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KINETICS OF NITROGEN DISSOLUTION IN ARC-MELTED STEELS

KINETYKA ROZPUSZCZANIA AZOTU W TOPIONYCH ŁUKOWO STALACH

The work refers to nitrogen absorption by the iron based liquid alloys. The industrial heats of the Fe-C-Mn (SpG1) type welding filler metals were selected for own research. The research of the nitrogen absorption kinetics was carried out in the TIG arc-melting conditions in the Ar+N₂ atmosphere. The thermodynamic and kinetic conditions of experiments were made possibly close to those existing in a molten metal drop in the arc welding processes. The nitrogen absorption process was analysed against a background of other metallurgical reactions occurring in the melted filler metals. It was demonstrated that the nitrogen absorption conditions by the arc-melted Fe-C-Mn type filler metals differ from mechanisms proposed for the pure Fe and solutions in the Fe-O system. Nitrogen absorption by the arc-melted Fe-C-Mn filler metals may be described by the first order kinetic expression. This indicates that nitrogen transfer in the liquid phase is the rate limiting step of its absorption. Separation is required in the arc-melting mathematical model of the liquid metal total surface into the electric arc affected zone and the one in contact with the cooler shielding gas. Temporal courses of nitrogen content, mass transfer coefficients β , and nitrogen absorption rates were determined basing on the above mentioned model. It was demonstrated that deoxidation with carbon taking place at high temperatures features the limiting factor of the nitrogen absorption by the arc-melted Fe-C-Mn filler metals. Nitrogen absorption rate decreases along with the increase of oxygen content in the arc-melted Fe-C-Mn filler metals in the Ar+N₂ atmosphere. Moreover, results obtained indicate that phenomena connected with nitrogen transport in the liquid metal result also in the increase of the nitrogen absorption intensity during arc-melting – apart from nitrogen activation processes in electric arc, stressed often in the literature.

Praca dotyczy absorpcji azotu przez ciekłe stopy na osnowie żelaza. Do badań własnych wybrano przemysłowe wytopy spoiw spawalniczych typu Fe-C-Mn (SpG1). Badania kinetyki absorpcji azotu przeprowadzono w warunkach topienia łukowego metodą TIG w atmosferze Ar+N₂. Warunki termodynamiczne i kinetyczne prowadzenia eksperymentów starano się zbliżyć do istniejących w kropli ciekłego metalu łukowych procesów spawania. Proces absorpcji azotu analizowano na tle innych reakcji metalurgicznych zachodzących w topionych spoiwach. Wykazano, że warunki absorpcji azotu przez topione łukowo spoiwa Fe-C-Mn odbiegają od mechanizmów proponowanych dla czystego Fe i roztworów w układzie Fe-O. Absorpcję azotu przez topione łukowo spoiwa Fe-C-Mn opisać można wyrażeniem kinetycznym I rzędu. Wskazuje to, że ogniwem limitującym przebieg absorpcji jest transport azotu w fazie ciekłej. W modelu matematycznym absorpcji azotu w czasie topienia łukowego całkowitą powierzchnię kropli rozdzielono na obszar oddziaływania łuku elektrycznego i obszar kontaktujący się z chłodniejszym gazem osłonowym. W oparciu o wymieniony model wyznaczono czasowe przebiegi zawartości azotu, współczynniki transportu masy β i szybkości absorpcji azotu. Wykazano, że czynnikiem ograniczającym absorpcję azotu przez topione łukowo spoiwa Fe-C-Mn jest zachodząca w wysokich temperaturach reakcja odtleniania węglem. Ze wzrostem zawartości tlenu w stopach Fe-C-Mn, topionych łukowo w atmosferze Ar+N₂, obniża się szybkość absorpcji azotu. Uzyskane wyniki wskazują ponadto, że na zwiększenie intensywności absorpcji azotu przy topieniu łukowym wpływają, obok często podkreślanych w literaturze procesów aktywowania azotu w łuku elektrycznym, zjawiska związane z transportem azotu w fazie ciekłej.

1. Introduction

Research of the kinetics of nitrogen absorption and desorption by liquid iron and its alloys has not explained unequivocally yet the mechanisms limiting the process flow, albeit the subjects of the investigation are usually

pure metals or binary alloys with the limited content of impurities.

