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**INVESTIGATION OF NITROGEN SOLUBILITY IN LIQUID Fe-V ALLOYS
WITH THE USE OF LEVITATION TECHNIQUE**

**BADANIE ROZPUSZCZALNOŚCI AZOTU W CIEKLYCH STOPACH Fe-V
PRZY UŻYCIU TECHNIKI TOPIENIA LEWITACYJNEGO**

A methodology and the results of experimental studies on nitrogen solubility in liquid Fe-V alloys are presented in the article. The investigations were carried out using the levitation metal melting technique. Liquid Fe-V alloys (%V — 1.5; 5.8; 7.8; 12.2) were saturated with nitrogen at the temperature 2173 K. Nitrogen partial pressure was varied within the range of 0.1–2.1 MPa. The experiment involved melting down a 1 g-mass sample in an electromagnetic field produced by a levitation coil, filling the reaction chamber with nitrogen up to the required pressure, and heating the sample up to the preset temperature.

The sample was held in this condition for 180 s. Then, the power supply of the coil was switched off and a metal drop fell by gravity into a small copper mould in which the metal solidified in the conditions of rapid crystallisation. Nitrogen contents were determined by the method of extraction to a neutral gas using a Leco TC-336 apparatus.

High nitrogen concentrations were obtained in metal samples as the result of high nitrogen partial pressures in the gaseous phase within the reaction chamber. In these conditions, all interactions of nitrogen in the alloy examined could be revealed, namely: nitrogen-vanadium, nitrogen-nitrogen, and nitrogen-nitrogen-vanadium interactions.

In the case of the liquid Fe-V alloy, a solid phase of vanadium nitride separates from the liquid after exceeding the nitrogen solubility limit. The tests were carried out within such a range of nitrogen concentrations where a given Fe-V alloy was still homogeneous.

Investigation results have shown a nonlinear dependence of the activity coefficient, f_N , not only on the vanadium content of alloy, but on its nitrogen content as well. Therefore, interaction between nitrogen atoms in liquid Fe-N-V alloys has been documented.

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Particularly clearly visible is the strong effect of nitrogen on its own activity coefficient in the case of higher vanadium contents of alloy. This is probably connected with the sensitivity threshold (error) of the experimental method employed in the investigations described.

Using experimental data and findings from the previous work on the liquid Fe-N alloy, temperature relationships for the following interaction parameters were derived: $e_N^{(V)}$, $r_N^{(V)}$, $r_N^{(N,V)}$ and $t_N^{(N,V,V)}$ have been determined for the temperature 2173 K.

The derived thermodynamic characteristics make a basis for conducting further studies on the Fe-N-V alloy, when the system in the state of equilibrium is composed of the liquid and separated vanadium nitrides. The results of such studies, with consideration being given to the effect of nitrogen partial pressure, will be the subject of a subsequent publication.

W pracy przedstawiono metodykę oraz wyniki badań eksperymentalnych nad rozpuszczalnością azotu w ciekłych stopach Fe-V. Badania przeprowadzone zostały przy użyciu techniki lewitacyjnego topienia metali. Ciekłe stopy Fe-V (%V — 1,5; 5,8; 7,8; 12,2) nasycano azotem przy temperaturze 2173 K. Ciśnienie cząstkowe azotu zmieniano w zakresie 0,1–2,1 MPa. Eksperyment polegał na roztopieniu próbki o masie 1 g w polu elektromagnetycznym wytworzonym przez cewkę lewitacyjną, napełnieniu komory reakcyjnej azotem do wymaganego ciśnienia i nagrzaniu próbki do zadanej temperatury. W takim stanie próbkę wytrzymywano przez 180 s. Następnie wyłączono zasilanie cewki i kropla metalu spadała grawitacyjnie do miedzianej wlewniczki, w której metal krzepł w warunkach szybkiej krystalizacji. Zawartości azotu określone były metodą ekstrakcji do gazu obojętnego przy użyciu aparatu Leco TC-336.

