AN UNIVERSAL FORMULA FOR THE CALCULATION OF NITROGEN SOLUBILITY IN LIQUID NITROGEN-ALLOYED STEELS

INTRODUCTION

In the production of micro-nitrogen steels and nitrogen steels, out of the three thermodynamic factors, i.e. chemical composition, temperature and pressure, only the first two are utilized. Focusing the attention on the third factor, which is associated with the construction of specialized equipment in order to operate at elevated and high pressures, has created conditions for extending the scope of the “old” concept of upgrading steel with nitrogen. More important, however, is the possibility of producing entirely new steels with a unique combination of properties by using the pressure steelmaking process. These new steels with higher – compared to $P_{\text{N}} = 0.1$ MPa – nitrogen contents have been called high-nitrogen steels, in the international nomenclature being denoted with the symbol HNS (High Nitrogen Steels) [1]. The application of nitrogen as an alloying element has been known in metallurgy for a long time; however, this application become widespread in the early 80s of the past century. Since 1988, high-nitrogen steels have been the subject of a dozen or so international and national scientific conferences. The publications show that the number of registered steel grades is already a 3-digit number.

Studies from recent years have shown that, at high contents of nitrogen, its dissolution in liquid iron alloys should not be considered as following Sieverts’ law, which was assumed previously; it is necessary to take into account the nitrogen-nitrogen self-interaction that occurs in it. This fact required the introduction of new self-interaction parameters in order to describe the activity of nitrogen in metal.

The main objective of the present work is to present the authors’ own thermodynamic model and to compare the results of calculation of nitrogen solubility in liquid steels of different types using the model in question, with calculation results obtained using data reported by other authors.

MEASUREMENT OF NITROGEN SOLUBILITY IN LIQUID METALS

Making use of the experience gained from the application of the magnetic field levitation melting (LM) method for the examination of nitrogen solubility in metals in numerous scientific centres, as well as results provided in relevant literature, a specialized measuring stand was built at the Czestochowa University of Technology. Its detailed description is provided in work [2], and its upgraded version enabling the digital recording of measurement monitoring is described in work [3].
THERMODYNAMIC BASES

The phenomenon of dissolution of two-atom molecules of gaseous nitrogen in liquid metal, under the assumption of thermodynamic equilibrium between nitrogen in the gaseous phase and in the solution, has been described in detail, e.g., in the author’s works [4].

Taking the concentrations in wt. percents, and assuming the standard state according to Henry’s law (and limiting the discussion to the interaction parameters of the 2nd order), then for the solutions Fe-N-X, the logarithm of the activity coefficient $f_N$ can be expressed by the following polynomial:

$$
\begin{align*}
\text{lg}[%N] &= \text{lg}K_{N(Fe)} - \text{lg} f_N^{(X)} - \text{lg} f_N^{(Y)} - \text{lg} f_N^{(Z)} \\
&= \frac{K_N}{P_{N_i}} - 0.999 - (\text{lg} f_N^{(X)} + \text{lg} f_N^{(Y)}) \\
&= \text{lg}A_N^{(X)} - \frac{K_N}{P_{N_i}} - 0.999 - (\text{lg} A_N^{(X)} + \text{lg} A_N^{(Y)})
\end{align*}
$$

(4)

In literature concerning in particular HNS steels, the proposals by Satir-Kolorz et al. [6], Medovar et al. [7] and initially by Stein, Menzel [8] are often used. In works [6] and [7], one self-interaction parameter of the first order, $e_N^{(X)}$, is used, which is determined, in the first case, at a temperature of 1973K ($e_N^{(X)}=0.13$), and in the other case, at a temperature of 2073K ($e_N^{(X)}=0.044$). Work [8], on the other hand, actually omits the nitrogen-nitrogen interaction and, besides, only considers the interaction parameters of the first order, $e_N^{(X)}$.

