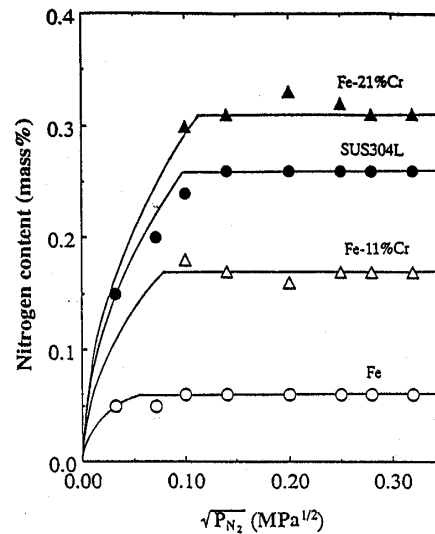


Figure 1.23 Experimental and calculated weld metal nitrogen contents as a function of the nitrogen partial pressure in Ar-N₂ shielding gas mixtures²⁷.

1.5 THE INFLUENCE OF ALLOYING ELEMENTS ON THE DISSOLUTION OF NITROGEN IN IRON DURING WELDING

The influence of alloying elements on the dissolution of nitrogen in iron alloys appears to be similar to the influence of the same elements on the equilibrium solubility, as considered in §1.2. However, the previous discussion did not take into consideration the influence of the base metal nitrogen content prior to welding, which is of particular significance in the case of high nitrogen stainless steels, nor the presence of surface active elements in the weld metal. The influence of each of these factors is discussed in the following section. The possible vaporisation of alloying elements from the weld pool due to the high temperatures associated with welding is an additional factor that may play a role in determining the solubility of nitrogen during welding. This factor is unlikely to influence the results obtained during this investigation to any significant extent, and will therefore not be considered further.

1.5.1 The influence of the base metal nitrogen content on the nitrogen content of welds

Limited information is currently available on the influence of the base metal nitrogen content on nitrogen dissolution in iron alloy welds. Okagawa *et al*⁶ studied the influence of nitrogen additions to argon shielding gas during autogenous gas tungsten arc welding on the nitrogen content of type 304L stainless steel welds. The authors reported that the final weld metal nitrogen content was not influenced by the base metal nitrogen content (0,025% nitrogen in the type 304L stainless steel investigated), and concluded that the base metal nitrogen was in a form that did not take part in the nitrogen dissolution reaction during welding. They based this conclusion on the observation that the weld metal nitrogen content was the same as that of the original base metal when pure argon shielding gas was used. Suutala³¹ studied autogenous gas tungsten arc welds in a number of austenitic stainless steels with base metal nitrogen levels varying between 0,008 and 0,076 wt%, and reported good correlation between the

nitrogen contents of the austenitic base metals and autogenous welds in the same materials with pure argon shielding gas, particularly in the presence of relatively high amounts of manganese. The results of Arata *et al*³² indicated that the total weld metal nitrogen content is the sum of the residual nitrogen content of the base metal and the nitrogen picked up from the shielding gas-metal interaction.

The nitrogen levels of the steels investigated by these authors were relatively low, compared to the nitrogen contents of high nitrogen austenitic stainless steels, and were probably well below the nitrogen solubility limit of the weld metal. This is further evidenced by the influence of manganese, as reported by Suutala³¹. For this reason it is unlikely that the conclusions of the authors described above can be extended to the case of high nitrogen alloys, where the base metal nitrogen content is significantly higher and closer to the solubility limit.

1.5.2 The influence of surface active elements on the nitrogen content of welds

Ample evidence exists to show that the presence of surface active elements, in particular sulphur and oxygen, has a significant influence on nitrogen dissolution in iron alloy welds. A number of these studies is considered below.

Lancaster¹ reported that the amount of nitrogen absorbed during arc welding increases in the presence of oxygen, and Ogawa *et al*³³ demonstrated that nitrogen-induced porosity in austenitic stainless steel welds can be curbed by welding in an atmosphere containing a small amount of oxidising gas. According to Blake¹¹, the presence of oxygen in the arc plasma or weld metal leads to lower nitrogen desorption rates. Uda and Ohno³⁴ studied the effects of surface active elements, including sulphur, oxygen and selenium, on the nitrogen content of iron under arc melting conditions in a number of Ar-N₂ shielding gas mixtures. The presence of these surface active elements markedly increased the nitrogen content of the iron, as shown in Figure 1.24 for a number of iron-oxygen alloys. It is evident that the level of supersaturation of nitrogen in the welds increases with increasing concentrations of oxygen. Sinha and Gupta³⁵ studied the rate of nitrogen absorption during the arc melting of stainless steel and observed that the rate of absorption decreased in the presence of surface active elements.

