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THERMODYNAMIC SECOND-ORDER INTERACTION COEFFICIENTS OF NITROGEN WITH NICKEL AND CHROMIUM IN LIQUID STEEL

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Abstract. The authors propose a simple theory of thermodynamic properties of liquid nitrogen solutions in alloys of the Fe–Ni and Fe–Cr systems. The theory is analogous to the theory of these systems proposed previously by the authors in 2019 and 2021. It is based on lattice model of the Fe–Ni and Fe–Cr solutions. The model assumes a FCC lattice. At the sites of this lattice are the atoms of iron, nickel and chromium. Nitrogen atoms are located in octahedral interstices. Nitrogen atom interacts only with the metal atoms located in the lattice sites neighboring to it. This interaction is pairwise. It is assumed that the energy of this interaction depends neither on composition nor on temperature and the liquid solutions of Fe–Ni and Fe–Cr systems are perfect. For an infinitely nitrogen-diluted solution of this element in the Fe–*j* alloy (*j* = Ni, Cr), a rational nitrogen activity coefficient γ_N^0 is determined. Next, we considered the expansion of the function $\ln\gamma_N^0$ at a constant temperature in a series in powers of the argument c_j, where c_j is the concentration of the *j* component, expressed in mole fractions. The coefficient J_n in the term of the n^{th} degree of this expansion is called the thermodynamic n^{th} order interaction coefficient of nitrogen with *j* element in liquid steel. In this case, $J_1 = \varepsilon_N^j$ is called Wagner interaction coefficient, $J_2 = \rho_N^j$ – the second order interaction coefficient. Within the framework of the presented theory the simplest relationship between the interaction coefficients ρ_N^j and ε_N^j was found. The formula looks like: $\rho_N^j = \frac{1}{12}\left(\varepsilon_N^j\right)^2$. To verify this formula, experimental data on the solubility of nitrogen in liquid alloys of the Fe–Ni and Fe–Cr systems at a temperature of 1873 K, obtained by Satir-Kolorz and Feichtinger (1991) were used. From these data follows: $\varepsilon_N^{Ni} = 2.6$; $\varepsilon_N^{Cr} = -10.2$; $\rho_N^{Ni} = 0.8$; $\rho_N^{Cr} = 6.3$. The theoretical values calculated using the above formula are as follows: $\rho_N^{Ni} = 0.56$; $\rho_N^{Cr} = 8.67$. Bearing in mind the significant uncertainty in the experimental determination of the second order interaction coefficient of nitrogen with alloying elements in iron-based binary alloys, the correspondence between the theoretical and experimental results should be considered satisfactory.

Keywords: thermodynamics, solution, nitrogen, iron, nickel, chromium, activity coefficient, n^{th} order interaction coefficient, Wagner interaction coefficient, Langenberg interaction coefficient

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ТЕРМОДИНАМИЧЕСКИЕ ПАРАМЕТРЫ ВЗАИМОДЕЙСТВИЯ ВТОРОГО ПОРЯДКА АЗОТА С НИКЕЛЕМ И ХРОМОМ В ЖИДКОЙ СТАЛИ

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Аннотация. Предложена простая теория термодинамических свойств жидких растворов азота в бинарных сплавах систем Fe–Ni и Fe–Cr, которая аналогична теории, предложенной авторами ранее (2019 – 2021). Данная теория основана на решеточной модели растворов Fe–Ni и Fe–Cr. Предполагается модельная решетка типа ГЦК, в узлах которой располагаются атомы железа, никеля и хрома. Атомы азота располагаются в октаэдрических междоузлиях. Атом азота взаимодействует лишь с атомами металлов, находящимися в соседних с этим атомом узлах решетки, и это взаимодействие парное. Предполагается, что энергия этого взаимодействия не зависит ни от состава сплава, ни от температуры, и жидкие растворы систем Fe–Ni и Fe–Cr являются совершенными. Для бесконечно разбавленного по азоту раствора этого элемента в сплаве Fe–*j* (*j* = Ni, Cr) рассматривается рациональный коэффициент активности азота γ_N^0. Далее анализируется разложение функции $\ln\gamma_N^0$ при постоянной температуре в ряд по степеням аргумента c_j, где c_j – концентрация компонента *j*, выраженная в мольных долях. Коэффициент J_n в члене *n*-й степени этого разложения называется термодинамическим параметром взаимодействия *n*-го порядка азота с элементом *j* в жидкой стали. При этом $J_1 = \varepsilon_N^j$ называется вагнеровским параметром взаимодействия, а $J_2 = \rho_N^j$ – параметром взаимодействия второго порядка. В рамках представленной теории найдена простая связь между параметрами

взаимодействия ρ_N^j и ε_N^j. Формула имеет вид $\rho_N^j = \frac{1}{12}\left(\varepsilon_N^j\right)^2$, для ее проверки были использованы экспериментальные данные по растворимости азота в жидких сплавах систем Fe–Ni и Fe–Cr при температуре 1873 К, полученные в работе Затир-Колорц и Файхтингера (1991 г.). Из этих данных следует: $\varepsilon_N^{Ni} = 2{,}6$; $\varepsilon_N^{Cr} = -10{,}2$; $\rho_N^{Ni} = 0{,}8$; $\rho_N^{Cr} = 6{,}3$. Теоретические значения, рассчитанные по приведенной формуле, получились следующими: $\rho_N^{Ni} = 0{,}56$; $\rho_N^{Cr} = 8{,}67$. Имея ввиду значительную экспериментальную неопределенность для параметров взаимодействия ρ_N^{Ni} и ρ_N^{Cr}, согласие теоретических результатов с экспериментальными следует признать удовлетворительным.

