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SOLUBILITY OF NITROGEN IN THE LIQUID Fe-Mo ALLOY

ROZPUSZCZALNOŚĆ AZOTU W CIEKŁYM STOPIE Fe-Mo

The solubility of nitrogen in liquid alloys of iron with molybdenum was previously determined experimentally in numerous works, and in one case by means of the thermodynamic calculations of phase diagrams. The influence of molybdenum contained in the alloy on nitrogen solubility was interpreted by employing interaction parameters of the first order, $e_N^{(Mo)}$, and the second order, $r_N^{(Mo)}$. In all cases, with the exception of one work, investigations were related to temperatures little deviating from $T = 1873$ K. Also, not very large (25% wt max) contents of molybdenum, with the relatively weak interaction of this element with nitrogen, might be the cause of the failure to reveal all possible interactions between nitrogen and molybdenum in the liquid iron alloy.

Bearing the above in mind, the author's own programme of experimental investigations was drawn up, in which such conditions were created that all possible interactions in the liquid Fe-N-Mo alloy would be revealed to such an extent that they could be measured using an appropriate experimental technique. By applying the levitation metal melting technique, nitrogen concentrations in the alloy of iron with molybdenum were determined in the conditions of thermodynamic equilibrium within a wide range of variation of thermodynamic factors, i.e. nitrogen pressure from 0.1 to 3.0 MPa, liquid metal temperature from 1973 to 2173 K, and molybdenum concentration from 10 to 50% wt.

The experimental results served for formulating the thermodynamic characteristics of activity coefficient, where one of the factors, for the first time, is the nitrogen concentration in the alloy. By using the results of the author's earlier work on the liquid Fe-N alloy, temperature relationships of all interaction parameters necessary for the Fe-N-Mo alloy have been defined.

The thermodynamic data obtained in the study will constitute part of an original base for building a thermodynamic model intended for the determination of nitrogen solubility in new generation steels, i.e. high-nitrogen steels that are designated by the international abbreviation HNS.

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Rozpuszczalność azotu w ciekłych stopach żelaza z molibdenem, wcześniej określano eksperymentalnie w wielu pracach oraz w jednym przypadku drogą termodynamicznych obliczeń diagramów fazowych. Wpływ zawartości molibdenu w stopie na rozpuszczalność azotu interpretowano przez użycie parametrów oddziaływania pierwszego rzędu $e_N^{(Mo)}$ i drugiego rzędu $r_N^{(Mo)}$. We wszystkich przypadkach, poza jedną pracą, badania odnosiły się do temperatur niewiele odbiegających od $T = 1873$ K. Również niezbyt duże zawartości molibdenu (maks. 25% mas.) przy stosunkowo słabym oddziaływaniu tego pierwiastka z azotem, mogły być przyczyną nie ujawnienia wszystkich możliwych oddziaływań między azotem a molibdenem w ciekłym stopie żelaza.

Mając to na uwadze, opracowano własny program badań eksperymentalnych, w których stworzono warunki dla ujawnienia się wszystkich możliwych oddziaływań w ciekłym stopie Fe-N-Mo i to w takim stopniu, że można je zmierzyć przy użyciu odpowiedniej techniki eksperymentalnej.

Stosując technikę lewitacyjnego topienia metali wyznaczono — w warunkach termodynamicznej równowagi — stężenia azotu w stopie żelaza z molibdenem w szerokim zakresie zmian czynników termodynamicznych, tj. ciśnienia azotu od 0,1 do 3,0 MPa, temperatury ciekłego metalu od 1973 do 2173 K i stężenia molibdenu od 10 do 50% mas.

Wyniki eksperymentów posłużyły do opracowania termodynamicznej charakterystyki współczynnika aktywności, w której po raz pierwszy jednym z czynników jest stężenie azotu w stopie. Wykorzystując wyniki wcześniejszej własnej pracy nad ciekłym stopem Fe-N, określono temperaturowe zależności wszystkich niezbędnych dla stopu Fe-N-Mo parametrów oddziaływania.

Uzyskane w pracy dane termodynamiczne będą stanowić część oryginalnej bazy dla budowy modelu termodynamicznego, służącego do wyznaczania rozpuszczalności azotu w stalach nowej generacji tj. stalach wysokoazotowych, które nazwano międzynarodowym skrótem HNS.