Three hypotheses have been offered to explain the apparently conflicting results describing the influence of surface active elements on nitrogen dissolution:

1. Blake¹¹ attributed the observed increased rate of dissolution and the lower desorption rate in the presence of oxygen to the formation of nitric oxide, NO, in preference to monatomic nitrogen in the arc. This hypothesis is probably inaccurate, due to the experimental and theoretical evidence for the influence of monatomic nitrogen on enhanced solubility. Blake's hypothesis also does not account for the influence of sulphur, which is similar to that of oxygen.
2. The presence of surface active elements, such as sulphur and oxygen, in the weld pool promotes convergent surface tension driven flow (Marangoni flow). In a pure metal, Marangoni flow is outwards across the weld pool surface, but the presence of surface active elements may cause the gradient of surface tension as a function of temperature to reverse and become positive. The surface

flow is then inwards, towards the arc root, causing nitrogen-rich weld metal to flow downward²¹. In iron-oxygen alloys the gradient of surface tension with temperature becomes positive at oxygen contents in the range of 60 to 100 ppm¹. This hypothesis is probably also unsound, since Marangoni flow generally plays only a minor role in determining mass flow patterns during welding, with the possible exception of low current gas tungsten arc welding. Divergent flow in a weld pool is usually a rare phenomenon.

- Surface active elements tend to occupy a fraction of the available sites on the metal surface, making it more difficult for nitrogen to adsorb on or desorb from the metal surface²¹. This is currently the most likely explanation for the influence of surface active elements on nitrogen dissolution and evolution, and was used by Katz and King²¹ to derive their kinetic model (to be considered in §1.7.1). In their study of nitrogen desorption kinetics, the authors found that in melts containing surface active elements, the rate of reaction was limited by the association of two adsorbed nitrogen atoms to form an adsorbed nitrogen molecule. On the other hand, when the melts contained low amounts of sulphur and oxygen, mass transport in the melt was the rate-limiting step for the desorption reaction.

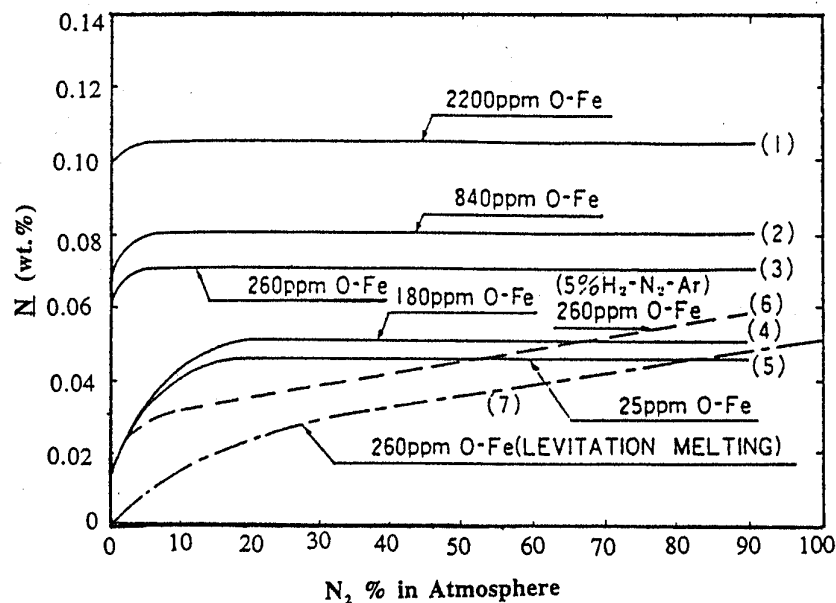


Figure 1.24 The nitrogen content of iron-oxygen alloys arc-melted at various nitrogen partial pressures³⁴.

The conflicting results discussed earlier were explained by Uda and Ohno³⁴, who proposed that the nitrogen content in iron is not an equilibrium value, but rather a steady-state concentration resulting from the absorption of nitrogen into the melt from the arc atmosphere and the evolution of nitrogen bubbles from the melt. Based on this steady-state assumption, the authors developed a model which is schematically illustrated in Figure 1.25. In this model, nitrogen is absorbed from the arc column, where the nitrogen exists in a number of activated states. Once absorbed into the melt, the nitrogen species are transported by fluid flow to the interior regions of the pool. The evolution of nitrogen bubbles from the melt occurs over the entire melt surface and is influenced by the characteristics of the surface in the

region not covered by the arc. If oxygen or sulphur covers part of the surface, nitrogen evolution is retarded. In the absence of surface active elements, nitrogen evolves much more readily. Sinha and Gupta³⁵ also stated that the final nitrogen content was the balance of nitrogen absorbed and desorbed over the range of exposure.