CALCULATION METHODOLOGY

In their publication [4], the author present the final version of the thermodynamic model for the calculation of nitrogen solubility in liquid multi-component iron alloys under the conditions of change in gaseous phase nitrogen pressure from 0.1 to 4.0 MPa and in temperature from 1873K to 2173K, with a possibility for extrapolation. The model includes a temperature relationship of the equilibrium constant $K_N(Fe)$, temperature relationships of the interaction parameters $e_N^{(X)}$ and $r_N^{(X)}$, and temperature relationships of the self-interaction parameters $e_N^{(X)}$, $r_N^{(X,X)}$, and $r_N^{(X,X,X)}$. For this calculation, the equation has the following form:

$$
\text{lg}[%N] = \text{lg}A_N^{(X)} - \frac{K_N}{P_{N_i}} - 0.999 - (\text{lg} A_N^{(X)} + \text{lg} A_N^{(Y)})
$$

(4)

Figure 1. Solubility of nitrogen in iron at $T=1873\,\text{K}$

Figure 1 shows curves representing variations in nitrogen solubility in liquid iron as a function of gaseous phase nitrogen pressure up to 4 MPa at a metal temperature of 1873K.

As is indicated by the position of the curves, the maximum absolute difference in nitrogen solubility values increases with increasing pressure ($P_{N_i}$ from 0.1 to 4.0 MPa) from 87 to 547 ppm.

The curves plotted based on the results of works [6-8] are rectilinear (i.e. the law of the square root of gaseous phase nitrogen partial pressure is satisfied here). The curve determined based on the results of the authors’ own studies [2] deviates negatively from the rectilinearity, which means a self-limiting of nitrogen solubility by the nitrogen dissolved in the liquid iron. This deviation becomes increasingly apparent with increasing nitrogen content, which is quite understandable. On this basis the author [2] have found that the self-interaction parameter $e_N^{(X)}$ can be described by the following temperature relationship:

$$
e_N^{(X)} = \frac{386}{T} - 0.158
$$

(5)
The increase in liquid iron temperature from 1873K to 2073K results in the decrease of the parameter $e_N$ from 0.048 to 0.028.

In turn, Figure 2 represents the results of calculation of nitrogen solubility in the liquid Fe-Cr alloy at a temperature of 1873K and an analogous change in gaseous phase nitrogen pressure, i.e. up to 4 MPa.

This deviation, as is marked in Figure 2, can be described in a given case with the value of the nitrogen activity coefficient, according to Equation (1). However, in the case of an alloy of iron with chromium, the self-interaction parameter $r_{N, Cr}^{(1)}$ should additionally be included. The identical procedure should be followed when calculating the solubility of nitrogen in HNS steels.

In order to demonstrate the universal nature of the developed model of nitrogen solubility, calculation results related to application alloys, corresponding to nitrogen-alloyed steels, are presented in Figures 3 to 6.

In the first case, the calculation concerns the most common high-strength austenitic HNS steel of the Cr18Mn18 type, called “supra austenite”. For a contrast, the subsequent figure shows calculation results for a high corrosion-resistant steel of the Cr24Ni20Mn7Mo7 type, whose chemical composition is more complex.

As can be seen from Figure 3, the position of the nitrogen solubility curves indicates considerable differences between the results of calculation based on literature data and those based on the authors’ own data. These differences grow with increasing gaseous phase nitrogen pressures and, as a result, with increasing nitrogen content of the steel types tested.

While for steel Cr18Mn18 the curves determined on the basis of literature data lie clearly above the curve corresponding to our thermodynamic model, for steel Cr24Ni20Mn7Mo7 the curve based on the data reported in [6] practically coincides with our curve in the entire range of variation of nitrogen content.

By comparing the behaviour of the curves related to the temperatures 1873K and 2073K and the calculated values of M$N_{eq}$ at pressures of 0.1 and 4.0 MPa it can be found that the increase in liquid metal temperature results in a decrease in nitrogen solubility in the steels under consideration.

This type of temperature effect is correct, as the process of nitrogen dissolution in steels including elements, such as chromium, manganese and molybdenum is an exothermic process.