1. Introduction

As reported in details in the author's own study [1], a search for a new, unknown until recently, effects of alloying elements on the properties of steels, revealed a significant role played by nitrogen. Intensive research and the implementation of research results to industrial practice have led to distinguishing a new group of alloy steels called high nitrogen steels (HNS).

It is was found that alloying elements which increase the solubility of nitrogen in the iron include the following (as shown in the decreasing order): vanadium, niobium, chromium, manganese, molybdenum and tungsten. Elements like carbon, silicon and aluminium, decrease the solubility of nitrogen (Fig. 1 — [2]).

From the point of view of the properties of HNS steels, when comparing the thermodynamic characteristics of liquid iron alloys with high nitrogen contents, consideration should be given to such alloying elements, as chromium, manganese, molybdenum, vanadium, nickel, carbon and silicon.

In high nitrogen steels, such a form of nitrogen is sought for, which will enable the nitrogen to transfer into the alloy matrix. Elements that most intensively

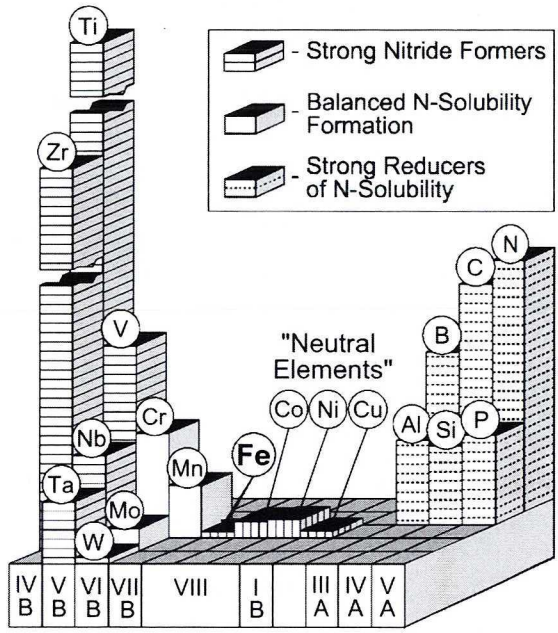

Fig. 1. Suitability of elements of HNS — metallurgy arranged in the periodic system [1]

dissolve nitrogen in the solid solution include chromium, manganese and molybdenum.

For the above reason, it is essential to determine, among other factors, the thermodynamic characteristics of the liquid Fe-N-Mo alloy.

The solubility of nitrogen in liquid alloys of iron with molybdenum was previously determined in works [3 – 7] using Sieverts's method, in works [8 – 13] using the sampling method, and in work [14] employing the levitation metal melting technique. The effect of the alloy content of molybdenum on the solubility of nitrogen was interpreted by utilizing the first order interaction parameter, $e_{\mathrm{N}}^{\mathrm{Mo}}$ — determined from studies on the Fe-Mo binary alloy, and by using this parameter in conjunction with the second order interaction parameter, $r_{\mathrm{N}}^{\mathrm{Mo}}$ — determined from studies on multi-component iron alloys, in which molybdenum was one of the alloying constituents. The solubility of nitrogen was also determined by means of the thermodynamic calculations of phase diagrams [15]. In all cases, except for one study [14], investigations were related to temperature deviating a little from $T = 1873\,\mathrm{K}$. Moreover, the rather small contents of molybdenum (25% wt., max.) with the relatively low interaction of this element with nitrogen, might have been the cause of the failure to disclose all possible interactions between nitrogen and molybdenum in the liquid iron alloy, which are considered in the Wagner-Chipman equation. This problem is explained in detail in the study [1].

In summary, it is justifiable to presume that the currently available database, though being sufficient for the description of alloys with low nitrogen contents, may become useless in describing alloys with high nitrogen contents.

Bearing the above in mind, the author's own programme of experimental studies was developed, in which conditions were created for to include all possible interactions in the liquid Fe-N-Mo alloy and to measure them using an appropriate experimental technique. It was assumed that obtained thermodynamic data would make up a part of the new base for building a thermodynamic model intended for the determination of the solubility of nitrogen in high nitrogen steels, HNS.