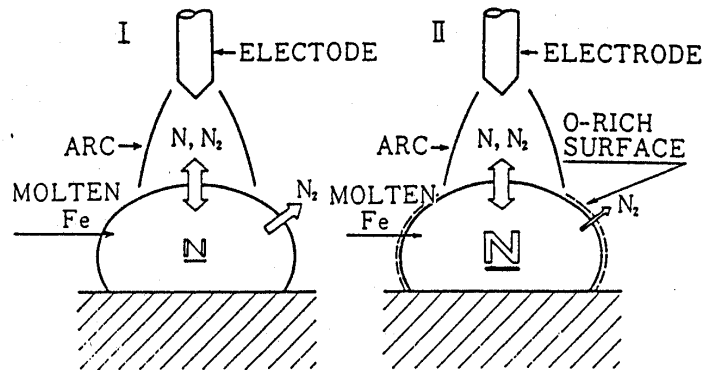


Figure 1.25 Schematic model of nitrogen dissolution and evolution from arc melted iron containing (I) low oxygen concentrations, and (II) high oxygen concentrations³⁴.

Uda and Ohno³⁶ also investigated the spattering of molten iron, containing 25 ppm and 260 ppm oxygen, under arc melting conditions in a nitrogen containing atmosphere. Spattering is a common phenomenon in the arc welding of steels and is driven by the high internal pressure and the high rate of bubble formation in liquid iron in the region of the arc spot. The authors explained the results of their spattering experiments using the model for the steady-state nitrogen concentration described above. At low oxygen concentrations (such as 25 ppm), the surface of the iron droplet outside of the arc column is not covered with an oxygen-rich film, thereby allowing the nitrogen, which is transported to this region by convection and diffusion, to be readily discharged from the surface. However, at high oxygen concentrations (such as 260 ppm), an oxygen-rich film forms on the surface of the droplet outside the jet impingement area, not allowing the nitrogen to evolve readily from the melt, and thereby increasing the nitrogen concentration within the drop.

1.6 THE INFLUENCE OF WELDING PARAMETERS ON THE NITROGEN CONTENT OF WELDS

Several researchers have reported that welding parameters, in particular the welding current, arc voltage, travel speed and electrode polarity, have a significant influence on nitrogen absorption and desorption reactions during welding. A number of these investigations are discussed below.

Kuwana and Kokawa¹⁹ and Kuwana *et al*²⁸ studied nitrogen absorption in pure iron and stainless steel (AISI type 304L) samples during autogenous gas tungsten arc welding in pure nitrogen shielding gas (0,1 MPa nitrogen pressure). As shown in Figure 1.26(a), the authors observed that the weld metal nitrogen content decreases with increasing welding current. This reduction in nitrogen content with increasing

current is more significant in stainless steel than in iron, and the nitrogen contents of the stainless steel welds are also considerably higher than those of the iron welds. The authors attributed the enhanced nitrogen solubility in the stainless steel welds to the presence of chromium. They also observed that the weld cross-sectional area increases considerably with an increase in welding current. The relationship between the nitrogen content of iron and stainless steel welds and the arc length during welding is shown in Figure 1.26(b). The nitrogen content appears to be almost independent of the arc length for both the stainless steel and iron welds. Since the arc voltage increases linearly with an increase in arc length, the results suggest that the weld metal nitrogen content is almost independent of the arc voltage. The weld cross-sectional area initially increases with an increase in arc voltage, but becomes constant at higher arc lengths. Figure 1.26(c) shows the relationship between the nitrogen content of the weld metal and the torch travel speed. It is evident that the weld metal nitrogen content increases with an increase in travel speed. This increase in nitrogen content is more significant in stainless steel than in iron. The weld cross-sectional area decreases markedly with an increase in travel speed.