Results of the previous research suggested that nitrogen absorption by the liquid iron is the first order reaction in relation to nitrogen content, and the rate-limiting step of the process is the nitrogen transfer in the liquid phase. Further investigations [1–7] revealed that the sur-

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face active components in the liquid iron and steel, like oxygen, sulphur, tellurium, and selenium, decrease the value of reaction constants of nitrogen absorption and change mechanisms limiting its flow in the induction or resistance melting conditions. The significant complexity of these processes may be attested by the fact that ranges of the limiting portions of the constituents, cited in the literature, at which the rate-limiting step of nitrogen absorption by the liquid Fe-O and Fe-S alloys changes from the diffusion to the chemical-adsorption one are very wide [2, 3, 8].

It is commonly considered that the nitrogen portions observed during arc-melting of iron and its alloys, much higher than coming from Sieverts law, are the result of the exceptional physical properties of the liquid metal – electric arc system. This statement is usually supported by the results of the thermodynamic analyses, from which appears that the processes of dissociation, ionisation and activation of the molecular nitrogen in the electric arc feature the main reason of the increased nitrogen absorption [9–11]. However, obtaining the equilibrium (in contact with the electric arc) nitrogen content is difficult because the electric arc encompasses usually only a part of the melted metal's surface. The final nitrogen content is a result of settling the dynamical equilibrium (pseudo-equilibrium) between the stream of nitrogen absorbed in the high-temperature part and coming out from the low-temperature part of the metal bath [12–15].

Oxygen fosters nitrogen absorption in the arc iron melting processes. Some publications [16] stress the role of the NO oxide facilitating nitrogen transport from the gaseous phase of the electric arc to the molten metal. The nitrogen absorption model in the arc-melted Fe-O systems presented in [13, 14] assumes that oxides contained in the surface that is not in touch with the electric

arc directly restrict nitrogen desorption, which fosters increase of its portion. The results cited above, pertaining to pure metals and binary alloys, as well experiments reproducing conditions close to the steelmaking process, have limited usability for analysis of nitrogen absorption taking place during welding.

Taking that into account, investigations of nitrogen dissolution in the arc melting conditions were carried out, striving to bring the experiment conditions to those taking place during welding of steel. The decision was taken to investigate the Fe-C-Mn complex alloys with the specified amount of impurities. This fact makes the detailed analysis of the elementary stages of nitrogen dissolution more difficult, yet brings the experiment conditions closer to those occurring in the actual technological processes.

2. Materials used in experiments

The industrial heats were investigated of the SpG1 grade filler metal according to PN-88/M-69420 standard with the chemical composition presented in Table 1.

Test pieces were cut out with the dimensions of $\varnothing 4 \times 6$ mm and weight of 0.6 g. The weight of the investigated test pieces was selected so that the melting conditions were close to those existing in the arc welding processes. This pertained in particular to the feasibility of obtaining the high temperature of the liquid metal, big F/V specific test piece surface, high heating rate, and possibility of melting in short time intervals.

Gas atmospheres in which melting process was carried out, were mixture of argon 99.995% purity (0.0005% O₂, 0.003% N₂, 0.0001% hydrocarbons, 0.0001% CO₂, 0.0005% humidity) with nitrogen 99.98% purity.

TABLE 1

Chemical composition of the investigated materials

Heat designation	Content of the alloying elements and impurities, %								
	C	Mn	Si	Cr	Ni	S	P	N	O
B	0.042	0.36	0.020	0.000	0.001	0.027	0.014	0.0063	0.0585
C	0.086	0.50	0.030	0.000	0.002	0.020	0.020	0.0060	0.0219
Composition acc. PN-88/M-69420	max 0.1	0.3–0.6	max 0.03	max 0.2	max 0.3	max 0.03	max 0.03	max 0.01	–

3. Testing equipment

The following subsystems were included in the testing equipment:

- system for controlling the chemical composition and flow rate of gas mixtures,

- TIG arc-melting system. The water cooled copper base $\varnothing 10$ mm was the anode, and the tungsten electrode $\varnothing 2.6$ mm was the cathode,
- melting time control system.

Moreover, the following testing equipment was used the investigations:

- TC-436 LECO oxygen and nitrogen content analyser,
- CS-mat 6500 STRÖHLEIN carbon and sulphur content analyser,
- ON-mat 8500 STRÖHLEIN oxygen and nitrogen content analyser,
- F SPECTROLAB spectral analyser.

4. Melting tests

The scope of tests of nitrogen absorption kinetics, melting parameters, and initial content of nitrogen, oxygen, and carbon in the examined test pieces are presented in Table 2.

