The Influence of Oxygen on Nitrogen Absorption during Arc Melting of Iron

Oxygen present during arc melting of iron results in the formation of an oxygen layer on the surface of the molten metal, which enhances nitrogen absorption

BY J. W. HOOIJMANS AND G. DEN OUDEN

ABSTRACT. In this paper, the results of a study dealing with the influence of oxygen on nitrogen absorption during arc melting of iron are presented. Arc melting experiments were carried out in an argon-nitrogen atmosphere on small samples of pure iron containing various amounts of oxygen. It was found that nitrogen absorption increases with oxygen content of the sample up to an oxygen level of about 0.008 wt-%. Above this level, no further increase of the nitrogen absorption was observed. The total amount of nitrogen absorbed is the result of two mutually independent processes: inflow of nitrogen through the interface between the arc and the liquid metal, and outflow of nitrogen through the entire outer surface of the liquid metal. It was shown that oxygen influences the nitrogen absorption predominantly through its effect on the outflow rate, its effect on the inflow rate being negligibly small. The results obtained can be understood in terms of the formation of an oxygen layer at the surface of the liquid metal, which hampers the outflow of nitrogen. This oxygen layer is destroyed directly under the arc, but remains intact outside the arc.

Introduction

One of the problems occurring when arc welding steel is the absorption of nitrogen by the weld metal. In most cases this nitrogen, originating from the surroundings, influences the mechanical properties of the weld in a negative way (Ref. 1). More specifically, nitrogen favors the conditions for aging, raising the yield stress and the tensile strength and lowering the ductility. At high levels nitrogen can also give rise to pore formation.

The absorption of nitrogen during arc melting (stationary arc) and arc welding (traveling arc) has been studied by various authors (Refs. 2–11). The results of these studies show that nitrogen absorption taking place under arc melting/arc welding conditions is a rather complex phenomenon with many factors playing a role.

One of the most striking features of the absorption phenomenon is the fact that the amount of nitrogen absorbed during arc melting or arc welding is considerably larger than the amount of nitrogen absorbed in the metal when melting under nonarc melting conditions, the latter corresponding with values predicted by Sievert's law (Ref. 12). Although not fully understood, this deviation from normal behavior is attributed to the dissociation of nitrogen in the relatively hot arc and based on the assumption that the absorption rate of atomic nitrogen is higher than that of molecular nitrogen (Ref. 13).

Another important aspect of the absorption phenomenon is the influence of oxygen on the amount of nitrogen absorbed. As reported by most investigators, the presence of small quantities of oxygen gives rise to a considerable increase in the total amount of nitrogen absorbed. Over the past years, various attempts have been made to explain this effect (Refs. 2, 6–8). In spite of these attempts, however, the role played by oxygen in the absorption process of nitrogen during arc melting/arc welding is still unclear. The aim of the study presented in this paper was to further clarify this role.

KEY WORDS

Arc Melting of Iron
Nitrogen Absorption
Oxygen Content
Nitrogen Inflow
Nitrogen Outflow
Weld Pool Surface
Oxygen layer
GTAW
Nitrogen Saturation
Surface Oxygen

Experimental Procedure

Arc melting experiments were carried out under stationary arc conditions, using the equipment described in detail elsewhere (Ref. 11). The central part of the equipment is a stainless steel chamber provided with a thoria-doped tungsten electrode, located in vertical position above a water-cooled copper table on which the sample to be melted was placed. The situation is schematically presented in Fig. 1. Arc melting was performed in an argon-0.4 vol-% nitrogen mixture (purity argon: 99.998%; purity nitrogen: 99.9990%). The two component gases were mixed in a mixing chamber consisting of a number of parallel plates in which small holes were drilled. The flow rate of both component gases was adjusted and measured using flow controllers with an accuracy of about 1%. The flow rate of the mixture was 10 L/min (4.7 ft^3/h). In order to remove unwanted gases, the chamber was twice evacuated before being filled with the desired gas mixture.

J. W. HOOIJMANS and G. den OUDEN are with the Department of Materials Science and Engineering, Delft University of Technology, Delft, The Netherlands.

