



# The kinetics of nitrogen dissolution in levitation and arc-melted Fe-C-Mn filler metals

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Received 27.03.2008; published in revised form 01.06.2008

## ABSTRACT

**Purpose:** The influence of melting method on the kinetics of nitrogen absorption by Fe-C-Mn filler metals has been analysed. The industrial heats of the Fe-C-Mn (SpG1) type welding filler metals were selected for own researches.

**Design/methodology/approach:** The research of the nitrogen absorption kinetics was carried out in the levitation and TIG arc-melting conditions in the Ar+N<sub>2</sub> atmosphere. The conditions of experiments were made possibly close to those existing in a molten metal drop in the welding processes.

**Findings:** Based on the models of nitrogen absorption during levitation and arc melting of Fe-C-Mn filler metals, the time-dependent changes of nitrogen content were determined as well as the mass transfer coefficients  $b$  and the rates of nitrogen absorption. Nitrogen absorption rate decreases along with the increase of oxygen content in the Fe-C-Mn filler metals arc-melted in the Ar+N<sub>2</sub> atmosphere.

**Research limitations/implications:** Investigation of the Fe-C-Mn complex alloys with the specified amount of impurities 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 welding processes.

**Practical implications:** Recognizing the mechanisms of nitrogen absorption under arc and non-arc melting to make possible the control of nitrogen level in the welds.

**Originality/value:** Obtained results explain the influence of oxygen and melting conditions on kinetics of nitrogen dissolution in Fe-C-Mn alloys.

**Keywords:** Welding; Nitrogen; Absorption; Arc melting; Levitation melting; Kinetics; Model

## MATERIALS MANUFACTURING AND PROCESSING

### 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 surface 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.

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 [8-10]. 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 [11-13]. Oxygen fosters nitrogen absorption in the arc iron melting processes. Some publications [14] 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 [12, 13] 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 and induction 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. Research equipment and work methodology

Details pertaining to the testing equipment and the levitation and TIG arc-melting conditions are presented in [16].

### 2.1. Materials used in experiments

The industrial heats were investigated of the SpG1 grade filler metal according to PN-88/M69420 standard with the chemical composition presented in Table 1. Test pieces were cut out with the dimensions of Ø 4 x 6 mm and weight of 0.6 g.

Table 1.  
Chemical composition of the investigated materials

Heat designation	Content of the alloying elements and impurities, %							
	C	Mn	Si	Ni	S	P	N	O
A	0.068	0.36	0.021	0.001	0.015	0.016	0.0060	0.0162
B	0.042	0.36	0.020	0.001	0.027	0.014	0.0063	0.0585
C	0.086	0.50	0.030	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 0.3	max 0.03	max 0.03	max 0.01	-

## 3. Results of researches

### 3.1. Levitation melting tests

Levitation melting tests in the Ar+1%N<sub>2</sub> atmosphere revealed that along with extension of the melting time the nitrogen content in the test pieces grows exponentially from its initial value of [N]<sub>0</sub>=60 ppm, reaching the equilibrium level of [N]=80 ppm after about 80 sec of melting. The temperature of the inductive melted test pieces, measured with the optical pyrometer was about 1550-1570°C. The reaction order and quantitative parameters characterising the nitrogen absorption kinetics in these conditions were determined basing on measurement results of nitrogen content.

The first order reaction was described with the formula:

$$\frac{d[N]_t}{dt} = k_1 \cdot \frac{F}{V} ([N] - [N]_t) \quad (1)$$

whose solution is as follows:

$$\ln \frac{[N] - [N]_t}{[N] - [N]_0} = k_1 \left( \frac{F}{V} \right) \cdot t \quad (2)$$

For the second order reaction:

$$\frac{d[N]_t}{d[t]} = k_2 \cdot \frac{F}{V} ([N]^2 - [N]_t^2) \quad (3)$$

therefore:

$$\frac{1}{2[N]} \left\{ \ln \left( \frac{[N] + [N]_t}{[N] - [N]_t} \right) + \ln \left( \frac{[N] - [N]_0}{[N] + [N]_0} \right) \right\} = k_2 \left( \frac{F}{V} \right) \cdot t \quad (4)$$

The following input data were used for determining the reaction order: [N]<sub>0</sub> = 60 ppm, (Table 1.), [N] = 80 ppm, F = 0.87 cm<sup>2</sup>, V = 0.076 cm<sup>3</sup>.