TABLE 2

Scope of tests of nitrogen absorption kinetics

Test series ID Heat	Initial content, %			Shielding atmosphere	Melting times, s	Melting method Parameters
	N	O	C			
1 C	0.0060	0.0219	0.086	Ar+2%N ₂	1,2,3,5,10,20,40	TIG 100A
2 B	0.0063	0.0585	0.042	Ar+2%N ₂	1,2,3,5,10,20,40	TIG 100A

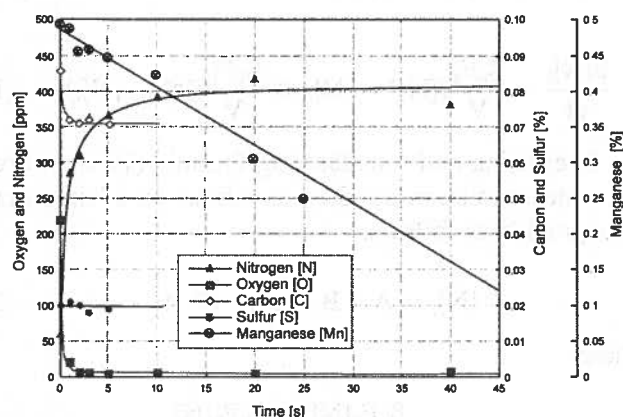


Fig. 1. Nitrogen, oxygen, carbon, manganese and sulfur contents in the steel heat C melted in the Ar+2%N₂ atmosphere, first test series

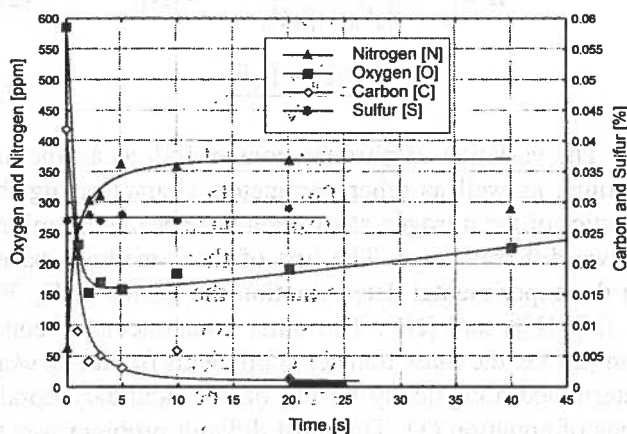


Fig. 2. Nitrogen, oxygen, carbon and sulfur contents in the steel heat B melted in the Ar+2%N₂ atmosphere, second test series

Details pertaining to the testing equipment and the TIG arc-melting conditions are presented in [19].

Temperature measurements made with the W-Mo \varnothing 0.2mm thermocouple have revealed that the molten metal reached the temperature of about 2400°C during

TIG melting of the test pieces weighing 0.6 g with the current of 100 A.

Contents of nitrogen, oxygen, carbon, and sulphur were determined in the arc-melted test pieces. In addition, manganese content was determined in the first test series. Test results are presented in Figures 1 and 2. The nitrogen and oxygen contents are given as average values out of five (second test series) or four (first test series) identical melting tests. Contents of carbon, sulphur, and manganese are given as average values out of three melting tests.

5. Discussion of the experimental results

The Fe-C-Mn filler metals with the similar nitrogen content and with the diversified oxygen and carbon contents (Table 2) were subjected to arc-melting with TIG method in the Ar+2%N₂ atmosphere. In first test series the C filler metal with the initial nitrogen content of 60 ppm reached 286 ppm of nitrogen after melting for 1 second, simultaneously the oxygen content dropped from 219 ppm to about 20 ppm. Nitrogen content was growing along with extension of melting time, to reach the pseudoequilibrium level of about 400 ppm after 10 seconds. Oxygen content settled at the level of about 5 ppm. Carbon content lowered from 0.086 to 0.072% (Fig. 1) along with oxygen content decrease. Changes of oxygen and carbon content correspond approximately to the stoichiometric ratio of the $C+O=CO_g$ reaction. This indicates that the deoxidation process of the SpGI filler metal at temperature of about 2400°C takes place mostly with carbon. This is also confirmed by calculations, carried out basing on data included in [18], of the ΔG free energy of the deoxidation reaction of steel with carbon and manganese. The ΔG of the reaction of steel

deoxidation with carbon at the temperature of 2400°C is (minus) 128 kJ/mole, and of the reaction of deoxidation with manganese it is about +42 kJ/mole. The deoxidation depth, to about 5 ppm O, may be explained by the nature of the gas shielding in which melting was taking place (Ar+N₂) and by low CO partial pressure over the metal bath (fast carrying away of reaction products).