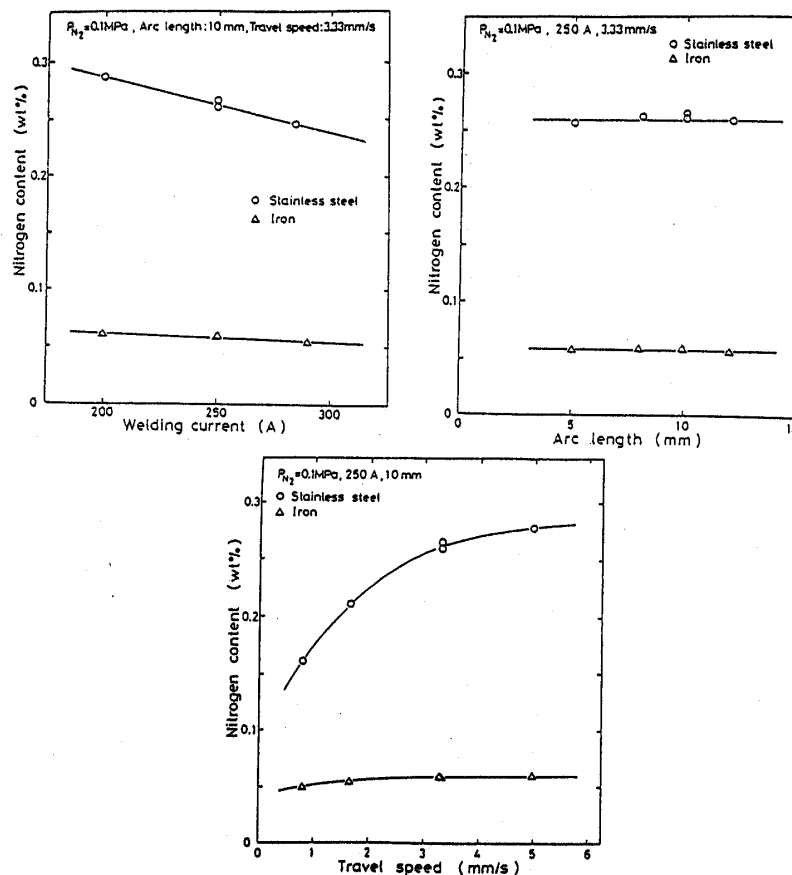


Figure 1.26 The relationship between the weld metal nitrogen content and the welding parameters during the autogenous gas tungsten arc welding of iron and stainless steel in 0,1 MPa nitrogen shielding gas: (a) the influence of welding current, (b) the influence of arc length, and (c) the influence of torch travel speed²⁸.

Kuwana *et al*²⁸ attributed these results to the influence of the welding parameters on the weld cross-sectional area. They observed that the weld metal nitrogen content generally decreases with increasing cross-sectional area and suggested that in the presence of pure nitrogen shielding gas, the nitrogen content

of the weld metal may be controlled mainly by nitrogen evolution during cooling. An increase in the weld cross-sectional area results in a decrease in the cooling rate after welding, thereby prolonging the period of time before solidification and resulting in an increase in the amount of evolved nitrogen. Figure 1.27 summarises the relationship between the nitrogen content of the weld metal and the weld metal cross-sectional area, and demonstrates that the nitrogen content of the weld metal decreases with an increase in weld cross-sectional area. The authors also observed that the nitrogen content of the weld metal decreases with an increase in the heat input during welding.

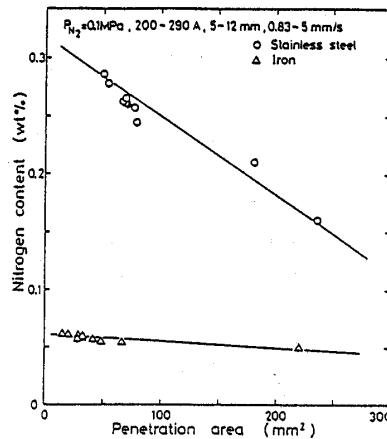


Figure 1.27 The relationship between the weld metal nitrogen content and the weld cross-sectional area during tungsten arc welding in pure nitrogen at a pressure of 0,1 MPa²⁸.

Kotecki³⁷ studied open-arc welding with self-shielded flux-cored stainless steel electrodes and reported that an increase in arc voltage causes the weld deposit nitrogen content to increase. This behaviour was attributed to the longer arc lengths associated with increasing arc voltage. At short arc lengths, the shielding gas atmosphere produced by shielding gas components in the flux has a low nitrogen content. As the arc length increases, more nitrogen from the surrounding atmosphere (air) is entrained in the arc plasma, thereby increasing the nitrogen content of the shielding gas atmosphere and resulting in high weld metal nitrogen contents. Kotecki also reported that increasing welding currents cause a decrease in the deposit nitrogen content. Increasing the current during flux-cored arc welding results in a higher wire electrode feed rate, which means that more metal per unit time passes through a given arc volume. Any nitrogen in the weld pool is diluted by the additional metal, resulting in a decreasing nitrogen content with increasing current.