W próbkach metalu uzyskiwano wysokie stężenia azotu, na skutek wytwarzania wysokich ciśnień cząstkowych azotu w fazie gazowej przestrzeni reakcyjnej. W takich warunkach mogły być ujawnione wszystkie oddziaływania azotu w badanym stopie a mianowicie: oddziaływania azot–wanad, azot–azot, azot–azot–wanad.

W przypadku ciekłego stopu Fe-V, po przekroczeniu granicy rozpuszczalności azotu, wydzieliła się z cieczy stała faza azotku wanadu. Badania prowadzono w takim zakresie stężeń azotu, przy którym dany stop Fe-V był jeszcze homogeniczny.

Wyniki badań wykazały nieliniową zależność współczynnika aktywności f_N nie tylko od zawartości wanadu w stopie ale również od zawartości w nim azotu. Zatem udokumentowano oddziaływanie pomiędzy atomami azotu w ciekłych roztworach Fe-N-V.

Szczególnie wyraźnie widoczny jest silny wpływ azotu na jego współczynnik aktywności w przypadku wyższych zawartości wanadu w stopie. Prawdopodobnie jest to związane z progmem czułości (uchybem) zastosowanej w tych badaniach metody eksperymentalnej.

Wykorzystując dane eksperymentalne oraz ustalenia wcześniejszej pracy nad ciekłym stopem Fe-N, opracowano wartości następujących parametrów oddziaływania: $e_N^{(V)}$, $r_N^{(V)}$, $r_N^{(N,V)}$ i $t_N^{(N,V,V)}$ dla temperatury 2173 K.

Opracowane charakterystyki termodynamiczne stanowią podstawę do prowadzenia dalszych badań nad stopem Fe-N-V, gdy w stanie równowagi układ będzie się składał z cieczy i wydzielonych azotków wanadu. Wyniki takich badań, z uwzględnieniem wpływu cząstkowego ciśnienia azotu, będą przedmiotem kolejnej publikacji.

1. Introduction

Modern technologies should be based on a reliable and very accurate thermodynamic and kinetic database. Studies on the solubility of nitrogen in liquid metals and alloys were carried out mainly in the 60's and 70's. Many of them were related to the temperature 1873 K and a nitrogen phase pressure of up to 0.1 MPa. Presently, alloys of a complex chemical composition are being investigated at gaseous phase pressures above 0.1 MPa.

The Department of Extraction and Recirculation of Metals of the Technical University of Częstochowa is one of few Poland's scientific institutions directed towards problems related to the theoretical and practical principles of producing steels with alloying nitrogen.

2. Basic thermodynamic relationships

The process of dissolution of gaseous nitrogen in liquid metal is preceded by the dissociation of the two-atom gas and, in the conditions of a chemical equilibrium between the nitrogen in the gaseous phase and in the metallic phase, it can be described by the following formula:

$$\frac{1}{2} \{N_2\} = [N]. \quad (1)$$

Nitrogen can be treated as a perfect gas even under high pressures; the difference between the gas volatility and its pressure is less than 1.2% to 5 MPa.

When determining concentrations in mass %, the equilibrium constant of reaction (1) can be described by the formula:

$$K_{N(\text{Me})} = \frac{[\%N] \cdot f_N}{\sqrt{P_{N_2}}}. \quad (2)$$

The coefficient f_N characterizes the deviation of the real gas solution from the ideal solution. For the evaluation of activity coefficients, the equation derived by Wagner and Chipman is widely used in metallurgy.

For the liquid Fe-N-X alloy, the value of the parameter f_N is expressed by the equation:

$$\log f_N = e_N^{(N)} \cdot [\%N] + e_N^{(X)} \cdot [\%X] + r_N^{(N)} \cdot [\%N]^2 + r_N^{(X)} \cdot [\%X]^2 + r_N^{(XN)} \cdot [\%N] \cdot [\%X]. \quad (3)$$

