The influence of gas tungsten arc (GTA) melting conditions in Ar+2% N₂ and Ar+2% N₂+0.2% O₂ atmospheres and oxygen content in filler metals on the kinetics of nitrogen absorption by Fe-C-Mn-type filler metals has been analyzed. This process was investigated in conjunction with other phenomena occurring in melted filler metals. The nitrogen absorption by arc-melted Fe-C-Mn-type filler metals has been described by the first-order kinetic expression, dividing the total surface area of the melted specimen by the region of the electric arc interaction and the region contacting with the cooler shielding gas. Based on this model, the time-dependent changes of nitrogen content were determined, as well as the mass transfer coefficients and the rates of the nitrogen absorption in various melting conditions. It has been shown that the conditions of nitrogen absorption by arc-melted Fe-C-Mn-type filler metals differ much from the mechanism suggested for pure Fe and solutions in the Fe-O system. The carbon deoxidation reaction running at high temperatures is a factor limiting the nitrogen absorption by arc-melted Fe-C-Mn-type filler metals. An increase of the nitrogen absorption rate and nitrogen content as a result of decreased melting current correlated with the reduction of carbon deoxidation and manganese evaporation, as well as with the formation of liquid oxides that reduce nitrogen desorption from the areas not subjected to the arc interaction.

Introduction

The development of welding is connected with the improvement of methods to protect the liquid metal from atmospheric nitrogen. This concerns, in particular, arc welding, in which the nitrogen content in welds may exceed many times the values resulting from Sievert's law (Refs. 1-3). This reduces the ductility of welds as well as the operational properties of welded structures, which are often made of high-quality steels, resistant to brittle cracking. On the other hand, in recent years the number of weldable steels in which nitrogen is an alloy element, e.g., duplex steels, has been constantly growing. Another problem is how to achieve welds with a strictly controlled nitrogen content, approaching the content of nitrogen in welded steels (Refs. 4, 5). Such problems can be solved only if the mechanisms of the nitrogen absorption and desorption during arc welding are thoroughly known. An investigation concerning the kinetics of nitrogen absorption and the influence of oxygen on these processes seems to be of crucial importance.

The complexity of phenomena associated with arc welding does not allow a univocal determination of those factors that influence the content of nitrogen in welds based merely on welding tests. Investigations of arc melting in controlled gaseous atmospheres have made it possible to explore the mechanisms and kinetics of nitrogen absorption more strictly. It is supposed that some of the main reasons for intensified absorption of nitrogen are dissociation, ionization, and activation of nitrogen occurring in the arc (Refs. 6-9). Oxygen as a factor affecting nitrogen absorption by liquid metals and alloys is also a matter for investigation. Contrary to arcless melting, oxygen is supposed to favor nitrogen absorption during arc melting and arc welding of steel and iron. Some authors (Refs. 10-12) emphasize the role of nitrogen oxide (NO) in facilitating nitrogen transport from the gaseous phase of the arc to the liquid metal. Another explanation has also been suggested (Refs. 13, 14) for the role of oxygen as an agent to increase nitrogen content in arc-melted Fe-O systems. The model of absorption presented by these authors assumes that the final nitrogen content results from the established dynamic equilibrium between the amount of absorbed nitrogen and the nitrogen desorbed from the liquid metal. The absorption takes place on the oxide-free metal surface contacting the arc. On the other hand, oxides restrict the desorption of nitrogen in those regions not subject to arc interaction, and favors the increase of nitrogen content.

Until now, most of the results presented concerning nitrogen absorption are devoted to pure iron or binary Fe matrix alloys, as well as experiments simulating conditions that are closer to steelmaking processes than to welding (Refs. 1, 2, 7, 13). In arc welding processes, nitrogen absorption is usually accompanied by other metallurgical reactions and intensive convection of liquid metal (Refs. 15-18). These investigations concerning the nitrogen absorption do not take into consideration these phenomena to a sufficient extent. In analyzing the processes of nitrogen absorption during arc melting and arc welding, the mentioned problems shouldn't be neglected. The starting point to formulate a thesis is the fact that the content of alloy elements and impurities in filler metals and welded materials corresponds approximately to the thermodynamic equilibrium of steelmaking processes. Significant differences between the thermodynamic and kinetic conditions of steelmaking processes, on the one hand, and arc welding, on the other, intensify metallurgical reactions during arc welding and affect the absorption of nitrogen.