Spherical shape of the test pieces from the Fe-C-Mn alloy, weighing 0.6 g, was assumed for evaluation of F and V values. Analysis of obtained data revealed that the relationship

$$\ln \left( \frac{[N] - [N]_t}{[N] - [N]_0} \right) = f(t) \quad (5)$$

(5) is closer to a linear one (linear correlation coefficient R = 0.989). This indicates, that nitrogen absorption by the investigated F-C-Mn alloy melted with the levitation method in the experiment conditions is the first order reaction in respect to nitrogen content, and nitrogen diffusion in the liquid phase is its rate-limiting step.

The reaction rate constant k<sub>1</sub> from the formula (1) equal to 0.0065 cm/s is the transfer coefficient of nitrogen β in the diffusion layer of the liquid metal.

### 3.2. Arc-melting tests

The Fe-C-Mn filler metals with the similar nitrogen content and with the diversified oxygen and carbon contents (Heat B and C, Table 1.) were subjected to arc-melting with TIG method in the Ar+2%N<sub>2</sub> atmosphere. Temperature measurements made with the W-Mo Ø 0.2 mm 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 100A. In second test series the C filler metal with the initial nitrogen content of 60 ppm reached 286 ppm of nitrogen after melting for

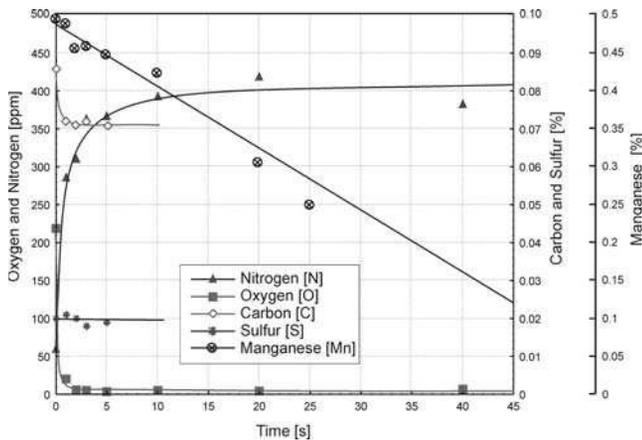


Fig. 1. Nitrogen, oxygen, carbon, manganese and sulfur contents in the steel heat C melted in the Ar+2%N<sub>2</sub> atmosphere, second test series

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<sub>g</sub> reaction. This indicates that the deoxidation process of the SpGl filler metal at temperature of about 2400°C takes place mostly with carbon.

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 third test series the B filler metal (Table 1.), 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 second 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.

### 3.3. 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 [11]. The following assumptions have been made:

- the surface of the melted drop was divided into the area F<sub>a</sub> subjected to contact with the electric arc and the area F<sub>b</sub> subjected to contact with the cooler shielding gas. The total surface of the melted specimen equals to F = F<sub>a</sub> + F<sub>b</sub>,

- 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 on the surface F<sub>a</sub> there exists an equilibrium concentration of nitrogen [N]<sup>\*</sup> in liquid metal contacting the electric arc, and on the surface F<sub>b</sub> an equilibrium concentration of nitrogen [N] in liquid metal contacting the cool shielding gas. During the initial stage of melting, when the nitrogen content in the liquid metal [N]<sub>t</sub> is lower than [N], the nitrogen penetrates into the liquid metal through the whole outer surface of the drop. When [N]<sub>t</sub> exceeds the value of [N], the absorption on the surface F<sub>a</sub> proceeds, whereas on the surface F<sub>b</sub> the nitrogen desorption occurs. 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]<sub>t</sub> = [N]<sup>r</sup> is maintained.

