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DETERMINATION OF PARAMETERS OF COOPERATION FOR NITROGEN IN LIQUID IRON ON EXPERIMENTAL DATA ARRAY WITH THE USE OF THERMODYNAMICS MODEL OF MULTICOMPONENT CONDENSED PHASE

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The reliable values of parameters of interaction of nitrogen in liquid iron are got both for energy of Gibbs and enthalpy. Graphic dependences for accordance of calculation and experimental values of solubility of nitrogen depending on content of alloying elements in the iron: manganese, vanadium, titan, chrome, molybdenum, niobium, tungsten, tantalum, aluminium, boron, nickel and silicon are built. Adequacy of thermodynamics model of the condensed phase for description of difficult multicomponent solutions is confirmed.

Keywords: parameters of Wagner, solubility of nitrogen, liquid iron, condensed pha-se, alloying elements

Parameters of Gibbs energy cooperating of nitrogen with chemical elements in the liquid alloys of iron was studied in a row of works, in particular [1], however until now there is a problem of receipt of their reliable numeral values. Parameters of cooperation are partials of logarithm of coefficient of activity of nitrogen γ_N on the mole rate of some chemical element of x_j at endless dilution of fusion:

$$\varepsilon_j^N = \varepsilon_N^j = \left(\frac{\partial \ln(\gamma_N)}{\partial x_j} \right)_{x_1=1}, \quad (1)$$

where x_1 is an element-solvent (iron).

In practice the enthalpy parameters of cooperation are used also:

$$\eta_j^N = \eta_N^j = \left(\frac{\partial h_N^M}{\partial x_j} \right)_{x_1=1}, \quad (2)$$

in which differentiate partial molar enthalpy of h_N^M nitrogen.

Parameters of cooperation are the key elements of thermodynamics analysis of solubility of nitrogen in liquid iron at its interaction with alloying elements. Any similar analysis supposes the use of some theoretical model of metallic solution, since the rows of Taylor series decompositions of Gibbs energy with empiric coefficients, first offered by K. Wagner [2], and concluding the new statistical model of the condensed phase [3].

In obedience to a model [3] for activity of nitrogen in three-component solution (in the standard of Raul) have:

$$\ln a_N^{mod} = \ln\left(x_i \cdot \psi_i\right) + 1 - \sum_{j=1}^{k} x_j \cdot \psi_j \cdot \beta_{ji} =$$

$$= 1 + \ln\left(\frac{x_N}{x_{Fe} \cdot \beta_{NFe} + x_R \cdot \beta_{NR} + x_N} \right) - \frac{x_N}{x_{Fe} \cdot \beta_{NFe} + x_R \cdot \beta_{NR} + x_N} - \frac{x_{Fe} \cdot \beta_{FeN}}{x_{Fe} + x_R \cdot \beta_{FeR} + x_N \cdot \beta_{FeN}} -$$

$$- \frac{x_R \cdot \beta_{RN}}{x_{Fe} \cdot \beta_{RFe} + x_R + x_N \cdot \beta_{RN}}, \quad (3)$$

where a_N^{mod} is activity of nitrogen in obedience to a model; *R* is the second component (*Mn*, *V*, *Ti*, …); x_i is a mole rate of i component; $\beta_{ij} = \exp\left(E_{ij}/R \cdot T\right)$, $\psi_i = 1/\sum_{j=1}^{k} x_i \beta_{ij}$; β_{ij}, E_{ij} are power parameters of solution model, cooperation's related to the sought after parameters by formulas [3]:

$$\varepsilon_j^N = \varepsilon_N^j = 1 + \beta_{1N} \cdot \beta_{1j} - \frac{\beta_{Nj}}{\beta_{N1}} - \frac{\beta_{jN}}{\beta_{j1}} \; ; \tag{4}$$

$$\eta_j^N = \eta_N^j = R \cdot T \cdot \left(\beta_{1N} \cdot \beta_{1j} \cdot \ln\left(\beta_{1N} \cdot \beta_{1j}\right) - \frac{\beta_{Nj}}{\beta_{N1}} \cdot ln\left(\frac{\beta_{Nj}}{\beta_{N1}}\right) - \frac{\beta_{jN}}{\beta_{j1}} \cdot \ln\left(\frac{\beta_{jN}}{\beta_{j1}}\right)\right) . \tag{5}$$

We suppose that in the conditions of dilute solution for energy parameters correlations $\beta_{ij} = \beta_{ji}$, $E_{ij} = E_{ji}$, as well as for the parameters of cooperation ε_j^i.