Experimental Procedure

Materials

The investigation concerned industrial melts of Fe-C-Mn-type filler metals, as presented in Table 1.

The kinetics of nitrogen absorption...
were investigated in gas tungsten arc (GTA) melting conditions aiming to achieve comparable conditions in the experiment to those taking place during the formation and existence of liquid metal drops in arc welding, in particular, the possibility of getting a high temperature for the liquid metal, a large specific surface area, and cooling rate, and melting at short time intervals. The mass of the melted specimens was equal to 0.6 g. The gaseous atmospheres in which the melting took place included argon (99.995%) containing less than 0.0005% O₂, 0.003% N₂, 0.0001% hydrocarbons, 0.0001% CO₂, 0.0005% moisture and its mixtures with nitrogen (99.9988%) and oxygen (99.5%) Ar+2%N₂ and Ar+2%N₂+0.2%O₂.

**Equipment**

The investigations were carried out on a test stand, as partially shown in Fig. 1. The melting process took place in a quartz tube with a diameter of 20 mm in the shielding gas flow. The anode consists of a water-cooled copper base of 10 mm diameter, the cathode was a thoriated tungsten electrode of 2.6 mm in diameter. An essential part of the test stand was a system for adjusting the chemical composition and flow rate of the gas mixtures. It was equipped with a gas mixer, electronic gas flow regulators, and a control system setting the time of melting. The arc, oxygen and nitrogen contents in the investigated samples were determined using ON-mat 6500 STROHLEIN analyzer, by the carrier gas method, through their fusion into outgassed graphite crucibles in the helium atmosphere. The methods of detection used were thermal conductivity measurement of gases for nitrogen and infrared absorption for oxygen determination. The error in measuring nitrogen content ranged from 3 to 5% of the measured quantity. The carbon and sulfur contents were measured using a SPECTROLAB F spectral analyzer.

**Table 1 — Chemical Composition of the Tested Filler Metals**

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<th>No.</th>
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<td>0.0060 0.0219 0.086</td>
<td>Ar+2%N₂ 1,2,3,5,10,20,40</td>
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<td>arc length about 1.5 mm</td>
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<tr>
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**Table 2 — Range of Investigation on the Kinetics of Nitrogen Absorption by Liquid Fe-C-Mn-Type Filler Metals**

<table>
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Measurement carried out using a 0.2-mm-diameter W-Mo thermocouple (Fig. 1) indicated that the 0.5-g specimens melted at a current of 60 A reached a liquid metal temperature of 2000°C. At a current of 100 A, the liquid metal drop reached a temperature of 2400°C. In the latter case, the results should be treated as approximate ones, due to the quick damage of the W-Mo thermocouples in the liquid metal.

In this investigation the following melting parameters were applied:
- Current, 100 or 60 A.
- Polarity, (−) tungsten electrode.
- Arc length, 2.5 mm (1.5 mm, third test series).
- Shielding gas, Ar+2%N₂ and Ar+2%N₂+0.2%O₂.
- Flow rate of the shielding gas, 10 L/min.
- Specimen melting times, 1, 2, 3, 5, 10, 20, and 40 s.

The nitrogen and oxygen contents in the melted samples were determined for all test series without removing the oxides created during melting from their surfaces. The samples were stored in an evacuated vessel for 24 hours before analysis. The contents of carbon and oxygen were determined using a CS-mat 6500 analyzer, by infrared absorption for oxygen determination. The error in measuring nitrogen content ranged from 3 to 5% of the measured quantity. The carbon and sulfur contents were measured using a SPECTROLAB F spectral analyzer.

**Arc Melting Experiment**

The scope of the research on the kinetics of nitrogen absorption, melting parameters, and initial contents of nitrogen, oxygen, and carbon in the specimens are presented in Table 2. After the melting conditions had been established, a specimen of the tested filler metal was placed on a copper base (Fig. 1) and the arc was ignited. After about 1.5 s at I = 100 A, the specimen was completely melted, and from that moment the electronic system started counting the time of melting. Then the specimen was cooled down in a flux of shielding gases to ambient temperature. The interval between the breaking off of the arc and solidification of the specimen did not exceed one second.