2. Experiments

Tests of the solubility of nitrogen in the liquid Fe-Mo alloy were carried out using the levitation metal melting technique. The testing stand and the experimental methodology are described in detail in previous works [1, 16, 17].

The liquid Fe-Mo alloy was saturated with nitrogen at the temperatures 1973, 2073 and 2173 K. The partial pressure of nitrogen was varied in the range 0.1 to 3.0 MPa. In total, 86 experimental points were obtained. The nitrogen content in Fe-N-Mo alloy specimens was determined by means of extraction to neutral gas using a LECO TC-336 analyzer.

3. Results and discussion

To describe thermodynamically the nitrogen gaseous phase system in equilibrium with the liquid Fe-N-Mo alloy system the following relationship was used:

$$\lg \frac{[\%\,\mathrm{N}]}{\sqrt{P_{N_2}}} = \lg K_{\mathrm{N(Fe)}} - \lg f_{\mathrm{N}} \tag{1}$$

on the basis of the obtained experimental results.

After considering a temperature dependence for the equilibrium constant of the reaction of nitrogen dissolution in liquid iron, as determined in the previous study [1], Equation (1) takes on the final form:

$$\lg f_{\mathrm{N}} = -\frac{664}{T} - 0.999 - \lg \frac{[\%\,\mathrm{N}]}{\sqrt{P_{N_2}}}\,. \tag{2}$$

Results of calculations using Equation (2) are shown in Figures 2 and 3.

As Figures 2 and 3 show, the values of the coefficient of activity of nitrogen, f_{N}, increase not only with increasing temperature, but also with increasing nitrogen

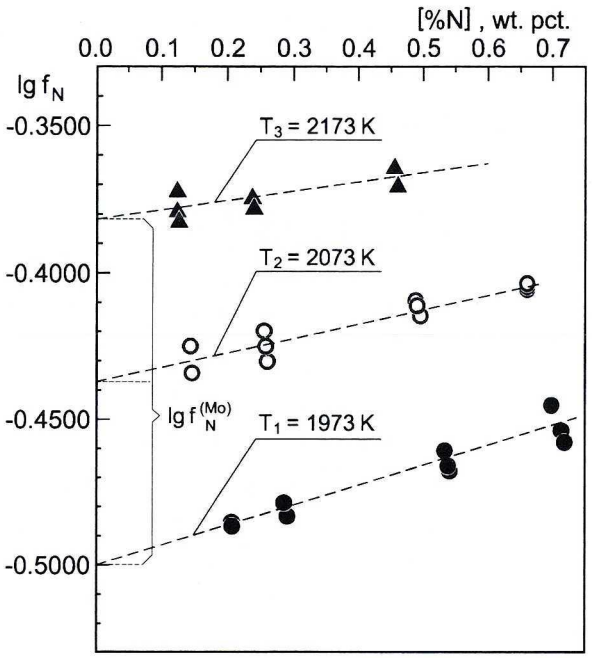

Fig. 2. Dependence of the coefficient of activity of nitrogen on the nitrogen concentration in the liquid Fe-N-Mo alloy 40% (the author's own studies — results of 28 measurements)

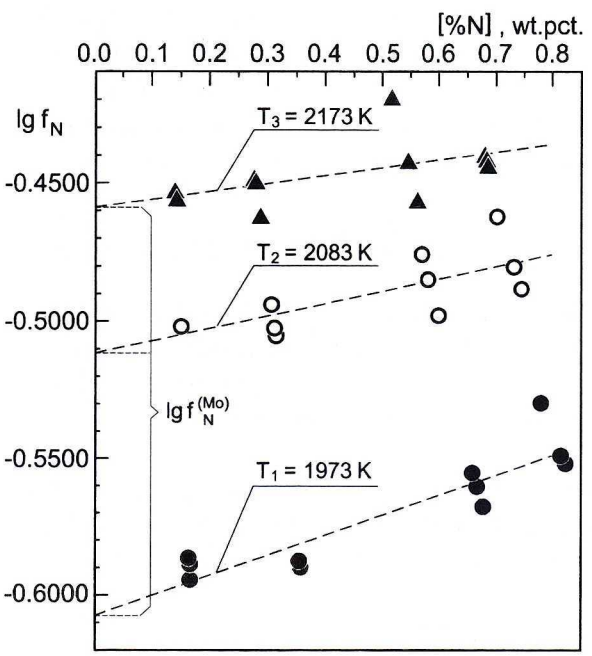

Fig. 3. Dependence of the coefficient of activity of nitrogen on the nitrogen concentration in the liquid Fe-N-Mo alloy 50% (the author's own studies — results of 35 measurements)

