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Short report
Краткое сообщение

WAGNER INTERACTION COEFFICIENT BETWEEN NITROGEN AND COBALT IN LIQUID STEEL

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Abstract. A simple theory of thermodynamic properties of liquid nitrogen solutions in Fe–Co alloys is proposed. This theory is completely analogous to the theory for liquid nitrogen solutions in alloys of the Fe–Cr system proposed previously by the authors in 2019. The theory is based on lattice model of the Fe–Co solutions. The model assumes FCC lattice. In the sites of this lattice are the atoms of Fe and Co. Nitrogen atoms are located in octahedral interstices. The nitrogen atom interacts only with the metal atoms located in the lattice sites neighboring to it. This interaction is pairwise. It is supposed that the liquid solutions of Fe–Co system are perfect. The initial values for the calculation are the Sieverts law constants for nitrogen solubility in liquid iron and in liquid cobalt. Result of the calculation is value of Wagner interaction coefficient in liquid iron-based alloys at 1873 K $\varepsilon_N^{Co} = 1.8$. This value is in good agreement with the experimental data obtained by Schenck, Frohberg and Graf, 1958; Maekawa and Nakagawa, 1960.

Keywords: thermodynamics, solutions, nitrogen, iron, cobalt, Wagner interaction coefficient, Langenberg interaction coefficient, Sieverts law

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ВАГНЕРОВСКИЙ ПАРАМЕТР ВЗАИМОДЕЙСТВИЯ АЗОТА С КОБАЛЬТОМ В ЖИДКОЙ СТАЛИ

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Аннотация. Предложена простая теория термодинамических свойств жидких растворов азота в сплавах системы Fe–Co. Эта теория полностью аналогична теории для жидких растворов азота в сплавах системы Fe– Cr, предложенной авторами в 2019 г. Теория основана на решеточной модели растворов Fe–Co. Предполагается модельная решетка типа ГЦК. В узлах этой решетки располагаются атомы железа и кобальта. Атомы азота располагаются в октаэдрических междоузлиях. Атом азота взаимодействует с атомами металлов, находящимися в соседних с этим атомом узлах решетки. Это взаимодействие парное. Предполагается, что жидкие растворы системы Fe–Co являются совершенными. В качестве исходных для расчетов взяты значения констант закона Сивертса для растворимости азота в жидком железе и в жидком кобальте. Результатом расчета является значение вагнеровского параметра взаимодействия в жидких сплавах на основе железа при температуре 1873 К $\varepsilon_N^{Co} = 1{,}8$. Это хорошо согласуется с экспериментальными данными, полученными Шенк, Фроберг, Граф в 1958 г. и Маекава, Накагава в 1960 г.

Ключевые слова: термодинамика, растворы, азот, железо, кобальт, вагнеровский параметр взаимодействия, лангенберговский параметр взаимодействия, закон Сивертса

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To predict the solubility of nitrogen in liquid steel, understanding the nitrogen solubility in liquid iron is crucial, along with at least obtaining the first order interaction coefficients between nitrogen and alloying elements. Typically, these coefficients are derived from experimental investigations of nitrogen solubility in the melts of binary metal systems like Fe – j, rwhere iron serves as the solvent and j represents the alloying element. Nevertheless, values obtained through this method often encompass experimental uncertainties, occasionally

of significant magnitude. This scenario also holds true for the interaction between nitrogen and cobalt.

Currently, cobalt finds diverse technological applications, including its use in alloying special steels known for their high-speed, magnetic, and heat-resistant properties. The significance of the Wagner interaction coefficient between nitrogen and cobalt in liquid steel lacks consensus. Hence, an intriguing avenue lies in investigating this matter from a theoretical perspective.

To delve into the thermodynamics of nitrogen solutions in the Fe – Co system's liquid alloys, we denote the concentrations of the components in molar fractions as c_{Fe}, c_{Co} and c_N. Alternatively, expressing these concentrations in mass percentages yields [% Fe], [% Co] and [% N]. Let a_N means present the thermodynamic activity of nitrogen in the solution, $\gamma_N = \frac{a_N}{c_N}$ – the rational coefficient of nitrogen activity in the solution, $f_N = \frac{a_N}{[\%\ N]}$ – the mass-percentage coefficient of nitrogen activity. The thermodynamic first order interaction coefficients between nitrogen and cobalt in liquid iron-based alloys of the Fe–Co–N systems are determined by the following formulas