Ключевые слова: термодинамика, раствор, азот, железо, никель, хром, коэффициент активности, параметр взаимодействия *n*-го порядка, вагнеровский параметр взаимодействия, лангенберговский параметр взаимодействия

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Nitrogen is an element that plays a significant role in steel production [1]. In recent decades, special attention has been given to the production and application of high-nitrogen steels [2; 3], as well as to the behavior of nitrogen in various manufacturing processes [4 – 6]. The solubility of nitrogen in liquid steel is of primary importance [7 – 10]. Research in this area aims to improve the accuracy of solubility predictions and the potential for nitride formation.

Let us consider the thermodynamics of nitrogen solutions in liquid binary Fe–*j* alloys, where j represents nickel and chromium. The concentrations of elements in the Fe–*j*–N solution, expressed in mole fractions, will be denoted as c_{Fe}, c_j and c_N, respectively. In practical metallurgy, these concentrations are typically expressed as mass percentages and designated as [% Fe], [% *j*] and [% N].

We will proceed from the concept of the absolute [11] activity of nitrogen in the solution, denoted as a_N. The rational activity coefficient will be represented as γ_N ($\gamma_N = a_N/c_N$). The mass-percent activity coefficient of nitrogen will be denoted as f_N ($f_N = a_N/[\%\ N]$). The activity coefficients in an infinitely nitrogen-diluted solution ($c_N \to 0$; [% N] → 0) will be denoted as γ_N^0 and f_N^0, respectively. These coefficients will be normalized based on the condition: $\gamma_N^0 \to 1$ as $c_{Fe} \to 1$; $f_N^0 \to 1$ as [% Fe] → 100.

The fundamental concept of the phenomenological thermodynamics of multicomponent dilute alloys was introduced by Wagner [12]. Wagner's idea was applied to the calculation of nitrogen solubility in steel by Langenberg [13]. A significant development of Wagner's approach was presented in [14]. According to this study, within a certain convergence interval, the following expansion holds

$$\ln\gamma_N^0 = \sum_{n=1}^{\infty} J_n c_j^n, \qquad (1)$$

where J_n is the rational *n*-th order interaction coefficient. A similar expansion can be written.

$$\lg f_N^0 = \sum_{n=1}^{\infty} \widetilde{J_n}[\%\ j]^n, \qquad (2)$$

where $\widetilde{J_n}$ is the mass-percent *n*-th order interaction coefficient.

For first- and second-order interaction coefficients, there exist more specific notations [12 – 14]: $J_1 = \varepsilon_N^j$; $J_2 = \rho_N^j$; $\widetilde{J}_1 = e_N^j$; $\widetilde{J_2} = r_N^j$, where ε_N^j and e_N^j are the Wagner and Langenberg interaction coefficients, respectively.

Next, we will limit our consideration to the condition of constant temperature T = const.

Under this condition, from the invariance of the differential of the logarithm of the activity coefficient, the following relationship was obtained [15]

$$\varepsilon_N^j = 230{,}3\frac{A_j}{A_{Fe}}e_N^j + \frac{A_{Fe} - A_j}{A_{Fe}}, \qquad (3)$$

where A_{Fe} is the atomic mass of iron, and A_j is the atomic mass of the alloying element *j*. Similarly, the following relationship was derived [14]

$$\rho_N^j = \frac{230{,}3}{A_{Fe}^2}\left[100A_j^2 r_N^j + A_j\left(A_{Fe} - A_j\right)e_N^j\right] + \frac{1}{2}\left(\frac{A_{Fe} - A_j}{A_{Fe}}\right)^2. \qquad (4)$$

To measure the thermodynamic parameters of nitrogen interaction with element *j* in liquid steel, it is, in principle, sufficient to experimentally study the dependence of nitrogen solubility in a binary Fe–*j* alloy on the concentration of element *j*. The solubility of nitrogen in liquid iron was first measured in 1938 [16]. Shortly thereafter, research on nitrogen solubility in liquid binary iron alloys began [17]. The first-order thermodynamic interaction parameters of nitrogen with alloying elements were thoroughly investigated in studies [18 – 21]. The results of the main stage of experimental research on these parameters were summarized in a review article [22]. Such studies continue to this day [23].