By regrouping the terms of the equation (3), we obtain:

$$\log f_N = \log f_N^{(X)} + \log f_N^{(N)}. \quad (4)$$

If such an E_N^N parameter is assumed that:

$$E_N^{(N)} = e_N^{(N)} + r_N^{(N)} \cdot [\%N] + r_N^{(XN)} \cdot [\%X] \quad (5)$$

then $\log f_N$ can be defined by the formula as below:

$$E_N^{(N)} = \frac{\log f_N^{(N)}}{[\%N]} \Rightarrow \log f_N^{(N)} = E_N^{(N)} \cdot [\%N]. \quad (6)$$

By substituting (4), (6) to equation (2) and then transforming it, the following equation will be obtained, which serves for the description of the experimental results of studies on the gaseous phase — liquid metal system:

$$\log \frac{[\%N]}{\sqrt{P_{N_2}}} = \log K_{N(\text{Fe})} - \log f_N^{(X)} - E_N^{(N)} \cdot [\%N]. \quad (7)$$

Relationship (7) can be interpreted with the use of mathematical statistics methods, and in particular using the commonly known regression equation in the form of the linear function $y = ax + b$.

3. Studies with the use of the levitation metal melting technique

If a conductor is placed in a variable magnetic field (an electromagnetic field component), then *eddy currents* will be induced in that conductor. These form closed circuits within the conductor and transform the electric energy into heat. A high-frequency electromagnetic field interacts with eddy currents in the metal, whereby the weight of the metal is counterbalanced and the metal is maintained in a state of levitation. The levitation melting of metals is a type of induction melting and is frequently referred to as crucibleless melting.

The advantages of levitation metal melting are the following:

- No crucible needed (avoiding the interaction of liquid metal with the crucible material).
- Wide range of used temperatures (1000 ÷ 3000 °C).
- Possibility of using predetermined atmosphere.
- Increasing the rates of chemical reactions between metal and the gaseous phase (an advantageous ratio of surface area to volume).
- High chemical homogeneity (perfect mixing of liquid metal with eddy currents).
- Possibility of reaching high metal cooling rates ($> 10^4$ K/s, e.g. by reducing the phenomenon of desorption of gases dissolved in the specimen).

The measurement of temperature is accomplished by a contactless method using an optical pyrometer, and in particular a two-colour pyrometer. The principle of operation of this pyrometer relies on the measurement of the ratio of energy emitted by the solid in two bands of electromagnetic waves. This enables a very

accurate measurement of the temperature of the solid surface, even when some objects which absorb part of the energy (such as smoke, metal vapours, dirt on the sight-glass, etc.) appear between the solid and the optical system.

The levitation metal melting technique is successfully applied in the studies on the solubility of gases in liquid metals. A specimen of the alloy examined is saturated with a gas (eg. nitrogen or hydrogen) until a state of thermodynamic equilibrium is reached. Then, it is cast into an ingot mould. In thus obtained specimen, the gas is assayed. It is important during the examination that the gas dissolved in the specimen in the state of thermodynamic equilibrium be fixed in the specimen. In the case of some liquid metals (including liquid iron) the solubility of gases decreases with decreasing temperature. Thus, the gas will desorb during solidification. This phenomenon, however, can be minimized by applying high rates of cooling the specimen, which are feasible with the levitation melting technique.

4. Studies on the solubility of nitrogen in liquid Fe-V alloys

Studies on the solubility of nitrogen in liquid Fe-V alloys were carried out mainly in the 60's and 70's. In those studies, the researchers used the Sieverts method — e.g. works [1–5], the sampling method [6], and the levitation melting technique [7] and [8]. More recent works, e.g. [9], relating to the solubility of nitrogen in the Fe-V alloy form compilations of earlier results done using computer techniques. Thus, unexplored areas are only “predicted” with the use of specialized applications. As the available literature shows, there are no new works that would be purely experimental in character.

5. Authors' own studies

Studies on the solubility of nitrogen in liquid Fe-N-V alloy were carried out using the levitation metal melting technique. A schematic diagram of the testing stand is shown in Fig. 1.