Neuschütz *et al*³⁸ heated liquid steel in a tundish with argon-stabilised plasma arcs in order to study the influence of changes in the characteristics of the arc on the enhanced dissolution of nitrogen. The authors performed experiments with the plasma torch operating in three different configurations, namely DCEP (direct current electrode positive), AC (alternating current), and DCEN (direct current electrode negative). Nitrogen dissolution results for these different arc configurations showed that the lowest nitrogen levels were found when melting was performed under DCEP conditions, and the highest nitrogen contents under

DCEN conditions. The authors concluded that the rate of nitrogen pick-up during arc melting is determined by mass transport in the melt and by the rate of nitrogen desorption in the arc-free area of the molten pool, and suggested that the arc polarity affects nitrogen dissolution mainly by influencing stirring in the weld pool. The impact of the arc agitates the melt, thereby enhancing mass transport in the weld pool, and increasing the rate of nitrogen absorption. The melt is more strongly agitated with the torch serving as cathode (DCEP) than as anode (DCEN).

The results obtained by Kuwana and Kokawa¹⁹ and Kuwana *et al*²⁸ for pure nitrogen shielding gas cannot be applied directly to gas tungsten arc welding in pure argon or argon-nitrogen shielding gas mixtures. Lower nitrogen levels in the arc atmosphere will probably change the relationship between the weld metal nitrogen content and the welding parameters. This is evidenced by the contradictory influence of the arc length on the weld metal nitrogen content as reported by Kuwana *et al*²⁸ and Kotecki³⁷.

1.7 KINETICS OF NITROGEN DESORPTION AND ABSORPTION DURING WELDING

The results published by Kuwana *et al*²⁷ described in §1.4.2 suggest that a kinetic approach may be more appropriate than a thermodynamic method for describing the dissolution of nitrogen in high alloy steels and stainless steels. This approach has not been investigated yet, with the majority of published kinetic studies focussing on the absorption and desorption of injected nitrogen gas in liquid iron melts in view of the practical importance of the control of the nitrogen content of steels. A notable exception is a study by Katz and King²¹ who investigated the kinetics of nitrogen absorption and desorption from liquid iron during arc melting. Even though greater volumes of molten metal are involved and the melting times are longer, arc melting is thought to provide some insight into the behaviour of nitrogen during welding due to the presence of a plasma phase above the melt. The model developed by Katz and King²¹ is considered below.

1.7.1 The Katz and King²¹ model for nitrogen absorption and desorption during arc melting

Katz and King²¹ studied the absorption and desorption kinetics of nitrogen during the arc melting of iron. The authors allowed samples to melt under a pure argon atmosphere and then changed to the appropriate mixed argon-nitrogen shielding gas atmosphere. Samples for chemical analysis were removed at one minute intervals, starting immediately after switching from pure argon to the mixed argon-nitrogen shielding gas. The nitrogen content of the liquid iron was found to increase with time until a steady-state value was reached, sometimes indicated by the escape of well-defined nitrogen bubbles from the surrounding melt. After reaching this plateau value, the nitrogen desorption reaction was investigated by changing back to pure argon shielding gas. A typical experimental plot of the nitrogen content of arc-melted iron as a function of melting time is shown in Figure 1.28. The curves characteristically exhibit three regions: absorption, the steady-state plateau and, finally, a region of desorption. Katz and King initiated their investigation into the kinetics of nitrogen absorption by studying nitrogen desorption kinetics as a prelude to understanding the absorption process. Their kinetic model is described in the following section.

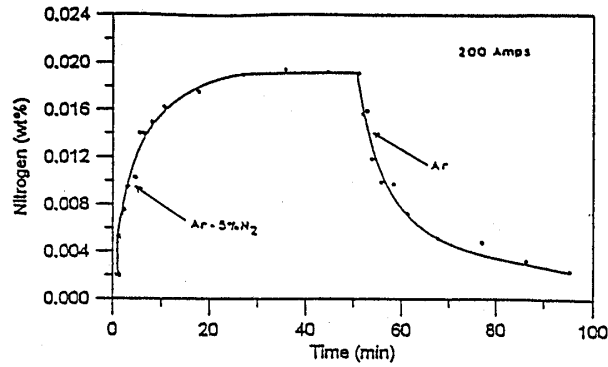
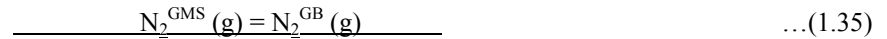


Figure 1.28 The nitrogen content of an arc-melted iron sample as a function of time for an Ar-5% nitrogen plasma.

a. Nitrogen desorption kinetics:

Katz and King studied the desorption of nitrogen from liquid iron into flowing argon during arc melting, based on the assumption that the following elementary steps, equations (1.31) to (1.35), apply to the desorption reaction, summarised by equation (1.36):



where: the superscript ^{MB} refers to the bulk metal,
 the superscript ^{GB} refers to the bulk gas,
 the superscript ^{MBL} refers to the metal-boundary layer, and
 the superscript ^{GMS} refers to the gas-metal surface.