**Equipment**

The investigations were carried out on a test stand, as partially shown in Fig. 1. The melting process took place in a quartz tube with a diameter of 20 mm in the shielding gas flow. The anode consists of a water-cooled copper base of 10 mm diameter, the cathode was a thoriated tungsten electrode of 2.6 mm in diameter. An essential part of the test stand was a system for adjusting the chemical composition and flow rate of the gas mixtures. It was equipped with a gas mixer, electronic gas flow regulators, and a control system setting the time of melting. The arc, oxygen and nitrogen contents in the investigated samples were determined using ON-mat 6500 STROHLEIN analyzer, by the carrier gas method, through their fusion into outgassed graphite crucibles in the helium atmosphere. The methods of detection used were thermal conductivity measurement of gases for nitrogen and infrared absorption for oxygen determination. The error in measuring nitrogen content ranged from 3 to 5% of the measured quantity. The carbon and sulfur contents were measured using a SPECTROLAB F spectral analyzer.

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The nitrogen and oxygen contents in the melted samples were determined for all test series without removing the oxides created during melting from their surfaces. The samples were stored in an evacuated vessel for 24 hours before analysis. The contents of carbon, manganese, and sulfur were determined for the samples under the same melting conditions. The results of these experiments are presented in Figs. 2-6. The contents of
nitrogen and oxygen were given as mean values from five (second, fourth, fifth, and sixth test series) or four (first and third test series) identical melting tests. The mean values of nitrogen shown in Figs. 2-6 were enlarged by the range x, x+s, x-s, where x is the mean value of nitrogen contents and s is the standard deviation. Because of the significant differences in the oxygen content results for the fifth test series, there are no mean values for oxygen content in Fig. 6. The carbon, manganese, and sulfur contents were given as mean values of three series of melting tests.

Discussion of Results

The filler metals used in this investigation had similar nitrogen contents but different oxygen and carbon contents. Experiments using GTA melting with currents of 100 and 60 A were carried out in an oxygen-free atmosphere of Ar+2%N2 as well as in a slightly oxidizing atmosphere of Ar+2%N2+0.2%O2 — Table 2.

In the first test series (Fig. 2, Table 2), the filler metal heat C, containing an initial nitrogen content of 60 ppm and an oxygen content of 219 ppm, was used. After one second of melting in an atmosphere of Ar+2%N2, the nitrogen content increased to approximately 286 ppm, whereas the oxygen content dropped in the same time to about 20 ppm. Simultaneously, the carbon content decreased from 0.086% to 0.072%, and in all cases of prolonged melting time its content remained unchanged. The changes of the oxygen and carbon contents correspond, more or less, to the stoichiometric ratio of the C + O = CO reaction. This indicates that the deoxidation process of Fe-C-Mn alloys, heated by an arc to a temperature of approximately 2400°C, runs mainly with carbon contribution. This also has been confirmed by Gibb's free-enthalpy calculations for steels deoxidizing reactions by carbon and manganese — Table 3.

The carbon deoxidation down to 5 ppm of oxygen (Fig. 2) can be explained by the shielding gas used (Ar+N2), and also by the two factors of the reaction products from above the liquid metal level. According to the law of mass action, the lower the partial pressure of CO above the metal bath, the higher the deoxidizing capability of carbon.

The reaction rate of deoxidation also deserves to be discussed. Deoxidation by carbon is a heterogeneous process, conditioned by the simultaneous presence of C and O at the phase boundary. If melting takes place in an atmosphere deprived of oxygen, the source of oxygen and carbon is the melted filler metal. The reactions run in the following order:

\[
[C] + M = \text{C}_{\text{ads}} \\
\text{O}_{\text{ad}} + M = \text{O}_{\text{ads}} \\
\text{C}_{\text{ads}} + \text{O}_{\text{ads}} - M = \text{CO}_{\text{ads}} \\
\text{CO}_{\text{ads}} - M = \text{CO}_{\text{g}} \uparrow \\
[C] + [O] = \text{CO}_{\text{g}}
\]

The high temperature, intensive convection of the liquid metal (Refs. 15-17), and large specific surface of the liquid metal drop facilitate the transfer of oxygen and carbon to the boundary of the liquid and gaseous phase. In such conditions the carbon deoxidation may have a bubbleless character (Refs. 20, 21).