Liquid Fe-V (%V — 1.5; 5.8; 7.8; 12.2) alloys were saturated with nitrogen at the temperature 2173 K. The nitrogen partial pressure was changed in the range 0.1–2.1 MPa. The experiment involved melting a 1 g specimen in an electromagnetic field produced by a levitation coil, filling the reaction chamber with nitrogen up to the required pressure, and heating the specimen up to the pre-set temperature. In this condition, the specimen was held by 180 s (i.e. the time required for attaining a thermodynamic equilibrium). Next, the power supply of the coil was switched off which resulted in falling of a metal drop by gravity into the small copper mould where the metal subsequently solidified. The nitrogen

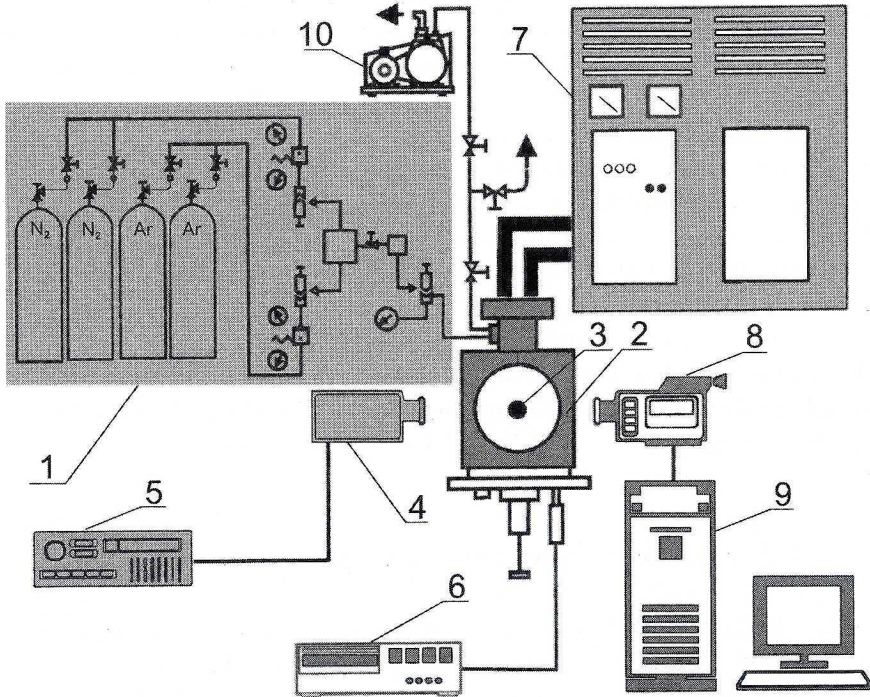


Fig. 1. Schematic diagram of the testing stand for levitation melting under variable pressure within the reaction chamber. 1 – block of supply with high-purity gases; 2 – hyperbaric reaction chamber with a levitation coil; 3 – levitating metal drop; 4 – Ircon Modline two-colour pyrometer; 5 – pyrometer indicating module; 6 – Endress-Hausser and MKS Instrument electronic pressure gauges; 7 – GIS 10 generator; 8 – vision camera; 9 – digital image recording system; 10 – rotary vacuum pump

contents were determined by the method of extraction to a neutral gas using a LECO TC-336 apparatus.

6. Test results

High nitrogen concentrations were obtained in the tests owing to the use of high nitrogen partial pressures in the gaseous phase. In these conditions, all interactions of nitrogen in the alloy examined were disclosed, namely: nitrogen–vanadium, nitrogen–nitrogen, and nitrogen–nitrogen–vanadium interactions. In the case of the Fe-V alloy, a solid phase of vanadium nitride precipitates from the liquid after the limit of nitrogen solubility has been exceeded. The precipitation of nitrides, whose melting temperature is higher than the temperature at which the liquid alloy had been saturated ($T_m = 2350$ K [10]), caused the solidification of the specimen. The nitrogen contained in the specimens did not correspond