Katz and King observed both first- and second-order kinetics during their investigation, depending on the composition, and in particular the surface active element concentration, of the alloy. Alloys containing high levels of surface active elements displayed second-order desorption kinetics, whereas alloys with low concentrations of these elements displayed first-order kinetics.

• Second-order kinetics:

Katz and King observed that the association of two adsorbed nitrogen atoms to form a nitrogen molecule at the metal surface, reaction (1.33), is rate-limiting in alloys containing surface active elements. For a reaction which is second order with respect to dissolved nitrogen, the initial apparent rate of desorption is expressed as:

$$-\left(\frac{dN(\text{wt}\%)}{dt}\right)_{t=0} = k^{\text{app}}[N_i(\text{wt}\%)]^2 - k^{\text{app}}P_{N_2}K' \quad \dots(1.37)$$

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 where: k^{app} is the apparent rate constant for the desorption reaction, and
 N_i is the initial nitrogen content of the melt (wt%).

Since desorption during the experiments occurred into pure argon, $P_{N_2} = 0$, and as the initial nitrogen content is the same as the steady-state value, the initial apparent rate equation reduces to:

$$-\left(\frac{dN(\text{wt}\%)}{dt}\right)_{t=0} = k^{app} [N_{ss}(\text{wt}\%)]^2 \quad \dots(1.38)$$

where: N_{ss} is the steady-state nitrogen content of the melt (wt%).

The initial rate of desorption divided by the steady-state nitrogen content squared is equal to the initial apparent rate constant for desorption:

$$k^{app} = \frac{-\left(\frac{dN(\text{wt}\%)}{dt}\right)_{t=0}}{[N_{ss}(\text{wt}\%)]^2} \quad \dots(1.39)$$

The initial rate of desorption can be obtained directly from plots such as Figure 1.28 by measuring the slope.

Katz and King's results indicate that the association of two adsorbed nitrogen atoms to form a nitrogen molecule at the surface (step (1.33)) is rate-limiting (as shown by the linear fit in Figure 1.29), with the apparent rate constant of the following form:

$$k^{app} = k^{bs} (1 - \theta_T)^2 \quad \dots(1.40)$$

where: k^{bs} is apparent rate constant on the bare melt surface, and
 $1 - \theta_T$ is the total fraction of vacant surface sites (or the surface availability).

The total fraction of vacant sites (the surface availability) is given as:

$$(1 - \theta_T) = \frac{1}{1 + K_O^{ads}(\text{wt}\% O) + K_S^{ads}(\text{wt}\% S)} \quad \dots(1.41)$$

where: $\log K_O^{ads} = \frac{12995}{T} - 4,96$, and

K_S^{ads} is equal to 67 and 65 per wt% S at 1550°C and 1600°C, respectively.

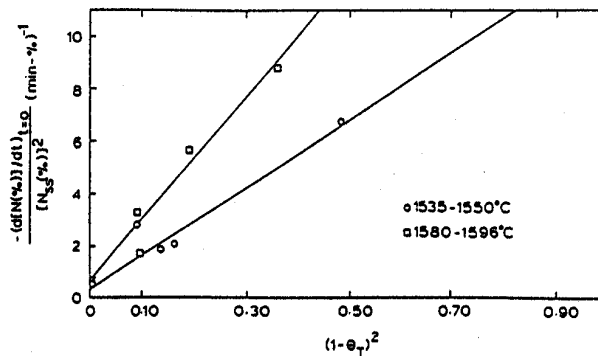


Figure 1.29 Initial apparent rate constants for desorption as a function of surface availability squared²¹.

It is evident that the initial rate of desorption is second order with respect to nitrogen and proportional to $(1-\theta_T)^2$.

The specific and apparent rate constants are related as follows:

$$k^{spec} = k^{app} \frac{V}{A} \quad \dots(1.42)$$

where: V is the melt volume, and
 A is the melt area.