$$\varepsilon_N^{Co} = \frac{\partial \ln \gamma_N}{\partial c_{Co}} \text{ при } c_{Fe} \to 1;$$

$$e_N^{Co} = \frac{\partial \lg f_N}{\partial [\%\ Co]} \text{ при } [\%\ Fe] \to 100,$$

where ε_N^{Co} is the Wagner interaction coefficient, while e_N^{Co} is the Langenberg interaction coefficient. A correlation between these parameters is presented in [1]:

$$\varepsilon_N^{Co} = 230{,}3\frac{A_{Co}}{A_{Fe}}e_N^{Co} + \frac{A_{Fe} - A_{Co}}{A_{Fe}}, \quad (1)$$

where A_{Fe} and A_{Co} are the atomic masses of the corresponding elements.

The solubility of nitrogen in liquid alloys of the Fe–Co system, expressed in mass percentage, is denoted as $[\%\ N]^*$. At a partial pressure of nitrogen in the liquid phase P_{N_2} approaching zero $P_{N_2} \to 0$, the square root law, also known as Sieverts law, applies:

$$[\%\ N]^* = K'\sqrt{\frac{P_{N_2}}{P_0}},$$

where P_0 is the standard pressure ($P_0 = 1$ atm $\approx$ ≈ 0.101 MPa); K' is the Sieverts law constant. Let $K' = K'(Fe)$ at $c_{Fe} = 1$ and $K' = K'(Co)$ at $c_{Co} = 1$.

Following the proposed simple theory regarding the thermodynamic properties of liquid nitrogen solutions in Fe–Co alloy systems, an alignment is observed with the theoretical framework governing nitrogen solutions in Fe–Cr and Ni–Cr alloy systems [2]. The abstract of this paper outlines the theoretical model. Utilizing the findings from [2], we arrive at the model presented below:

$$\varepsilon_N^{Co} = 6\left(1 - \sqrt[6]{\frac{A_{Co}K'(Co)}{A_{Fe}K'(Fe)}}\right). \quad (2)$$

At a temperature of $T = 1873$ K $K'(Fe) = 0.044$ wt. % [3] and $K'(Co) = 0.0047$ wt. % [4]. With $A_{Fe} = 55.847$ and $A_{Co} = 58.9332$. applying formula (2) yields the theoretical Wagner interaction coefficient between nitrogen and cobalt in liquid steel at $T = 1873$ K as $\varepsilon_N^{Co} = 1.8$. Subsequently, equation (1) provides the corresponding value of the Langenberg interaction coefficient $e_N^{Co} = 0.0076$.

Consideration of experimental values of the e_N^{Co} coefficient in liquid steel at $T = 1873$ K reveals various findings. In [5], nitrogen solubility in Fe–Co alloys was studied by quenching samples to a concentration of [% Co] = 24 wt. %, resulting in an estimated $e_N^{Co} = 0.0072$. Continuation of this study in [6] up to [% Co] = 100 wt. % produced an estimate for nitrogen solubility in liquid cobalt, $K'(Co) = 0.0044$ wt. %, which closely aligns with the value used in this paper, $K'(Co) = 0.0047$ wt. %.

In [7], an experimental value of $e_N^{Co} = 0.007$ was reported.

Additionally, [8] investigated the nitrogen solubility in melts of the Fe–Co system using the Sieverts method, determining an experimental estimate of the interaction coefficient at 1873 K as $e_N^{Co} = 0.011$.

Comparing these estimates of the Langenberg interaction coefficient at $T = 1873$ K: $e_N^{Co} = 0.0072$ [5] and $e_N^{Co} = 0.007$ [7] are closer to the theoretical estimate $e_N^{Co} = 0.0076$ than the experimental one $e_N^{Co} = 0.011$ [8]. Consequently, based on the theory presented in this paper, the estimates from [5] and [7] appear more plausible than the one described in [8].

Conclusions

Theoretical estimates for the thermodynamic first-order interaction coefficients between nitrogen and cobalt in liquid steel at $T = 1873$ K: $\varepsilon_N^{Co} = 1.8$; $e_N^{Co} = 0.0076$.

The experimental estimates of the Langenberg interaction coefficient $e_N^{Co} = 0.0072$ [5] and $e_N^{Co} = 0.007$ [7] appear more credible or reliable compared to the estimate $e_N^{Co} = 0.011$ [8].

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E. L. Bol'shova – translation of English articles, translation into English of the abstract and references.

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