equilibrium concentration. For this reason, for further considerations the activity coefficient is defined as follows:

$$\lg f_{\mathrm{N}} = \lg f_{\mathrm{N}}^{(\mathrm{Mo})} + \lg f_{\mathrm{N}}^{(\mathrm{N})}. \tag{3}$$

If we assume that

$$E_{\mathrm{N}}^{(\mathrm{N})} = e_{\mathrm{N}}^{(\mathrm{N})} + r_{\mathrm{N}}^{(\mathrm{N})} \cdot [\%\mathrm{N}] + r_{\mathrm{N}}^{(\mathrm{N,Mo})} \cdot [\%\mathrm{Mo}], \tag{4}$$

then Equation (3) will take on the following form:

$$\lg f_{\mathrm{N}} = \lg f_{\mathrm{N}}^{(\mathrm{Mo})} + E_{\mathrm{N}}^{(\mathrm{N})} \cdot [\%\mathrm{N}]. \tag{5}$$

In work [1], when studying, e.g., the liquid Fe-N alloy, a temperature relationship was determined for the parameter $e_{\mathrm{N}}^{(\mathrm{N})}$; whereas in work [16] involving studies on the Cr-N liquid alloy, a possibility of neglecting the second order parameter $r_{\mathrm{N}}^{(\mathrm{N})}$ in Equation (4) was demonstrated.

Using the above findings and performing the analysis of the linear regression function in the form of

$$y(x) = a + b \cdot x \tag{6}$$

the values of the coefficients a and b were determined by the least squares method, which in the case of Equation (5) correspond to the values $\lg f_{\mathrm{N}}^{(\mathrm{Mo})}$ and $E_{\mathrm{N}}^{(\mathrm{N})}$ for a given liquid metal temperature. Consequently, using the statistical model of linear regression function (6), the value of the interaction parameter $r_{\mathrm{N}}^{(\mathrm{N,Mo})}$ was determined. It was found the free term in the model equation was very close to zero. The temperature relationship of the complex parameter $r_{\mathrm{N}}^{(\mathrm{N,Mo})}$ has the following form:

$$r_{\mathrm{N}}^{(\mathrm{N,Mo})} = \frac{10.7 \pm 2}{T} - 0.0047 \pm (0.0010). \tag{7}$$

Relationship (7) is shown in Figure 4. It should be emphasized here, that the distribution of points and the calculations results identify uniquely this new interaction parameter which has not been reported in the literature so far.

Figure 5 shows the effect of molybdenum concentration on the coefficient of activity $f_{\mathrm{N}}^{(\mathrm{Mo})}$.

A strong effect for the change in the concentration of this element in the Fe-N-Mo alloy and the fact that this relationship is curvilinear are visible here. For this reason, further processing of experimental data was conducted in the following way:

$$\frac{\lg f_{\mathrm{N}}^{(\mathrm{Mo})}}{[\%\mathrm{Mo}]} = e_{\mathrm{N}}^{(\mathrm{Mo})} + r_{\mathrm{N}}^{(\mathrm{Mo})} \cdot [\%\mathrm{Mo}]. \tag{8}$$