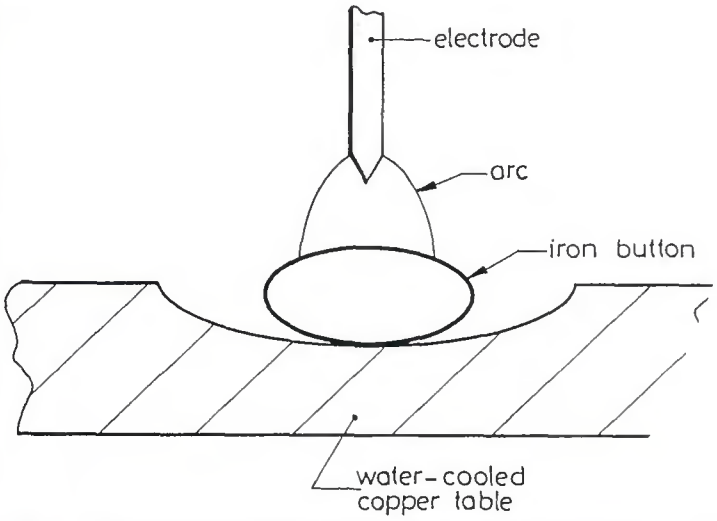

Fig. 1 — Schematic presentation of the central part of the equipment used.

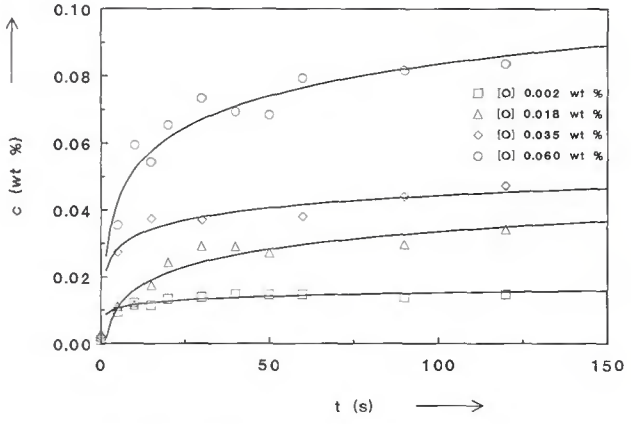

Fig. 2 — Nitrogen concentration as a function of arc time for four samples with different oxygen concentrations.

The material used was technically pure iron (Armco) in the form of small buttons (approximately 1 g). The samples were cut from bulk wire and, after cleaning, premelted in a pure argon atmosphere using a 100-A arc. In this way, the samples obtained their button-like shape, whereas the nitrogen concentration in the material was reduced to approximately 0.001 wt-% and the oxygen concentration to approximately 0.002 wt-%.

To acquire different oxygen concentrations in the metal, the buttons were melted in various argon-oxygen atmospheres during certain periods of time. In this way, samples containing oxygen concentrations between 0.002 and 0.180 wt-% were obtained, while the nitrogen concentration remained unchanged (0.001 wt-%).

Arc melting was carried out using a DC welding power source (Oerlikon TDG 160) provided with high-frequency ignition facilities. Arc voltage and arc current were measured continuously and were registered by means of an x-t recorder. The arc melting conditions used are listed in Table 1.

After solidification and subsequent cooling of the samples at the end of the arc melting experiments, the total nitrogen content and the total oxygen content of the samples were measured using Strohlein equipment of the types NSA-MAT 450 and OSA-MAT 350, respectively.

Table 1 — Arc Melting Conditions

Arc current	100 A
Arc voltage	11 V
Arc length	3 mm
Electrode diameter	3.2 mm
Electrode top angle	60 deg
Shielding gas composition	Ar-0.4 vol-% N_2
Shielding gas flow rate	10 L/min

Results and Discussion

In a first series of experiments, the nitrogen absorption of samples having different oxygen concentrations was measured as a function of arc time. This was done by melting the samples in an Ar-0.4 vol-% N_2 atmosphere for various arc times and determining the absorbed nitrogen after each experiment. The results of measurements on four samples are shown in Fig. 2. In this figure, each point represents the average of at least five measurements, with the scatter in measured nitrogen concentration being maximal 10%. It can be seen in Fig. 2 that the shape of the nitrogen vs. arc time curves is similar for all values of the oxygen content: after a fast initial increase of the nitrogen concentration, a saturation level is reached. This nitrogen saturation level increases with increasing oxygen content. The saturation concentration of the samples containing 0.06 wt-% oxygen, for instance, is about six times higher than the saturation concentration of the samples containing 0.002 wt-% oxygen.