Increasing the time of melting of the filler metal heat C causes the content of nitrogen to grow, reaching a steady-state content of about 400 ppm after 10 seconds (which is not the equilibrium of nitrogen in thermodynamic means, but the moment at which an equilibrium is reached between the amount of absorbed and desorbed nitrogen by the melted metal specimen). The linear decrease of the manganese content of about 0.01% Mn/s is mainly due to losses caused by intensive evaporation.

In the second test series (Fig. 3, Table 2), the filler metal heat B was used with an extremely high oxygen content (585 ppm) and low carbon content (0.042%). It was melted under the same conditions. The deoxidation process took place until the carbon content dropped to several thou-
sandwich percent and the oxygen went down to 150 ppm. After that the oxygen content showed a slight increase. After five seconds of melting, the nitrogen content stabilized on a level of about 360 ppm. The high oxygen content compared with the first test series did not affect the increase of the steady-state nitrogen content. The tendency to a slower increase of the nitrogen content was observed.

In the third series of tests (Fig. 4, Table 2) the filler metal heat C was melted in the Ar+2%N₂ atmosphere at the current of 100 A. This filler metal had been preliminarily melted in an atmosphere of pure argon with the GTA melting process. After this premelting, the oxygen content was approximately 3.5 ppm and the nitrogen content was 22 ppm. It was found that the nitrogen content increased with the growing time of melting, similarly as in the first and second series of investigation. The oxygen content remained unchanged in the melted specimens.

In the specimens from the fourth series of tests, the changes in oxygen and nitrogen contents proceeded in a different way. The specimens were melted in the Ar+2%N₂+0.2%O₂ atmosphere containing oxygen — Fig. 5, Table 2. The filler metal heat C that was melted contained 219 ppm of oxygen, 60 ppm of nitrogen, and 0.086% of carbon. Initially the oxygen content dropped from 219 ppm to about 150 ppm and remained on this level for about 10 seconds. In the same time, the nitrogen content increased slowly reaching a steady-state content at about 300 ppm, which was a level lower than the previously melted filler metal from heat C in the Ar+2%N₂ atmosphere — Fig. 2. After 20 seconds of melting, the carbon content dropped almost to zero (0.0038%), whereas the oxygen increased to 380 ppm, while simultaneously the nitrogen content went to about 390 ppm. A prolongation of the melting time to 25 seconds resulted in a nitric boiling of the liquid metal, an increase of nitrogen content to 624 ppm and oxygen content to 760 ppm. The rapid growth of the nitrogen content started only after the carbon had been combusted, with the simultaneous increase of the oxygen content. Deoxidation with carbon affects essentially the nitrogen content in arc-melted Fe-C-Mn alloys. During the initial melting phase, deoxidation with carbon reduced the oxygen content in the investigated filler metal from 219 ppm to about 150 ppm. Our current knowledge of the influence of oxygen on the nitrogen absorption by arc-melted iron (Fe) indicates that this might be considered suffi-
The reduction of manganese during melting in the Ar+2%N₂ atmosphere amounted to about 0.016% Mn/s, and was markedly higher than the same filler metal melting in the Ar+2%N₂ atmosphere — Figs. 4, 5. The character of deoxidation of Fe-C-Mn type filler metals during arc melting in an oxidizing atmosphere is more complex than in an oxygen-free atmosphere. The atmosphere in which melting is carried out is an additional source of oxygen. Apart from the process described by Equation 1, the following reaction may take place on the surface of liquid metal contacting the oxidizing atmosphere:

\[
[C] + M = C_{ads} \quad (2a)
\]
\[
O_g + M = O_{ads} \quad (2b)
\]
\[
C_{ads} + O_{ads} - M = CO_{ads} \quad (2c)
\]
\[
CO_{ads} - M = CO_g \quad (2d)
\]
\[
[C] + O_g = CO_g \quad (2)
\]

The rapid simultaneous increase of the oxygen and nitrogen after oxidation of carbon (Fig. 5) suggests that nitrogen is absorbed in compliance with the opinion expressed in Refs. 3 and 10, i.e., according to the reaction NO + Fe = [FeO] + [N].