Truncating the power series expansions (1) and (2) while retaining only the linear terms does not allow for an adequate description of the concentration dependence of nitrogen solubility in liquid binary iron alloys for a number of systems. Therefore, it is necessary to account for at least the quadratic terms as well. The technical

capabilities of experimental methods allow for the reliable determination of second-order thermodynamic interaction parameters of nitrogen with an alloying metal only in specific cases. Therefore, a theoretical approach capable of predicting these values would be useful for assessing the reliability of the obtained experimental results.

In this study, we propose a simple model of nitrogen solutions in liquid Fe–j (j = Ni, Cr) alloys that allows expressing the second-order thermodynamic interaction coefficient ρ_N^j in terms of the Wagner interaction coefficient ε_N^j. The theory is based on a lattice model of Fe–j solution. The model assumes a face-centered cubic (FCC) lattice, where the lattice sites are occupied by iron atoms and atoms of element j. Nitrogen atoms are located in octahedral interstices. A nitrogen atom interacts only with metal atoms occupying the neighboring lattice sites, and this interaction is pairwise. It is assumed that the energy of this interaction is independent of the alloy composition and temperature. The liquid solutions in the Fe–j system are considered ideal. Within the framework of the proposed theory, we express the logarithm of the nitrogen activity coefficient, $\ln\gamma_N^0$, in an infinitely nitrogen-diluted solution as a function of the concentration c_j. In doing so, we use the result obtained in studies [24; 25]:

$$\ln\gamma_N^0 = -\delta\ln\left(1-\frac{1}{\delta}\varepsilon_N^j c_j\right), \qquad (5)$$

where δ is the number of FCC lattice sites surrounding an octahedral interstice (δ = 6).

Next, we use the logarithmic expansion

$$\ln(1+x) = \sum_{n=1}^{\infty}(-1)^{n+1}\frac{x^n}{n}.$$

It follows that

$$\ln(1-x) = -\sum_{n=1}^{\infty}\frac{x^n}{n}. \qquad (6)$$

The radius of convergence for these expansions is equal to 1.

From expressions (5) and (6), we obtain

$$\ln\gamma_N = \delta\sum_{n=1}^{\infty}\frac{1}{n}\left(\frac{\varepsilon_N^j c_j}{\delta}\right)^n. \qquad (7)$$

Thus, for the n-th order interaction coefficient of nitrogen with element j, we have

$$J_n = \frac{1}{n}\frac{\left(\varepsilon_N^j\right)^n}{\delta^{n-1}}$$

or

$$J_n = \frac{6^{1-n}}{n}\left(\varepsilon_N^j\right)^n.$$

The radius of convergence of expansion (7) is $\frac{6}{\left|\varepsilon_N^j\right|}$.

For the second-order interaction coefficient $\rho_N^j = J_2$ we obtain

$$\rho_N^j = \frac{1}{12}\left(\varepsilon_N^j\right)^2. \qquad (8)$$

As an experimental validation of equation (8), this study utilizes the results of nitrogen solubility measurements in liquid binary Fe–Ni and Fe–Cr alloys at a temperature of 1873 K and partial nitrogen pressures P_{N_2} up to 100 bar [26]. A comparison between the theoretical predictions and experimental data is presented in the Table. The results obtained in [26] appear to be more reliable than the data reported in [7 – 10].

From the Table, it follows that the theoretical calculations based on equation (8) show satisfactory agreement with the experimental data from [26].

Conclusions

A model-based theory of structure and interatomic interaction has been applied to nitrogen solutions in liquid alloys of the Fe–Ni and Fe–Cr systems.

Equation (8) has been derived, expressing the second-order thermodynamic interaction coefficients ρ_N^{Ni} and ρ_N^{Cr} in liquid steel in terms of the Wagner interaction coefficients ε_N^{Ni} and ε_N^{Cr} in liquid iron-based alloys. The equation is given by $\rho_N^j = \frac{1}{12}\left(\varepsilon_N^j\right)^2$, where j = Ni, Cr.

Theoretical values of the second-order interaction coefficients in liquid steel at T = 1873 K were obtained: $\rho_N^{Ni} = 0.56$ and $\rho_N^{Cr} = 8.67$, which show satisfactory agreement with the experimental estimates: $\rho_N^{Ni} = 0.8$ and $\rho_N^{Cr} = 6.3$, as reported in [26].

Thermodynamic interaction coefficients of nitrogen with nickel and chromium in liquid steel

Термодинамические параметры взаимодействия азота с никелем и хромом в жидкой стали

j	Experiment [26]				Theory
	e_N^j	ε_N^j, equation (3)	$r_N^j\cdot10^5$	ρ_N^j, equation (4)	ρ_N^j, equation (8)
Ni	0.110	2.6	3.5	0.8	0.56
Cr	–0.048	–10.2	35.0	6.3	8.67

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L. A. Bol'shov – formation of the article idea, writing the text.
S. K. Korneichuk – verification of the proposed method and results, formatting the paper and accompanying documents.
E. L. Bol'shova – translation of English articles, translation into English of the abstract and references.

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