to the equilibrium values for the liquid alloy — nitrogen phase system. For this reason, the tests were conducted in the homogeneous range of the Fe-V alloy. Directly from the experiment, the concentrations of nitrogen in the alloy were obtained for a given temperature and nitrogen partial pressure. It was found that the coefficient of activity, $\log f_N$, depended on the nitrogen content (Fig. 2), thus interaction between nitrogen atoms appears in the Fe-N-V alloys tested. A strong effect of nitrogen on $\log f_N$ is particularly noticeable for higher vanadium concentrations in the alloy. This is an obvious fact as it is connected with the higher solubility of nitrogen. Using formula (7), experimental data and the relationship for $K_{N(\text{Fe})}$ reported in work [11], the values of the experimental parameter E_N^N were calculated. Figure 3 shows the dependence of the parameter E_N^N on the vanadium content of alloy, which is clearly nonlinear. Thus, it should have been expected that not only nitrogen–nitrogen, but also nitrogen–nitrogen–vanadium and nitrogen–nitrogen–vanadium–vanadium interactions would be revealed. Using the temperature relationship for the parameter $e_N^{(N)}$ [11] and the authors' own data, the interaction parameters were calculated. The value of the parameter $r_N^{(N,V)}$ is 0.0443 ± 0.0085 , whereas this for the parameter $t_N^{(N,V,V)}$ being equal to -0.0032 ± 0.0011 . The parameter $r_N^{(N)}$ on the basis of the previous data [12], was assumed as being equal to zero.

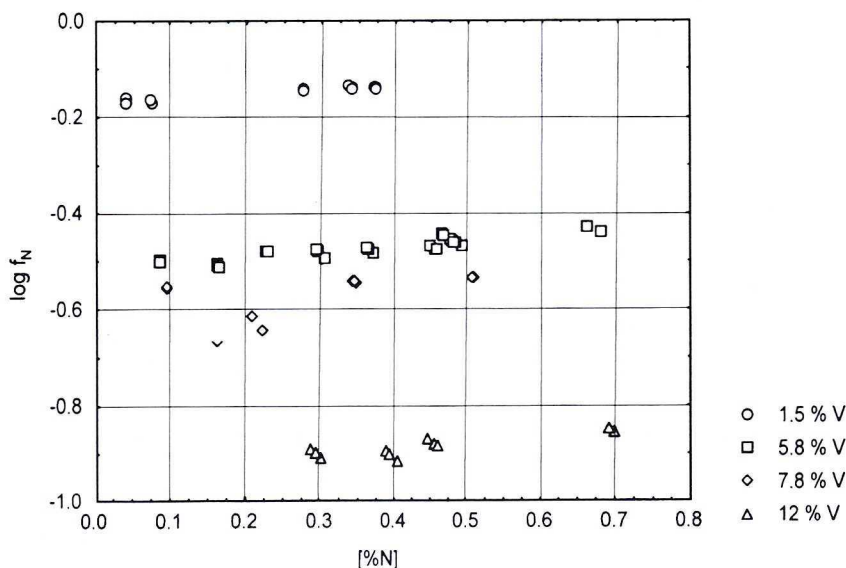


Fig. 2. Dependence of $\log f_N$ on the vanadium concentration in Fe-N-V alloys

Upon further processing of experimental data, the value of the activity coefficient $\log f_N^{(V)}$ was obtained. Figure 4 shows the dependence of this parameter on the concentration of vanadium in the liquid alloy. It follows from the figure that