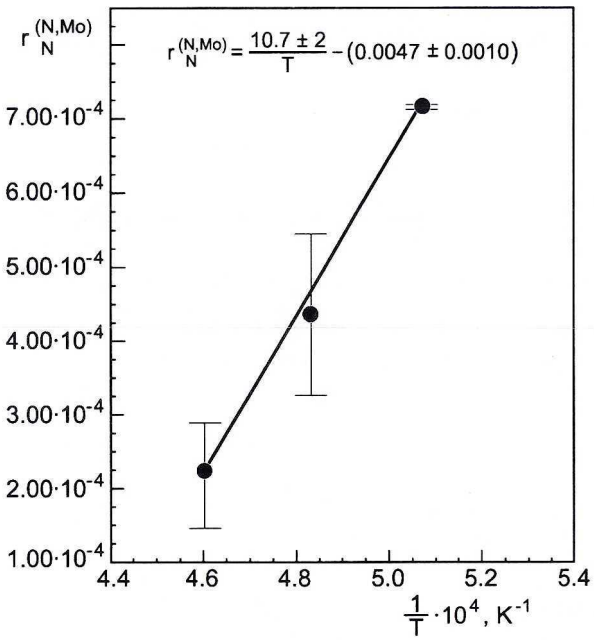

Fig. 4. Dependence of the parameter $r_N^{(N,Mo)}$ on temperature — results of the author's own studies

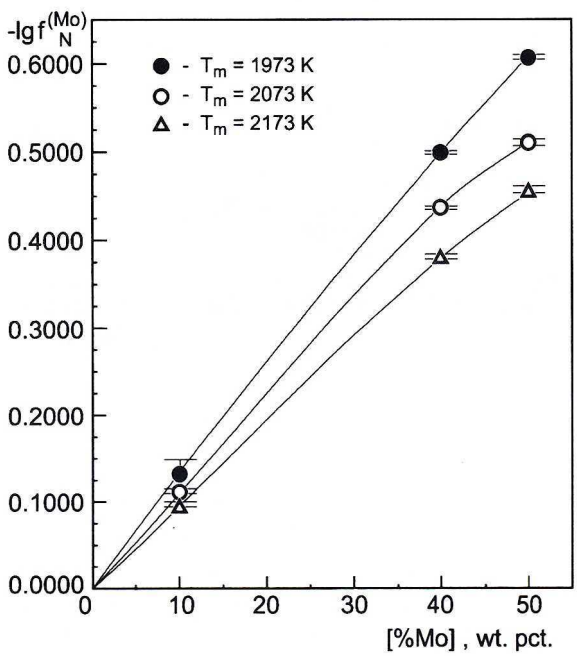

Fig. 5. Dependence of the coefficient of activity of nitrogen on the molybdenum concentration in the liquid Fe-N-Mo alloy (the author's own studies)

After determining the coefficients, i.e. the interaction parameters for particular metal temperatures, their temperature dependence was derived in the following form:

$$e_N^{(Mo)} = -\frac{77 \pm 1}{T} + 0.0257(\pm 0.0005), \tag{9}$$

$$r_N^{(Mo)} = \frac{0.32 \pm 0.08}{T} - 1.36 \cdot 10^{-4}(\pm 0.30 \cdot 10^{-4}). \tag{10}$$

Finally, the author's own data are compared with the literature data in Figures 6 and 7. This comparison was not possible for the parameter $r_N^{(N,Mo)}$, since, as has already been mentioned, it was determined for the first time by the author in his own studies.

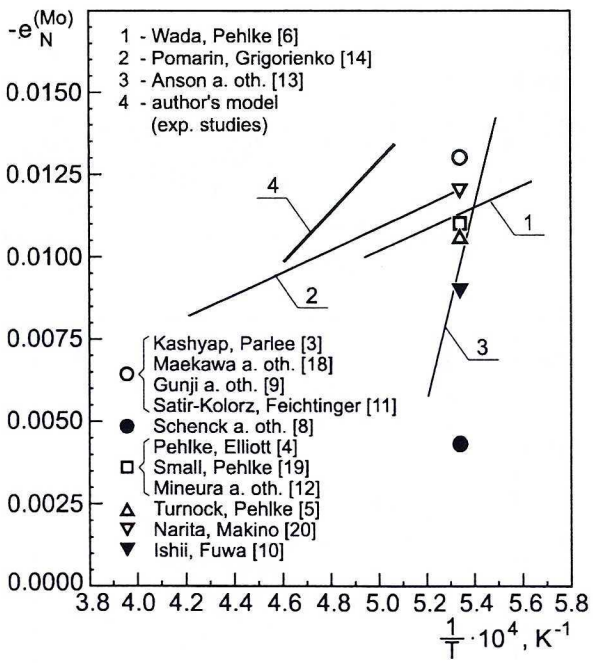

Fig. 6. Comparison of the results of the author's own studies with the literature data concerning the interaction parameter $e_N^{(Mo)}$