The influence of oxygen on the nitrogen absorption can best be demonstrated by plotting the nitrogen saturation level as a function of the oxygen concentration — Fig. 3. As can be seen in this figure, the nitrogen saturation level increases rapidly with increasing oxygen concentration until the saturation concentration reaches a level of approximately 0.09 wt-%. This concentration is apparently the highest possible under the present conditions and is reached at an oxygen concentration in the liquid metal of about 0.08 wt-%.

The present results are in good agreement with the results obtained by other investigators carrying out experiments under arc melting conditions (Ref. 7) and also agree with the results of experiments carried out on iron and steel under non-arc melting conditions (Refs. 12, 13).

In order to check whether all oxygen originally present in the sample remains in the sample during the arc melting experiment, two series of samples containing different amounts of oxygen (0.018 and 0.12 wt-%, respectively) were first saturated with nitrogen and subsequently degassed by arc melting in pure argon during increasing periods of time. After each melting experiment, the oxygen concentration of the sample was measured. In Fig. 4, the measured oxygen concentration of the samples is plotted as a function of degassing time. Although there is some scatter in the results, it appears that the oxygen concentration in the samples scarcely changes with degassing time. In the case of the sample with relatively high oxygen level (0.12 wt-%) only a slight decrease can be observed, whereas in the case of the sample with relatively low oxygen level (0.018 wt-%) the concentration remains virtually constant.

In the next series of experiments the nitrogen desorption was measured. Samples containing three different oxygen levels (0.002, 0.018 and 0.060 wt-%, respectively) were saturated with nitrogen and subsequently degassed by arc melting in a pure argon atmosphere during increasing periods of time. After each melting experiment, the nitrogen concentration of the sample was measured. The results of these measurements are given in Fig. 5. In this figure, the nitrogen concentration is plotted as a func-

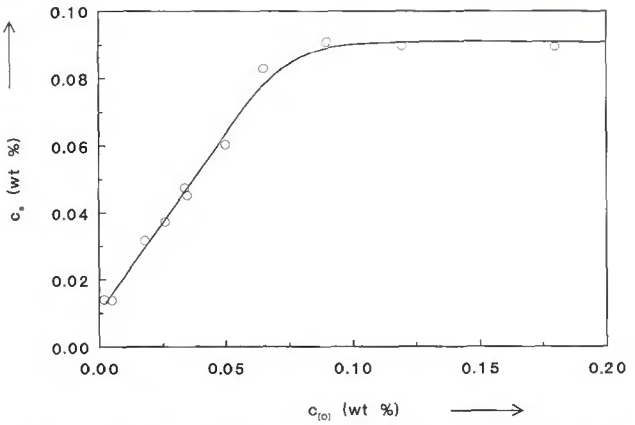

Fig. 3 — Nitrogen saturation concentration as a function of oxygen concentration.

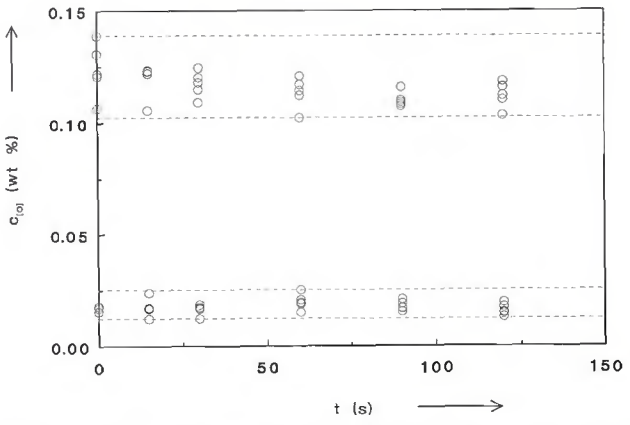

Fig. 4 — Oxygen concentration as a function of degassing time for two series of samples with different initial oxygen concentrations.

tion of degassing time. Again each point represents the average of at least five measurements. Figure 5 clearly shows that the nitrogen concentration decreases with degassing time, the decrease being slower when more oxygen is present in the liquid metal. Obviously, oxygen hampers the desorption of nitrogen.