The linear drop of manganese content of about 0.01%Mn/s in the entire melting time range indicates that this is the loss connected with its evaporation. Sulphur content in the remelted test pieces remained at the unchanged level (Fig. 1).

In the second test series (Fig. 2) the B filler metal (Table 2), with the very high oxygen content of 585 ppm and low carbon content of 0.042%, was melted in the same conditions. The deoxidation process progressed to the moment when carbon content dropped to several thousandths % and of oxygen content drop to the level of about 150 ppm. The oxygen content demonstrated the tendency to slight increase afterwards. The nitrogen content settled at the level of about 360 ppm. The oxygen content, higher than in first test series, did not result in the increased pseudoequilibrium nitrogen content. However, the tendency to a slower nitrogen content growth was observed at shorter melting time values.

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 basing on the model, the idea of which was discussed in [12]. The following assumptions have been made:

- the surface of the melted drop was divided into the area F_a subjected to contact with the electric arc and the area F_b subjected to contact with the cooler shielding gas. The total surface of the melted specimen equals to $F = F_a + F_b$ (Fig. 3),
- 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 phase.

Thus, it may be assumed that in the course of melting at the electric arc – liquid metal interface F_a there exists a concentration of nitrogen $[N]^*$ and at the shielding gas – liquid metal interface F_b an concentration of nitrogen $[N]$. During the initial stage of melting, when the nitrogen content in the liquid metal $[N]_t$ is lower than $[N]$, the nitrogen penetrates into the liquid metal through the whole outer surface of the drop. When $[N]_t$ exceeds the value of $[N]$, the absorption on the surface F_a proceeds, whereas on the surface F_b the nitrogen desorption occurs (Fig. 3). 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 $[N]_t = [N]^*$ is maintained.

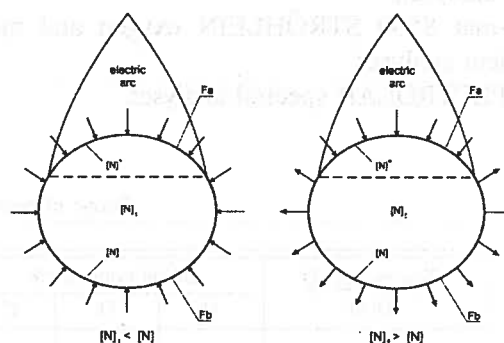


Fig. 3. Nitrogen absorption process in the course of arc melting

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

$$\frac{d[N]_t}{dt} = \frac{\beta_a F_a}{V} ([N]^* - [N]_t) + \frac{\beta_b F_b}{V} ([N] - [N]_t) \quad (1)$$

Integrating and transforming formula (1), the nitrogen concentration in the drop as a function of time may be expressed as follows:

$$[N]_t = A - B \cdot \exp(-C) \cdot t \quad (2)$$

where:

$$A = \frac{\beta_a F_a [N]^* + \beta_b F_b [N]}{\beta_a F_a + \beta_b F_b} \quad (2a)$$

$$B = \frac{\beta_a F_a [N]^* + \beta_b F_b [N]}{\beta_a F_a + \beta_b F_b} - [N]_0 \quad (2b)$$

$$C = \frac{\beta_a F_a + \beta_b F_b}{V} \quad (2c)$$

The variation of nitrogen content $[N]_t$ 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 based on the experimental determination the values of F_a , F_b , V , $[N]$, $[N]_0$ and $[N]^*$. The other components of equation (2), i.e. the mass transfer coefficients β_a and β_b were determined analytically basing on the boundary conditions of equation (1). The most difficult problem was to determine the value of $[N]^*$. Furthermore, no empirical relations exist which might make it possible to determine the value of $[N]^*$. Therefore, it was assumed that $[N]^* = 624$ ppm in both 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.

The equilibrium concentration of nitrogen $[N]$ at the boundary F_b between the liquid phase and the shielding

gas has been assumed to be equal 90ppm ($P_{N_2} = 2000 \text{ Pa}$, the temperature of the liquid metal about 2400°C).

For the electric arc length of 2,5 mm it has been assumed that $F_a/F_b = 1/2$.

Spherical shape of the test pieces of the Fe-C-Mn alloy, weighing 0.6g, was assumed for evaluation of F and V values.