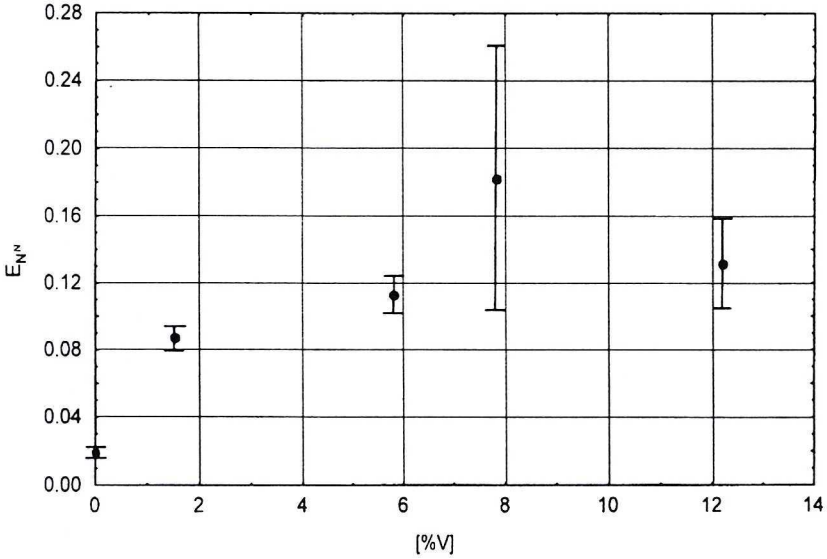


Fig. 3. Dependence of E_N^N on the vanadium concentration in Fe-N-V alloys

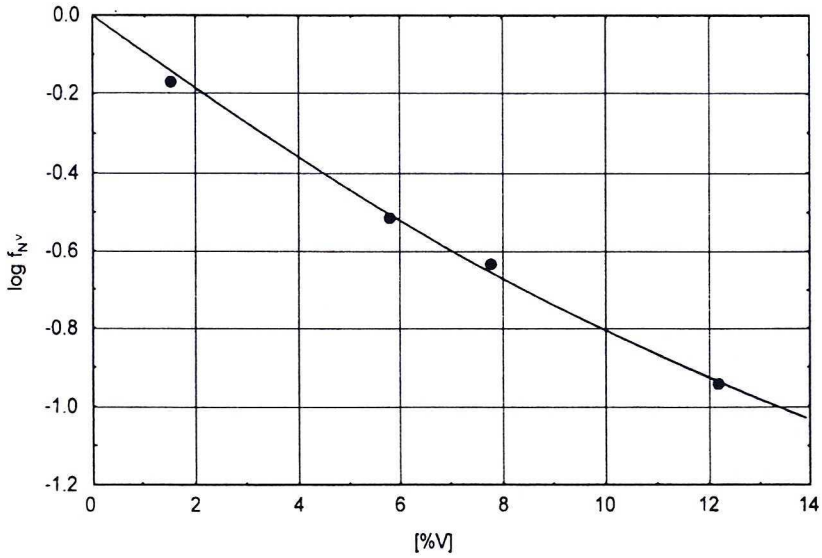


Fig. 4. Dependence of the coefficient of activity of nitrogen on the vanadium concentration in Fe-N-V alloys

this dependence is not linear in character. Thus, it should have been expected that the coefficient of activity $\log f_N^{(V)}$, would be described by at least two interaction parameters, namely those of the 1st and the 2nd order. The parameters were determined by applying nonlinear estimation.

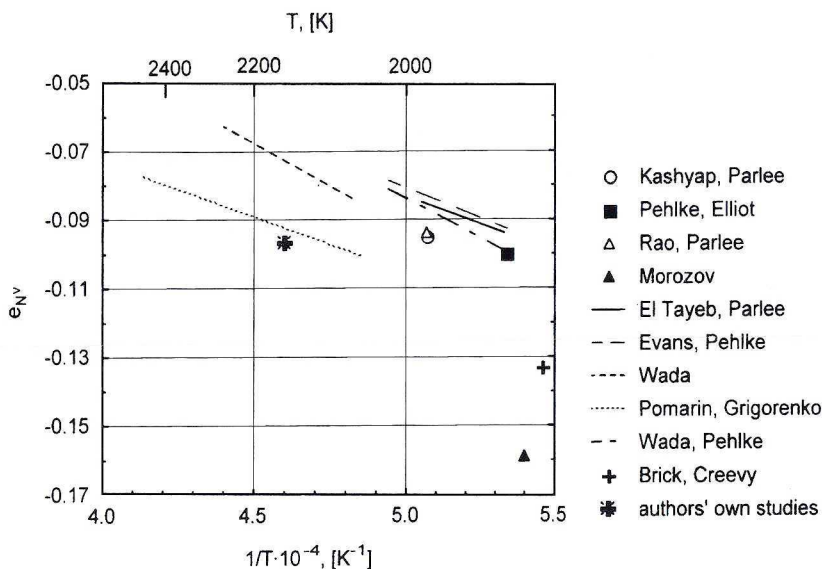


Fig. 5. Comparison of the authors' own examination results with literature data

The values of the interaction parameters of the 1st and 2nd order for the temperature 2173 K are, respectively: $e_N^{(V)} = -0.0967 \pm 0.0016$, $r_N^{(V)} = 0.0067 \pm 0.0006$.