The results described in the foregoing seem to suggest that the effect of oxygen on the nitrogen absorption is directly related to the surface activity of oxygen. In particular, it appears that the oxygen at the surface impedes the escape of nitrogen, giving rise to higher nitrogen levels in the material.

In order to verify this conclusion and to obtain more quantitative insight in the role of oxygen, the mechanism of nitrogen absorption during arc melting will be considered in more detail.

Recently, Den Ouden and Griebling (Ref. 11) proposed a simple model of nitrogen absorption during arc welding. According to their model, the nitrogen concentration in the melt is the result of two mutually independent processes: inflow and outflow. Inflow of nitrogen takes place exclusively through the interface between the arc and the liquid metal, the inflow rate being determined by the arc conditions (notably the partial pressure of the nitrogen in the arc and the temperature of the arc). Outflow of nitrogen takes place through the entire outer surface of the liquid metal (including that part of the surface which is covered by the arc), the outflow rate being proportional to the nitrogen concentration in the liquid metal. On this basis, the time-dependent change in nitrogen concentration can be described by the equation

$$\frac{dN}{dt} = W\frac{dc}{dt} = \alpha A - \beta B c \qquad (1)$$

with N the amount of nitrogen present in the liquid metal, c the nitrogen concentration in the liquid metal, t the time, W the sample weight, A the interface area between the arc and the liquid metal, B the interface area between the liquid metal and the surrounding gas phase, α the inflow coefficient (the amount of nitrogen entering the liquid metal per unit area per unit time) and β the outflow coefficient (the amount of nitrogen leaving the liquid metal per unit area per unit time).

The solution of differential Equation 1 can be written as:

$$c(t) = \frac{\alpha A}{\beta B}\left[1 - exp\left(-\frac{\beta B}{W}t\right)\right] \qquad (2)$$

Saturation occurs when the amount of nitrogen entering the liquid metal per unit time equals the amount of nitrogen leaving the liquid metal per unit time. The saturation value c_s can be obtained by substituting $t = \infty$ in Equation 2, which leads to:

$$c_s = \frac{\alpha A}{\beta B} \qquad (3)$$

Using Equations 1, 2 and 3 and the experimental data presented in Figs. 2 and 5, values of α and β were calculated

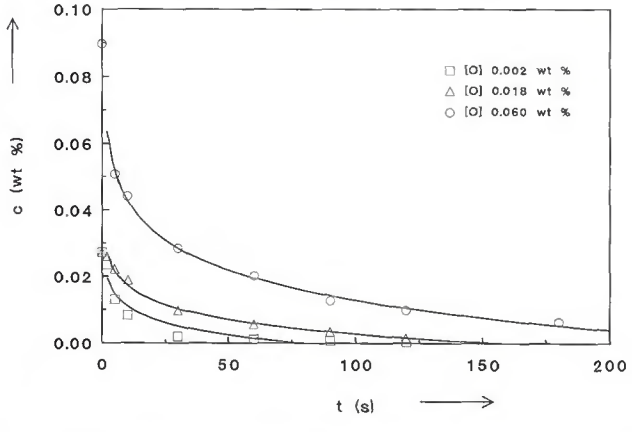

Fig. 5 — Nitrogen concentration as a function of degassing time for three series of samples with different oxygen concentrations.

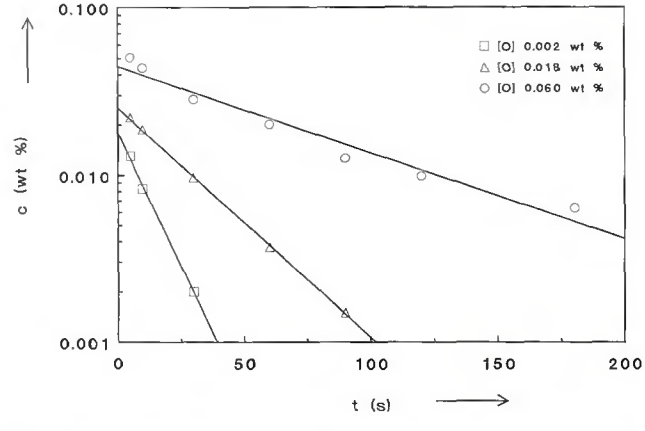

Fig. 6 — Logarithm of nitrogen concentration as a function of degassing time for three samples with different initial nitrogen concentrations (semilogarithmic plot of the experimental data presented in Fig. 5).