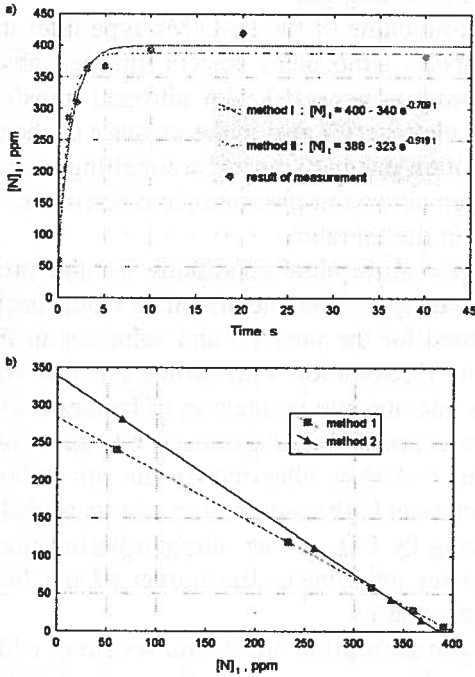


Fig. 4. Calculation results of the concentration (a) and the absorption rate (b) of nitrogen in the arc melted steel heat C, first test series

In the second method of calculation, the constants A, B and C in equation (2) were calculated applying the least squares method for a non-linear model, making use of the existing procedure for solving optimization problems, contained in the SOLVER option of the Microsoft EXCEL. Calculations were carried out basing on the average nitrogen contents in the melted specimens. Calculations of the A, B and C constants using the least squares method allowed to correct the earlier determined values of β_a and β_b , applying the equations (2a), (2b) and (2c). The values of F_a , F_b , $[N]^*$, $[N]$, $[N]_o$ and V remained on the same level as in the first method of calculation.

The graphical results of calculation of $[N]_t$ and the absorption rate of nitrogen $d[N]_t/dt = f[N]_t$, based on the model (1) for the both test series have been shown in Fig. 4 and 5.

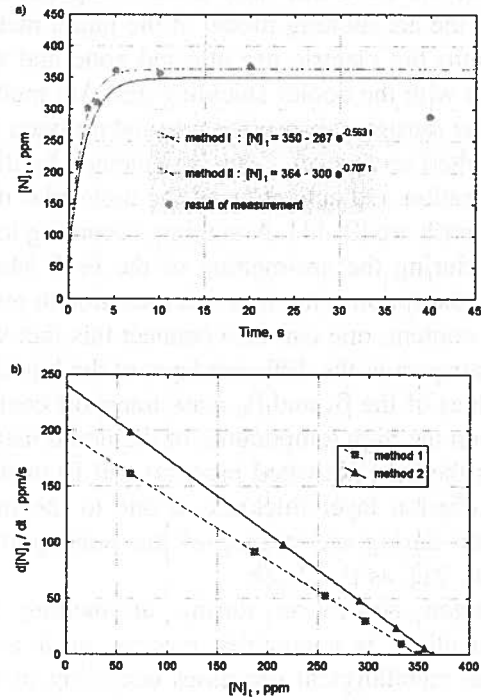


Fig. 5. Calculation results of the concentration (a) and the absorption rate (b) of nitrogen in the arc melted steel heat B, second test series

The linear relation $d[N]_t/dt = f[N]_t$ can be expressed in the following form:

$$d[N]_t/dt = -C \cdot [N]_t + F \tag{3}$$

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

The whole set of parameters, characterizing the kinetics of nitrogen absorption calculated basing on the model (1) has been shown in Table 3. The values of $d[N]_t/dt$ were determined for $[N]_t = [N]_o$. It corresponds to the initial stages of the filler metal melting. Such conditions may exist, for instance, in the arc welding processes during the formation and transition of the liquid metal drops to the weld pool.

TABLE 3

Influence of the initial oxygen content on the kinetics of nitrogen absorption by arc melting Fe-C-Mn alloys

Test series	Initial content, ppm		Mass transfer coefficient β , cm/s				$d[N]_t/dt$, ppm/s for $[N]_t = [N]_o$	
			β_a		β_b		Method I	Method II
	N	O	Method I	Method II	Method I	Method II		
1	60	219	0.1087	0.1286	0.0386	0.0510	241.2	276.3
2	63	585	0.0723	0.0896	0.0376	0.0420	161.4	198.9