If we look at the curves determined by calculation based on the data provided by work [8], we can see that...
they are rectilinear and lie above the remaining curves. On the basis of the current knowledge, they can be regarded as unreliable, because, as has been proven in several works, it is necessary to allow for nitrogen-nitrogen self-interaction in calculations, which has not been complied with by the authors of work [91].

Moreover, in their proposal, as has been noted earlier, the nitrogen activity coefficient is calculated by including the first-order interaction parameters $e_{N}^{(X)}$ only. The significant differences between the nitrogen solubility results obtained using our own formula and the calculation results obtained based on works [6] and [7] can be explained by a different method of determining the nitrogen activity coefficient used by the authors of those works. Namely, in their works, the authors propose using the following polynomial for activity coefficient calculation:

$$
\lg f_{N} = e_{N}^{(N)} \cdot [\%N] + e_{N}^{(X)} \cdot [\%X] + r_{N}^{(X)} \cdot [\%X]^2
$$

When comparing the polynomials expressed by Equations (1) and (6) it is easy to notice that Equation (6) contains fewer terms compared to Equation (1). The most important difference stems from the lack of the term $r_{N}^{(X)} \cdot [\%N] \cdot [\%X]$ in Equation (6), which is a substantive mistake from the point of view of the phenomenological thermodynamics.

Admittedly, the omission of some terms in the Taylor series expansion of a polynomial will be acceptable, but only when the right to do so has been proved experimentally. In this case, there is no such a right, as the significance of the self-interaction between nitrogen and nitrogen; nitrogen, nitrogen and component X, especially in steels containing chromium, manganese, molybdenum and vanadium, has been proved experimentally in some works, including those by the authors of the present work.

To quantitatively substantiate the differences in the positions of the curves in Figures 3 to 6, the following generalized equation is used, which is convenient in terms of calculation:

$$
\lg [\%N] + \lg f_{N}^{(N)} = \lg \frac{P}{P_{N}} - \lg K_{N(P)} - \lg f_{N}^{(X)}
$$

**SUMMARY**

The study has compared the results of calculation of nitrogen solubility in liquid steels, where nitrogen is an alloying element. In the calculations, model equations were used, which are given in relevant literature and are most often used by specialists in nitrogen-alloyed steels (including High Nitrogen Steels), as well as a model equation developed on the basis of the authors’ experimental measurements. As a basic assumption, it was decided that the calculations would be related to a wide range of nitrogen partial pressure and liquid metal temperature, in order that the results could be utilized in industrial technologies. Namely, calculation results related to 0.1 MPa can yield information useful for developing assumptions for the melting of micro-nitrogen steels and nitrogen steels, and concerning higher pressures of melting high-nitrogen steels.

The substantially differing temperatures, i.e. 1873 and 2073K, have also relevance to melting technologies. Indeed, at a temperature close to 1873K steels are melted in induction furnaces (e.g. according to the Bulgarian technology [9]) and in electric arc furnaces, while at higher temperatures – in electroslag remelting installations, according to e.g. the German technology [10], as well as in plasma installations. The most advanced tech-
nology applied in industrial conditions is a process that is commercially implemented in the Böhler works in Austria [11].

Taking into account the findings of the present study, it should be noted that the proper understanding of nitrogen solubility will make it possible, on the one hand, to avoid the porous structure of the steel ingot and the excessive consumption of ferroalloys (nitrogen carriers) in the case of melting in steelmaking furnaces, and, on the other hand, to determine the proper driving force of reaction of liquid metal saturation in the case electroslag steel remelting installations. The high gaseous phase nitrogen pressure (up to 4 MPa) applied there is intended to create a very large difference in nitrogen potentials in the two reaction phases. This potential difference has a strong effect on the rate, and thus the efficiency of the process.

REFERENCES


Nomenclature

E experimental coefficient
K thermodynamic equilibrium constant
P pressure / MPa
T temperature / K
X alloying element
f activity coefficient
e inter- and self-interaction parameter of the first order
r inter- and self-interaction parameter of the second order
t self-interaction parameter of the third order

Note: Language consultant: Czeslaw Grochowina, Częstochowa, Poland