In Figure 5, the obtained values of $e_N^{(V)}$ are compared with literature data. As the figure shows, the values of the authors' own parameters fit perfectly the literature data.

7. Summary

The solubility of nitrogen in liquid Fe-N-V alloys with different vanadium contents has been examined. Saturation with nitrogen was carried out at the temperature 2173 K with the use of the levitation metal melting technique. The parameters $e_N^{(V)}$, $r_N^{(V)}$ have been estimated, and interactions of nitrogen–nitrogen and nitrogen–nitrogen–vanadium types have been disclosed in liquid Fe-N-V alloys. Therefore, in the thermodynamic description of the solubility of nitrogen in liquid Fe-N-V alloys not only the $e_N^{(V)}$, $r_N^{(V)}$ parameters, but also the $e_N^{(N)}$, $r_N^{(N,V)}$, $t_N^{(N,V,V)}$ parameters should be taken into consideration.

Using the experimental data and the findings of the previous study on the liquid Fe-N alloy, the values of the interaction parameters $e_N^{(V)}$, $r_N^{(V)}$, $r_N^{(N,V)}$ and $t_N^{(N,V,V)}$ have been determined for the temperature 2173 K (Tab).

The present experimental studies are being continued for the liquid metal temperatures 2073 and 2273 K. The thermodynamic characteristics as developed complexly will be presented in subsequent publications.

Values of interaction parameters for the temperature 2173 K

$e_N^{(V)}$	$r_N^{(V)}$	$r_N^{(N,V)}$	$t_N^{(N,V,V)}$
-0.0967 ± 0.0016	0.0067 ± 0.0006	0.0443 ± 0.0085	-0.0032 ± 0.0011

Note: This work constitutes a fragment of research carried out within the framework of the KBN Grant No 7T08B 04517 "The thermodynamic characteristics of the Fe-V binary alloy with nitrogen in hyperbaric conditions".

REFERENCES

- [1] E. Schürmann, C. Zellerfeld, W. Kättlitz, *Archiv. Eisen.* **52** 219–224 (1981).
- [2] H. Wada, R.D. Pehlke, *Metall. Trans. B* **12B** 333–339 (1981).
- [3] D. B. Evans, R.D. Pehlke, *Trans. Met. Soc. AIME* **233** 1620–1624 (1965).
- [4] M. R. Rao, N. Parlee, *Mem. Sc. Rev. Metall.* **1**, 52–60 (1961).
- [5] R. D. Pehlke, J. F. Elliot, *Trans. Met. Soc. AIME* **218**, 1088–1101 (1960).
- [6] F. Ishii, T. Fuwa, *Tetsu-to-hagane* **68**, 1560–1568 (1982).
- [7] H. Wada, *Trans. ISIJ* **9**, 399–403 (1969).
- [8] Yu. M. Pomarin, G. M. Grigorenko, V. I. Lakomskij, *Izv. Akad. Nauk SSSR Metall.* **5**, 75–79 (1975).
- [9] H. Ohtani, M. Hillert, *CALPHAD* **15**, 25–39 (1991).
- [10] O. Knacke, O. Kubashevski, K. Hesselman, *Thermochemical Properties of Inorganic Substances*, Springer-Verlag Berlin, Heidelberg (1991), 2249.
- [11] J. Siwka, *Rozpuszczalność azotu w ciekłym żelazie, chromie i innych stopach oraz elementy wytapiania stali wysokoazotowych przy użyciu plazmy*, Politechnika Częstochowska (1999), *Rozprawa habilitacyjna*.
- [12] J. Siwka, *Archives of Metallurgy* **43**, 67–82 (1998).

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