Discussion summary

Experiments carried out and calculations confirmed the usefulness of the assumed kinetic model for the nitrogen absorption analysis in the conditions of the arc melting of the Fe-C-Mn filler metals. Separation is required in the arc-melting model of the liquid metal total surface into the electric arc affected zone and the one in contact with the cooler shielding gas. Arc melting increases the nitrogen absorption rate and nitrogen content in the melted test pieces. This is explained by dissociation, ionisation and activation of the molecular nitrogen in the electric arc [9, 11]. Assuming, according to model (1), that during the arc-melting of the Fe-C-Mn alloys nitrogen absorption is the first order reaction in respect to nitrogen content, one can also connect this fact with nitrogen transport in the diffusion layer of the liquid metal. High values of the β_a and β_b mass transport coefficients result from the high temperature of the liquid metal (diffusion is the heat activated process) and from decrease of the diffusion layer thickness δ due to the intensive convection during arc-melting of the small portions of metal [20, 21], as $\beta = D_g/\delta$.

Nitrogen absorption during arc-melting of the Fe-C-Mn alloys is a complex process, as it is affected by the metallurgical processes occurring in parallel with absorption. The contents of the alloying elements and impurities of the Fe-C-Mn filler metals correspond approximately to the thermodynamic equilibrium of the steel making process. The significant differences of the thermodynamic and kinetic conditions of the steel making and arc-melting processes (welding), force the intensive flow of the metallurgical processes, affecting nitrogen absorption. Deoxidation with carbon dominates when the liquid metal, like in case of arc-welding, reaches the temperature of about 2400°C. Increase of oxygen content in the arc-melted Fe-C-Mn type filler metal lowers nitrogen absorption rate at the beginning of the melting phase and lowers values of β_a i β_b (Table 3). The probable nitrogen absorption inhibiting mechanism due to carbon oxide formation at high temperatures is connected with lowering by CO_g of the nitrogen partial pressure in the zone adjacent to the border of the liquid and gaseous phases. Calculation results of the parameters characterising the nitrogen absorption kinetics confirm the general thesis about the significant effect of the metallurgical processes occurring during arc-melting of the Fe-C-Mn type filler metals on the nitrogen absorption process. Even in case when the deoxidation with carbon takes place at the initial melting phases only, as it is in case of melting the low mass of test pieces in the Ar+N₂ oxygen-free atmosphere, it has an influence on the nitrogen absorption rate.

6. Conclusions

1. Nitrogen absorption by the arc-melted Fe-C-Mn filler metals may be described by the first order kinetic expressions. Separation is required in the arc-melting model of the liquid metal total surface into the electric arc affected zone and the one in contact with the cooler shielding gas.
2. The arc-melting of the Fe-C-Mn type filler metals in the Ar+N₂ atmosphere fosters nitrogen absorption. Phenomena connected with nitrogen transfer in the liquid metal result also in the increase of the nitrogen absorption intensity during arc-melting – apart from nitrogen activation processes in electric arc, stressed often in the literature.
3. Nitrogen absorption conditions by the arc-melted Fe-C-Mn type filler metals differ from mechanisms proposed for the pure Fe and solutions in the Fe-O system. Deoxidation with carbon reaction should be taken into account in analysis of factors deciding nitrogen absorption. Limiting of nitrogen absorption by the Fe-C-Mn filler metals due to carbon oxide formation at high temperatures results probably from lowering by CO_g of the nitrogen partial pressure in the zones adjacent to the border of the liquid and gaseous phases.
4. Nitrogen absorption rate decreases along with the increase of oxygen content in the arc-melted Fe-C-Mn filler metals in the Ar+N₂ atmosphere.

List of symbols

- [N]₀ – initial content of nitrogen in the liquid metal, ppm
 [N]_t – nitrogen content in the liquid metal in time t, ppm
 [N]^r – steady-state content of nitrogen in liquid metal, ppm
 [N]^{*} – concentration of nitrogen at the electric arc – liquid metal interface, ppm
 [N] – concentration of nitrogen at the shielding gas – liquid metal interface, ppm
 ΔG – Gibbs free enthalpy, kJ/mol
 A, B, C, D, E, F - constants
 F – surface, cm²
 F_a – surface of liquid metal contacting the electric arc, cm²
 F_b – surface of liquid metal contacting the cool shielding gas, cm²
 V – volume, cm³
 t – time, s
 β – mass transfer coefficient, cm/s
 β_a – mass transfer coefficient on the surface contacting the electric arc, cm/s

β_b – mass transfer coefficient on the surface contacting the cool shielding gas, cm/s

D – diffusion coefficient, cm²/s

δ – diffusion layer thickness, cm

_g – index at the bottom of the symbol denotes the gaseous phase

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