Table 2 — The Inflow Coefficient α and the Outflow Coefficient β for Samples with Different Oxygen Concentrations

[O] (wt-%)	α (g/sm^2)	β (g/sm^2)
0.002	0.55	0.95×10^3
0.018	0.52	0.40×10^3
0.060	0.45	0.13×10^3

as follows:

First, the linear plot of Fig. 5 (nitrogen concentration vs. degassing time) was converted to the semilogarithmic plot of Fig. 6 (logarithm of nitrogen concentration vs. degassing time). In this semilogarithmic plot, nitrogen concentrations below 0.001 wt-% have been omitted. As can be seen, the experimental data presented in Fig. 6 can be easily approximated by straight lines. From the slope of these lines and measured values of B, values of β were calculated with the help of Equation 2, taking into account that $\alpha = 0$ (degassing).

From the obtained values of β and the saturation concentrations c_S given in Fig. 2, values of α were calculated using Equation 3. In Table 2, values of α and β calculated in this way are given for the three oxygen levels. It appears that α decreases only slightly, whereas β decreases rapidly with increasing oxygen level. This leads to the conclusion that oxygen influences the nitrogen absorption predominantly through its effect on the outflow rate, with its effect on the inflow rate being negligibly small.

This behavior can be understood by assuming that, as in the case of nonarc melting of iron and steel (Refs. 14, 15), oxygen forms an electrostatic double-layer of O^{2-} and Fe^{2+} on the surface of the liquid metal, which hampers the passage of nitrogen atoms. Directly under the arc, this surface layer is virtually destroyed due to the high temperature of the arc plasma and by the impinging plasma jet so that the inflow rate will scarcely be affected. However, outside the arc the surface layer remains intact and the escape of nitrogen atoms (*i.e.* the outflow) is hampered.

As can be seen in Fig. 3, oxygen is only active in the concentration range up to approximately 0.08 wt-%. Increasing the oxygen concentration above this level does not affect the nitrogen absorption any further. This can be understood by assuming that the oxygen layer at the surface of the liquid metal builds up with increasing oxygen concentration until at a level of 0.08 wt-% the formation of the layer is completed.

It is interesting to note that in melting experiments under nonarc equilibrium conditions (Refs. 14, 15), the threshold level above which the oxygen is not active any more is considerably smaller (0.02–0.04 wt-%) than that found in the present work under arc melting conditions (0.08 wt-%). This apparent discrepancy can be explained by realizing that in the case of arc melting more vigorous stirring of the liquid metal occurs. This type of stirring is due to electromagnetic- and surface tension-induced forces (Ref. 16) that are absent in the case of nonarc melting. Due to stirring of the liquid metal in the case of arc melting, a higher overall oxygen concentration is required for the surface to be completely covered by an oxygen layer.

Conclusions

On the basis of the results presented in this paper, the following conclusions can be drawn:

1) The absorption of nitrogen during arc melting and arc welding of iron is strongly affected by the presence of oxygen in the material: the nitrogen saturation level increases with increasing oxygen concentration up to an oxygen concentration of about 0.08 wt-%, becoming constant for oxygen concentrations above this value.

2) The total amount of nitrogen absorbed is the result of two mutually independent processes: inflow of nitrogen through the interface between the arc and the liquid metal, and outflow of nitrogen through the entire outer surface of the liquid metal. Oxygen influences the nitrogen absorption predominantly through its effect on the outflow rate. The effect of oxygen on the inflow rate appears to be negligibly small.

3) The role of oxygen can be understood by assuming that oxygen forms a layer on the surface of the liquid metal that hampers the passage of nitrogen atoms. Directly below the arc, this layer is virtually destroyed by the arc plasma, and consequently, the inflow of nitrogen is only slightly affected. Outside the arc, the layer remains intact, which results in a considerable reduction of the outflow rate.

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