The second-order integrated rate equation is obtained by integrating from $\underline{N}(\text{wt}\%) = \underline{N}_{ss}(\text{wt}\%)$, to $\underline{N}(\text{wt}\%) = \underline{N}_t(\text{wt}\%)$ to obtain:

$$k^{app} t = \frac{1}{\underline{N}_t(\text{wt}\%)} - \frac{1}{\underline{N}_{ss}(\text{wt}\%)} \quad \dots(1.43)$$

where: $\underline{N}_t(\text{wt}\%)$ is the nitrogen content of the melt at time t .

- First-order kinetics:

For melts with low levels of surface-active elements, Katz and King reported that the second-order form of the integrated rate equation does not fit the data well. For these melts, a plot of the rate equation as a function of time is parabolic. These results are better represented by the first-order integrated rate equation which produces a more linear plot. The rate constants were found to correlate with superheat rather than surface coverage. Superheat was calculated by subtracting the liquidus temperature of the iron melt from the actual melt temperature. Since a plot against superheat produces the best correlation (refer to Figure 1.30), the first-order behaviour observed in this study seems to indicate that mass transport in the melt is the rate-limiting step.

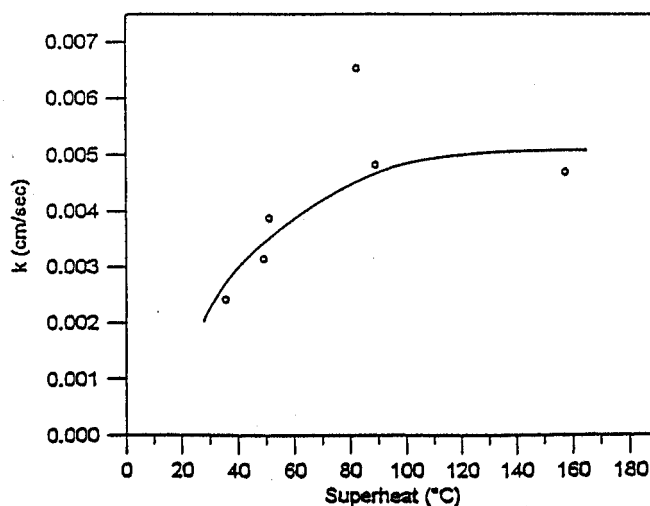


Figure 1.30 First-order rate constants for desorption vs. superheat.

b. Nitrogen absorption kinetics:

Katz and King studied nitrogen absorption kinetics during the arc melting of iron by assuming that the absorption process can be divided into the following sequence of steps:

1. the rate of supply of nitrogen,
2. mass transport through the gas-boundary layer,
3. chemical reaction control, and
4. mass transport through the melt-boundary layer.

Their investigation showed a first-order dependence with respect to nitrogen, which is consistent with mass transport through the melt-boundary layer. The surface-active element concentration was found to have a significant influence on the steady-state nitrogen content and the initial rate of absorption. Mass transfer in the melt appeared to be rate-limiting, and the rate constant was proportional to $(1-\theta_T)^{-1}$.

The initial rate of nitrogen absorption is dependent on the nitrogen content of the plasma. In general, the higher the nitrogen content, the higher the absorption rate. Based on the results shown in Figure 1.31, Katz and King concluded that the initial rate of nitrogen absorption is proportional to $(1-\theta_T)^{-1}[N_e(\text{wt}\%)]$. Examination of this figure, however, suggests that the initial rate of absorption is less dependent on $(1-\theta_T)$ than proposed by these authors.

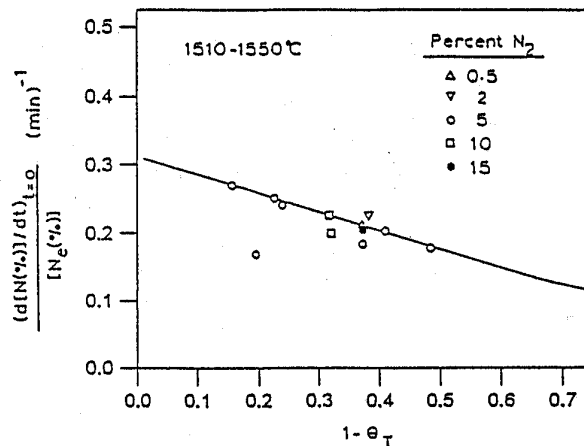


Figure 1.31 Initial rate of absorption divided by the equilibrium nitrogen content as a function of surface availability.