As seen from Figure 6, the curve derived from the author's study lies above the literature data, whereas in Figure 7 this curve lies below those data. The occurred situation is similar to that found in the case of the Fe-N-Cr alloy (the author's earlier work [16]). As commonly known, chromium and molybdenum are elements that behave similarly in relation to nitrogen, with chromium exhibiting a stronger effect. Monograph [1] explains in detail a similar position of the values of interaction parameters, as determined therein, in relation to the literature data.

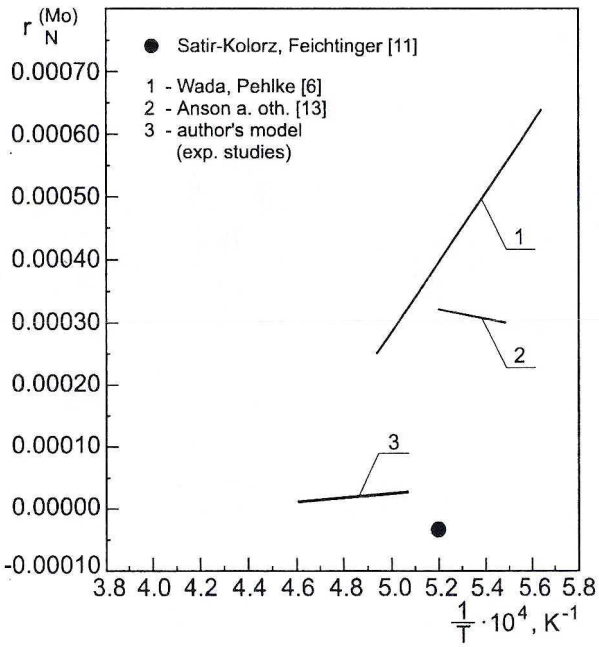

Fig. 7. Comparison of the results of the author's own studies with the literature data concerning the interaction parameter $r_N^{(Mo)}$

This position seems to be justifiable, because no parameters have been defined in the literature, which could allow for the effect of nitrogen concentration on the coefficient of activity, but instead the whole of this effect has been transferred to either chromium or molybdenum. Thus, with the nitrogen effect actually existing, the literature data could not reveal it.

4. Summary

Studies on the thermodynamics of the liquid Fe-Mo alloy — nitrogen containing gaseous phase system have been conducted so far at relatively low concentrations of nitrogen in the metal. Presumably for this reason all interactions among the alloy constituents, which determine the activity of nitrogen, have not been disclosed yet.

This study presents investigation results (pressure, P_{N_2} was up to 3.0 MPa), which indicate an increase in the activity of nitrogen as a result of increased nitrogen concentration in the liquid alloy of iron with molybdenum. This effect can be expressed quantitatively in terms of the interaction parameter, $e_N^{(N)}$, and the mixed interaction parameter, $r_N^{(N,Mo)}$ — this latter being determined experimentally in this study for the first time.

The solubility of nitrogen in the liquid Fe-Mo alloy can be determined using the following equation:

$$\lg[\%N] = 0.5 \lg P_{N_2} - \frac{664}{T} - 0.999 - \\ + \left\{\left(-\frac{77}{T} + 0.0257\right)\cdot[\%\mathrm{Mo}] + \left(\frac{386}{T} - 0.158\right)\cdot[\%\mathrm{N}] + \right. \\ \left. + \left(\frac{0.32}{T} - 1.36\cdot 10^{-4}\right)\cdot[\%\mathrm{Mo}]^2 + \left(\frac{10.7}{T} - 0.047\right)\cdot[\%\mathrm{N}]\cdot[\%\mathrm{Mo}]\right\}. \quad (11)$$

Note: This study represents a fragment of research conducted within the framework of KBN research project No. 7T08B 023 13 "Development of a thermodynamic model of liquid alloys of iron with nitrogen that correspond to the new group of HNS steels".

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