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

$$\frac{d[N]_t}{dt} = \frac{\beta_a F_a}{V} ([N]^* - [N]_t) + \frac{\beta_b F_b}{V} ([N] - [N]_t) \quad (6)$$

Integrating and transforming formula (6), the nitrogen concentration in the drop as a function of time may be expressed as follows:

$$[N]_t = A - B \cdot \exp(-C) \cdot t \quad (7)$$

$$A = \frac{\beta_a F_a [N]^* + \beta_b F_b [N]}{\beta_a F_a + \beta_b F_b} \quad (7a)$$

$$B = \frac{\beta_a F_a [N]^* + \beta_b F_b [N]}{\beta_a F_a + \beta_b F_b} - [N]_0 \quad (7b)$$

$$C = \frac{\beta_a F_a + \beta_b F_b}{V} \quad (7c)$$

The variation of nitrogen content [N]<sub>t</sub> 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<sub>a</sub>, F<sub>b</sub>, V, [N], [N]<sub>0</sub> and [N]<sup>r</sup>. The other components of equation (7), i.e. the mass transfer coefficients β<sub>a</sub> and β<sub>b</sub> were determined analytically basing on the boundary conditions of equation (6). The following input data were used: [N]<sup>r</sup>=624 ppm, [N]=90 ppm, F<sub>a</sub>/F<sub>b</sub> = 1/2, F = 0.87 cm<sup>2</sup>, V = 0.076 cm<sup>3</sup>.

In the second method of calculation, the constants A, B and C in equation (7) 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.

The parameters, characterizing the kinetics of nitrogen absorption calculated basing on the model (6) has been shown in Table 2. The values of d[N]<sub>t</sub>/dt were determined for [N]<sub>t</sub> = [N]<sub>0</sub>. 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 2.

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

Test series	Initial content, ppm		Mass transfer coefficient $\beta$ , cm/s				$d[N]_i/dt$ , ppm/s for $[N]_i=[N]_0$	
			$\beta_a$		$\beta_b$		Method I	Method II
	N	O	Method I	Method II	Method I	Method II		
II	60	219	0.1087	0.1286	0.0386	0.0510	241.2	276.3
III	63	585	0.0723	0.0896	0.0376	0.0420	161.4	198.9

#### 4. Conclusions

- Nitrogen absorption by the Fe-C-Mn filler metals levitation and arc-melted 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.
- Compared to the inductive melting, the arc-melting of the Fe-C-Mn type filler metals in the Ar+N<sub>2</sub> atmosphere fosters nitrogen absorption, increasing both the absorption rate and nitrogen content in the filler metal.
- 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<sub>g</sub> of the nitrogen partial pressure in the zones adjacent to the border of the liquid and gaseous phases.
- Nitrogen absorption rate decreases along with the increase of oxygen content in the Fe-C-Mn filler metals arc-melted in the Ar+N<sub>2</sub> atmosphere.

#### 5. List of symbols

- [N] - equilibrium content of nitrogen in liquid metal contacting the shielding gas, ppm  
 [N]<sub>0</sub> - initial content of nitrogen in the liquid metal, ppm  
 [N]<sub>t</sub> - nitrogen content in the liquid metal in time t, ppm  
 [N]<sup>\*</sup> - steady-state content of nitrogen in liquid metal, ppm  
 [N]<sup>\*</sup> - equilibrium content of nitrogen in liquid metal contacting the electric arc, ppm  
 A, B, C, D, E, F - constants  
 F - surface, cm<sup>2</sup>  
 F<sub>a</sub> - surface of liquid metal contacting the electric arc, cm<sup>2</sup>  
 F<sub>b</sub> - surface of liquid metal contacting the cool shielding gas, cm<sup>2</sup>  
 V - volume, cm<sup>3</sup>  
 t - time, s  
 $\beta$  - mass transfer coefficient, cm/s  
 $\beta_a$  - mass transfer coefficient on the surface contacting the electric arc, cm/s  
 $\beta_b$  - mass transfer coefficient on the surface contacting the cool shielding gas, cm/s  
 D - diffusion coefficient, cm<sup>2</sup>/s  
 $\delta$  - diffusion layer thickness, cm  
 g - index at the bottom of the symbol denotes the gaseous phase

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