The thermodynamical analysis confirms the possibility of a nitrogen oxide (NO) reaction with iron (Fe), accompanied by the simultaneous solution of oxygen and nitrogen — Table 3. However, in the fourth series of measurements, the simultaneous increase of oxygen and nitrogen occurred only after the deoxidation with carbon had been completed, which indicates that the sharp growth of the nitrogen content is related to the lack of balance between the absorbed and desorbed nitrogen caused by the formation of liquid oxides, as suggested in Refs. 13, 14.

The reduction of manganese during melting in the Ar+2%N₂+0.2%O₂ atmosphere proved the significant effect liquid oxides have on nitrogen absorption in arc melting conditions. The filler metal heat C was melted in a Ar+2%N₂+0.2%O₂ atmosphere with a current of 60 A. When the melting time exceeded three seconds, a noticeable porosity in the specimens was observed, making determination of nitrogen content impossible. After switching off the arc, in most cases, the formation of a single large bubble was observed (the specimen visibly enlarged its volume). This can be explained by the limited solubility of nitrogen in the liquid metal while solidifying and confining desorption from the sample due to the presence of liquid oxides on its surface.

After reducing the current with GTA melting from 100 to 60 A in the Ar+2%N₂+0.2%O₂ atmosphere, the manganese content in the melted samples decreased from 0.016% to about 0.005% Mn/s — Figs. 5, 6. This also intensifies the nitrogen absorption in Fe-C type filler metal melting.

The values for standard deviations in nitrogen measurements range mostly from a several to 20% of the mean value — Figs. 2-6. Only in one case (Fig. 5) was the value of standard deviation greater than 20% when the molten metal (for 20 s melting time) was passing from the quasi-equilibrium state to the nitrogen boiling state.

**Kinetic Model of Nitrogen Absorption in Arc Melting Conditions**

The quantitative parameters characterizing the kinetics of nitrogen absorption in arc melting conditions have been determined, based on the model discussed in Ref. 23. The following assumptions have been made:

The surface of the melted drop was divided into the area F_b subjected to contact with the electric arc and the area F_a subjected to contact with an oxidant:
jected to contact with the cooler shielding gas. The total surface of the melted specimen equals \( F = F_a + F_b \) (Fig. 7).

Under the analyzed conditions, the nitrogen absorption is subjected to the first-order reaction in respect to nitrogen concentration. The rate-limiting step is the transfer of nitrogen in the liquid metal (Refs. 7, 18, 24, 25).

Thus, it may be assumed that in the course of melting on the surface \( F_a \) there exists an equilibrium concentration of nitrogen \([N]^*\) in the liquid metal in contact with the arc, and on the surface \( F_b \) an equilibrium concentration of nitrogen \([N]_o\) in the liquid metal in contact with the cool shielding gas. During the initial stage of melting, when the nitrogen content in the liquid metal \([N]_o\) is lower than \([N]^*\), the nitrogen penetrates into the liquid metal through the whole outer surface of the drop. When \([N]_o\) exceeds the value of \([N]^*\), the absorption on the surface \( F_b \) proceeds, whereas on the surface \( F_a \), nitrogen desorption occurs — Fig. 7. If the fluxes of the absorbed and desorbed nitrogen reach the same level, the nitrogen content in the specimen does not undergo any changes and the steady-state level \([N]^*\) is maintained.

Taking into consideration these assumptions, it can be expressed by the equation

\[
\frac{d[N]^*}{dt} = \frac{\beta F_a}{V} \left( [N]^* - [N]_o \right) + \frac{\beta_b F_b}{V} \left( [N] - [N]^* \right)
\]  \hspace{1cm} (3)

Integrating and transforming Equation 3, the nitrogen concentration in the drop as a function of time may be expressed as follows:

\[
[N]_o = A - B \exp(-C) \cdot t
\]  \hspace{1cm} (4)

where

\[
A = \frac{\beta_b F_a}{\beta_b F_b} [N]^* + \frac{\beta_a F_a}{\beta_b F_b} [N]_o
\]

\[
B = \frac{\beta_b F_a}{\beta_b F_b} [N]^* + \frac{\beta_a F_a}{\beta_b F_b} [N]_o - [N]^*
\]

\[
C = \frac{\beta_b F_a}{\beta_b F_b} + \frac{\beta_a F_a}{\beta_b F_b}
\]