- The forward rate constant and nitrogen potential:

So far, the rate of absorption has been shown to be first order with respect to atomic nitrogen and limited by mass transfer in the melt. Two more parameters, however, are needed to characterise the absorption process fully: the forward rate constant and the atomic nitrogen potential of the arc. As shown earlier, the atomic nitrogen potential of the plasma arc exceeds the equilibrium value. The melt nitrogen content in equilibrium with the atomic nitrogen potential of the plasma arc will be denoted by $[N_f(\text{wt}\%)]$. The initial rate of absorption has been demonstrated experimentally to have the form shown in equation (1.44).

$$\left(\frac{dN(\text{wt}\%)}{dt} \right)_{t=0} = k_F A [N_e(\text{wt}\%)] \quad \dots(1.44)$$

where: k_F is the forward rate constant,
 $N_e(\text{wt}\%)$ is the equilibrium nitrogen content of the melt, and
 A is a constant.

Since the steady-state nitrogen content exceeds $[N_e(\text{wt}\%)]$, the initial rate of absorption can be expressed as:

$$\left(\frac{dN(\text{wt}\%)}{dt} \right)_{t=0} = k_F [N_f(\text{wt}\%)] \quad \dots(1.45)$$

where: $[N_f(\text{wt}\%)]$ is the nitrogen content of a melt in equilibrium with the atomic nitrogen potential of the plasma arc.

It then follows that $[N_f(\text{wt}\%)] = A[N_e(\text{wt}\%)]$, i.e. the atomic nitrogen potential of the arc is proportional to the equilibrium nitrogen potential. Since there are two unknowns, $[N_f(\text{wt}\%)]$ and k_F , they can be solved for if there are two independent equations relating them. The first is simply the initial rate of absorption (equation (1.45)). The second is provided by the steady-state condition. At steady-state, absorption under the arc is balanced by desorption over the remainder of the melt surface. The condition is represented by the following equation:

$$k_F \{ [N_f(\text{wt}\%)] - [N_{ss}(\text{wt}\%)] \} = k_B \{ [N_e(\text{wt}\%)]^2 - [N_{ss}(\text{wt}\%)]^2 \} \quad \dots(1.46)$$

where: k_B is the backward rate constant.

Substituting to eliminate $[N_f(\text{wt}\%)]$:

$$\left(\frac{dN(\text{wt}\%)}{dt} \right)_{t=0} - k_F [N_{ss}(\text{wt}\%)] = k_B \{ [N_e(\text{wt}\%)]^2 - [N_{ss}(\text{wt}\%)]^2 \} \quad \dots(1.47)$$

This equation may be solved if k_F is the only unknown. Values for k_B , $[N_{ss}(\text{wt}\%)]$, $\{dN(\text{wt}\%)/dt\}_{t=0}$, k_F and $[N_f(\text{wt}\%)^{ss}]$ can be obtained from Figure 1.29. The specific forward rate constant can now be calculated for a particular surface coverage and plasma impingement area. Since the rate of mass transfer in the melt is rate-limiting, the specific forward rate constant is the same as the mass transfer coefficient.

Melt mass transfer in a transferred plasma system is complex and can be influenced by at least four factors: electromagnetic stirring, natural convection, momentum transfer from impingement of the plasma jet and surface tension-driven flow. The only dependence of melt mass transfer observed in this study, as determined through measurement of the absorption rate at constant $N_e(\text{wt}\%)$, was with the concentration of surface-active elements. Katz and King concluded that surface tension-driven flow, i.e. Marangoni convection, is an important, if not dominant, contribution to melt mass transfer in the plasma furnace.

The Katz and King kinetic model appears to provide a promising approach to the modelling of nitrogen absorption and desorption during welding, even though the model has to be adjusted to incorporate the influence of alloying elements and welding parameters.

1.8 CONCLUSIONS

The nitrogen content of welds cannot be predicted using relationships, such as Sievert's law, derived under equilibrium conditions. Several researchers have reported nitrogen contents in weld metal far in excess of the values predicted under equilibrium conditions. This has been attributed to the presence of monatomic nitrogen in the arc plasma, formed as a result of the partial dissociation of diatomic nitrogen. A number of thermodynamic models have been developed to describe nitrogen dissolution in welds, but these models are generally highly simplified and do not consider several of the factors known to influence nitrogen absorption and desorption. These factors include the alloying element content of the weld metal, the prior nitrogen content and the surface active element concentration of the weld, and the weld parameters. Results published by Kuwana *et al* for nitrogen dissolution in stainless steel suggest that a kinetic approach may be more appropriate than a thermodynamic method for describing the dissolution of nitrogen in high alloy steels and stainless steels. Katz and King developed a kinetic model for nitrogen dissolution in iron under arc melting conditions, but such an approach has not yet been attempted for high alloy steels.

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