There is also another way of calculation of activity of nitrogen in fusion $\ln a_N$ in the same standard, coming from partial pressure of nitrogen above ferrous fusion:

where p_{N_2} is pressure of molecular nitrogen; $\ln K_{solN_2} = \frac{\Delta G_{solN_2}}{R \cdot T} + \ln \frac{100 A_N}{A_{Fe}} - \ln \gamma_N^{\infty}$ is a constant of dissolution of nitrogen in a gland, resulted to the standard of Raul; A_N; A_{Fe} are the atomic masses nitrogen and ferrous accordingly.

Concordantly, in particular, to Lyupis [4], molar Gibbs energy dissolutions of nitrogen in liquid iron are made $\Delta G_{solN_2} = 3600{,}6 + 23{,}907T$. In obedience to a model [3], $\ln \gamma_N^{\infty} = 1 - \beta_{FeN} - \ln \beta_{NFe}$.

Thus, for activity of nitrogen have:

$$\ln a_N = 0{,}5 \ln p_{N_2} - \frac{3600{,}6 + 23{,}907T}{R \cdot T} - \ln\left(\frac{100 \cdot 14{,}0067}{55{,}847}\right) + 1 - \beta_{FeN} - \ln \beta_{NFe} \; , \tag{7}$$

where T is a temperature, K; R = 8,314472 Jou/(mole·K) - universal gas constant.

Equating to activity of nitrogen, got by two methods, get equation for nonlinear regression:

$$\ln a_N - \ln a_N^{mod} = F_l\left(x_{Fe}, x_R, x_N, E_{FeN}, E_{RN}, T, p_{N_2}\right) = 0 \; , \tag{8}$$

where *l* is a number of alloys;

We apply multiple nonlinear regression on all array of melting of Fe-R-N and find the power parameters of model of the condensed phase E_{ij} on the minimum sum of squares of rejections $\sum_l F_l\left(x_{Fe}, x_R, x_N, E_{FeN}, E_{RN}, T, p_{N_2}\right)^2$, and then on formulas (4) and (5) are the sought after parameters of cooperation of nitrogen.

The power parameters of model β_{ij} must in every alloy be calculated as $\beta_{ij} = \exp\left(-E_{ij}/R \cdot T\right)$, id est taking into account the actual temperature of every experimental point. Further on formulas (4) and (5) find the sought after values of parameters of cooperation.

Except for determination of parameters from equation of regression (8) with the known sizes E_{FeN}, E_{RN} for every alloy find calculation solubility of nitrogen x_N, set by

values x_R, p_{N_2}, T considering that $x_{Fe} = 1 - x_R - x_N$. Such approach, requiring the decision of nonlinear equation with one unknown x_N

$$F(x_{Fe}, x_R, x_N, E_{FeN}, E_{RN}, T, p_{N_2}) = 0, \quad (9)$$

allows graphically to estimate adequacy of thermodynamics model of multicomponent solution [3]. This equation is equalization of the state of the system Fe-R-N with one degree of freedom. With its help any of four variables x_R, x_N, p_{N_2}, T it is possible to define, knowing three other sizes.

In all more than 2500 experimental points about solubility of nitrogen in liquid iron were analyzed in work in presence different alloying elements and calculated solubility of nitrogen depending on maintenance of tungsten, tantalum, aluminium, boron, nickel and silicon in liquid iron.

Conclusions. The reliable values of parameters of cooperation of nitrogen in liquid iron got in work both for Gibbs energy and enthalpy can be used for thermodynamics description of processes of the special electrometallurgy, used for the receipt of steels, both with subzero and by high content of nitrogen. The built graphic dependences of accordance of calculation and experimental values to solubility of nitrogen depending on maintenance in the iron of alloying elements confirm adequacy of thermodynamics model of the condensed phase [3] for description of difficult multicomponent solutions in the wide range of concentrations.

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