The variation of nitrogen content \([N]_n\), as a function of time, as well as other parameters characterizing the kinetics of the nitrogen absorption have been determined in two different ways. The first of these methods is based on the experimental determination of values for \( F_a, F_b, V, [N], [N]^* \). The other components of Equation 4, i.e., the mass transfer coefficients \( \beta_a \) and \( \beta_b \), were determined analytically based on the boundary conditions of Equation 3. The most difficult problem was to determine the value of \([N]^*\), i.e., the equilibrium concentration of nitrogen in liquid metal contacting the arc. In order to determine the value of \([N]^*\) experimentally, the whole surface of the drop should contact the electric arc atmosphere. It was impossible to create such conditions during the test carried out. Furthermore, no empirical relations exist that might make it possible to determine the value of \([N]^*\). Therefore, it was assumed that \([N]^* = 624 \text{ ppm}\) in all test series on the \( F_a\) surface. This is the level of nitrogen at which nitrogen boiling of the arc-melted Fe-C-Mn-type filler metal has been observed. Such phenomena occurred in the fourth series of tests when the melting lasted longer than 25 s — Fig. 5. The equilibrium concentrations of \([N]^*\) may be different somewhat in the respective series of tests, as these values depend on the parameters of the arc and the chemical composition of the melted filler metal.

According to Ref. 18, the equilibrium concentration of nitrogen \([N]^*\) at the boundary between the liquid phase \( F_b\) and the shielding gas has been assumed to be equal to the following:

\[
[N] = 90 \text{ ppm} \text{ in the first to fourth series of tests} \quad (I = 100 \text{ A, } P_{N2} = 2026 \text{ Pa}, \text{ for the temperature of the liquid metal at about } 2400^\circ C)
\]

\[
[N] = 85 \text{ ppm} \text{ in the fifth and sixth series of tests} \quad (I = 60 \text{ A, } P_{N2} = 2026 \text{ Pa}, \text{ for the temperature of the liquid metal at about } 2000^\circ C)
\]

For the arc length of 2.5 mm, it has been assumed that \( F_a/F_b = \frac{1}{3} \). In the third series of tests with the length of the arc shortened to 1.5 mm, the calculations were based on the assumption that \( F_a/F_b = \frac{1}{2} \).

In the second method of calculation, the constants \( A, B, C \) in Equation 4 were calculated applying the least squares method for a nonlinear model, making use of the existing procedure for solving optimization problems, contained in the SOLVER option of Microsoft® Excel. Calculations were carried out based on the average nitrogen contents in the melted specimens. Calculations of the \( A, B, C \) constants using the least squares method allowed for correction to earlier determined values for \( \beta_a \) and \( \beta_b \), applying the

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<td>Initial Content (ppm)</td>
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| Nitrogen Content | | | | | | |
| \([N] = A - B \exp(-C) \cdot t, (ppm)\) | Method I | Method II | Method I | Method II |
| \([N]_o = 60 \text{ ppm}\) | | | | | | |
Equations 4a, 4b, and 4c. The values of $F_a$, $F_b$, $[N]^*$, $[N]^*$, $[N]$, and $V$ remained on the same level as in the first method of calculation.

The graphical results for calculations of $[N]^*$ and the absorption rate of nitrogen $d[N]/dt = f[N]$, based on Model 3 for the first test series, are shown in Fig. 8. The linear relation $d[N]/dt = f[N]$ can be expressed in the following form:

$$d[N]/dt = -C [N] + F$$

(5)

The constant $F$ expresses the absorption rate of nitrogen for $[N] = 0$. The constant $C$ characterizes the rate at which the system attains the steady-state level.

The whole set of parameters for all series of tests, characterizing the kinetics of nitrogen absorption calculated based on Model 3, is shown in Table 4. The values of $d[N]/dt$ were determined for $[N] = 60$ ppm. They approach the value of the initial nitrogen content in the tested filler metals, which corresponds to the initial stages of the filler metal melting. Such conditions may exist, for instance, in arc welding processes during the formation and transition of the liquid metal drops to the weld pool. In the case of the fourth test series, the presented relations and values are valid until the carbon in the melted specimen is completely oxidized.

Discussion on the Model of Nitrogen Absorption

The results obtained from the calculation proved the usability of Model 3 for the analysis of nitrogen absorption during arc melting. The absorption of nitrogen by arc-melted Fe-C-Mn-type filler metals may be described by the first-order kinetic expression, which indicates that the rate-limiting step is the transfer of nitrogen in the liquid phase. The mass transfer coefficients in the region contacting the electric arc $F_a$ and the cooler shielding gas $F_b$ for the assumed melting conditions (Table 4) are at least one order higher than the value of $F$ determined for the inductive melting of the same filler metals (Ref. 18).

The high temperature of the liquid metal (diffusion is a thermally activated process) and the decreased thickness of the diffusion layer $\delta$ due to the intensive convection of liquid metal during arc melting (Refs. 15-17) can be explained by the high temperature of the liquid metal and the increased absorption rate due to the formation of carbon oxide at high temperatures.

After a full oxidation of carbon, the presence of liquid oxides also drastically increased the nitrogen content in the samples melted with the high-intensity current in Ar+2%N$_2$+0.2%O$_2$ atmosphere (fourth test series, Fig. 5). Thus, Model 3 shows the non-linear behavior of the phenomenon that occurs during arc melting of Fe-C-Mn-type filler metals. A different approach to explain the influence of temperature on gas absorption was presented in Ref. 26. On the basis of thermodynamic analysis, it has been shown that the most intensive absorption of hydrogen during arc welding should take place in the outer regions of the weld pool with lower temperatures. It was assumed in this analysis that in the course of arc welding the system reaches its thermodynamic equilibrium state.

In other test series (first to fourth), in which the specimens were melted at higher current intensities, the calculated functions for $[N] = f(t)$ approached the results presented in Fig. 8. The flow charts for $[N] = f(t)$ were calculated according to the second calculation method, which matched the results of measurements more closely.

An analysis of the data presented in Table 4 confirms earlier observations. Contrary to solutions in the Fe-O system, an increase of the oxygen content in the Fe-C-Mn-type filler metal reduces the value of $F_a$ and absorption rate of nitrogen (first and second test series). This was also proved by the results of third test series, where the decrease of the initial oxygen content to about 3 ppm leads to an increase of the nitrogen absorption rate.

The limited absorption of nitrogen due to the increased oxygen content in the Fe-C-Mn-type filler metal and in the atmosphere in which it is being performed, is connected to carbon deoxidation. The following mechanisms may be responsible for limiting the nitrogen absorption due to the formation of carbon oxide at high temperatures:

1) The decrease in partial pressure of nitrogen in the CO presence in the region adjacent to the boundary of the liquid and gaseous phase. In Model 3 we may assume that the values of $F_a$ and $F_b$ remain unaltered for the constant arc parameters, whereas the values of $[N]^*$ and $[N]$ are subjected to changes that differentiate the process of nitrogen absorption. Assuming, for instance, that the first test series is a standard one ($[N]^* = 624$ ppm, $[N] = 90$ ppm) and substituting $F_a$ and $F_b$ of series 1 into series 2 and 4, gives for the second test series:

$$[N]^* = 580.8\,\text{ppm},\, [N] = 89.3\,\text{ppm}$$

for the fourth test series:

$$[N]^* = 470.1\,\text{ppm},\, [N] = 87.5\,\text{ppm}$$

The reduction of the equilibrium levels $[N]^*$ and $[N]$, if compared with the first test series, at the same constant parameters of the arc, may be due to the lower partial pressure of nitrogen above the metal bath.

2) Higher desorption rate from the liquid metal. Nucleation and formation of CO at high temperatures facilitate the denitrifying of the liquid metal. Carbon and carbon oxide may also reduce the liquid oxides formed on the surface $F_b$ not contacting the arc, affecting the equilibrium between the amount of absorbed and desorbed nitrogen. The lowest $d[N]/dt$ values determined, depending on the applied method of calculation, range from 150 to 210 ppm/s (Table 4) during melting of filler metal with a high oxygen content in the Ar+N$_2$ atmosphere at a current of 100 A (second test series) or melting in a slightly oxidizing atmosphere of Ar+N$_2$+O$_2$ (fourth test series). Decreasing the current of the arc to 60 A, with other parameters remaining unchanged, caused an increase of the value of $d[N]/dt$ to about 470 ppm/s.

In this case, substantial differences were found in the nitrogen absorption rate between the first and second methods of calculation. It was caused by an unfortunate choice of boundary conditions in calculation according to the first method in the fifth and sixth test series, as well as the complexity of the process of the nitrogen absorption, in which the liquid oxide phases were involved. The $[N] = f(t)$ function, calculated according to the first method "lag distinctly behind" the results coming from the measurements. For that reason, the results obtained from the second calculation method for the fifth and sixth test series are more reliable.

The calculated parameters that characterize the kinetics of nitrogen absorption confirmed the general theorem concerning the essential influence of metallurgical processes occurring during arc melting of Fe-C-Mn-type filler metals on the absorption of nitrogen. Even if the carbon deoxidation reaction occurs only during the initial stage of melting, as in the case of samples with a small mass in oxygen-free Ar+N$_2$ atmospheres, it affects the absorption rate of nitrogen.

Conclusions

The conditions of nitrogen absorption during arc melting of Fe-C-Mn-type filler metals differ from the mechanisms that have been proposed for pure Fe and Fe-O systems. While analyzing the factors crucial for nitrogen absorption, the reaction of carbon deoxidation must be taken into account. Nitrogen absorption in Fe-C-Mn-type filler metals is restricted due to the formation of carbon oxide at high temperatures. The carbon oxide decreases the
nitrogen partial pressure in the area adjacent to the boundary of the liquid and gaseous phases. The increase of the oxygen content in arc-melted Fe-C-Mn-type filler metals in an Ar+N₂ atmosphere is accompanied by a reduction in nitrogen absorption rate. In the case of small specimen, rapid carbon deoxidation occurs together with the absorption of nitrogen only in the initial phases of melting.

Carbon deoxidation that takes place during arc melting of Fe-C-Mn-type filler metals in an Ar+N₂+O₂ atmosphere reduces the absorption rate of nitrogen and the steady-state level of nitrogen. After the full oxidation of carbon, as a result of the liquid oxide formation restricting the desorption of nitrogen, the contents of oxygen and nitrogen violently increase simultaneously.

Nitrogen absorption in arc-melted Fe-C-Mn-type filler metals can be described by the first-order kinetic expression. This indicates that the rate-limiting step for absorption is the transfer of nitrogen in the liquid phase and that the progress of the absorption is substantially affected by high temperature and convection of the liquid metal. In the arc melting model, the entire surface of the liquid metal must be divided into regions subjected to arc interaction and the region that contacts the cooler shielding gas.

Reducing current in the GTA melting of Fe-C-Mn-type filler metals in Ar+N₂ and Ar+N₂+O₂ atmospheres causes the absorption rate and the content of nitrogen to increase. This is connected to the limited carbon deoxidation and the vaporization of manganese, as well as the formation of liquid oxides restricting the desorption of nitrogen from the surface that is not directly affected by the arc.

Acknowledgment

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References


List of Symbols

[N] — equilibrium content of nitrogen in liquid metal contacting the shielding gas (ppm)

[N]₀ — initial content of nitrogen in the liquid metal (ppm)

[N] — nitrogen content in liquid metal in time t (ppm)

[N]₀ — steady-state content of nitrogen in liquid metal (ppm)

[N] — equilibrium content of nitrogen in liquid metal contacting the electric arc (ppm)

P — pressure (Pa)

T — temperature (K)

ΔG — Gibbs free enthalpy (kJ/mol)

P(N₂) — partial pressure of molecular nitrogen (Pa)

A, B, C, D, E, F — constants

M — vacant site on the surface of the liquid metal (ppm)

Fₐ — surface area (cm²)

Fₙ — surface of liquid metal contacting the electric arc (cm²)

Fₚ — surface of liquid metal contacting the cold shielding gas (cm²)

V — volume (cm³)

t — time (s)

β — mass transfer coefficient (cm/s)

βₚ — mass transfer coefficient on the surface contacting the electric arc (cm/s)

δ — diffusion layer thickness (cm)

s — specific surface, s = F/N (1/cm)

() — slag component

[] — component solved in liquid metal

( ) — surface of liquid metal contacting the cool shielding gas (cm²)

° — index at the bottom of the symbol denotes the gaseous phase

ads — index at the bottom of the symbol denotes the adsorbed component