In the initial period of steel production with nitrogen as an alloy addition, from among the three thermodynamic factors, i.e. chemical composition, temperature and pressure, use was made of the first and the second factor only. Consideration given to the third factor created conditions for the realization of the "old" idea of steel ennoblement using nitrogen. An experimental setup for the investigation of the equilibrium state of chemical reactions in the gaseous phase–liquid metal system in the pressure range from 0.001 to 3.2 MPa and at temperatures not exceeding 2 423 K has been constructed and is presented in this paper. This setup relies on the levitation metal melting technique, whereby the ceramic crucible is eliminated and does not take part in the reaction phenomena. Intensive induction mixing of the liquid metal and the rapid cooling of samples in the experiment period provide the reproducibility of a given state through chemical analysis of the frozen samples of metal. The solubility of nitrogen in liquid iron, chromium, nickel, cobalt, vanadium and iron alloys in the pressure range 0.001 to 3.2 MPa at various temperatures, was determined. The determined characteristics made it possible to develop a thermodynamic model describing the solubility of nitrogen, temperature and chemical composition in a wide range of variation of these factors. The established nitrogen–nitrogen interaction reduces the effectiveness of nitrogen introduced to the liquid steel.

KEY WORDS: metals and iron alloys; levitation melting technique; nitrogen; high pressure; thermodynamics.

1. Introduction

The basic directions of contemporary studies involve searching for methods for economical nitrogen alloying in the production of nitrogen and high-nitrogen steels. Due to a relatively low thermodynamic nitrogen activity, high nitrogen contents are difficult to achieve. Hence, any operation of increasing the limiting nitrogen contents of steel requires appropriate technologies to be developed.

Nitrogen, as an admixture, exhibits a considerable influence on the properties of steel, even at its small content, and can serve as an alloying element. The application of nitrogen as an alloying element has been known in metalurgy for a long time; however, this application became 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 (held, e.g., in France, Bulgaria, Germany, Ukraine, Poland, Japan, Finland, Sweden, the USA, India, Switzerland, Spain, Belgium and China). The published materials show that the number of registered grades is already a 3-digit number, with high-nitrogen steels being designated with the symbol HNS (High Nitrogen Steels) in the international nomenclature.

Nitrogen in steel exercises an influence on its properties by taking up interstitial sites in the solid solution and through the precipitations of nitrides and carbonitrides. It appears that the most adequate generalization concerning the application of HNS steels is the following view of J. Foc, expressed in his work: "The following expectations of societies may positively influence the development of alloying steels with nitrogen:

- safety in the field of transport (telecommunication cables, aircraft undercarriage parts, train wheels, car bodies, double shell plating of tankers),
- reliability and new possibilities in civil engineering,
- development of the sport and recreation industry (high demands concerning the ultimate strength and lightness of equipment), and
- the defence and space industries".

Studies from recent years have shown that, at high contents of nitrogen, its solution in liquid iron alloys should not be regarded as obeying the Sieverts' law, as 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.

For more than a decade, relevant literature has been quoting experimental data were obtained by the authors of works. These experimental data, valuable from the point of view of the thermodynamics of liquid high-nitrogen metallic alloys, were interpreted incorrectly in that the principles of phenomenological thermodynamics were not obeyed. Namely, the nitrogen–nitrogen self-interaction parameter, i.e. the parameter $e_{ij}^{(N)}$, determined on their basis, is not a parameter in the physical sense and is solely an experimental coefficient. Thus, its application to the calculation of the activity coefficient $f_{i}^{N}$ is limited to the ranges of variation of thermodynamic factors (in particular variations in chemical composition of alloys), for which it has been determined.

In this situation, the conclusion concerning the need for acquiring a large collection of experimental data on the thermodynamic properties of liquid metallic alloys with ni -
trogen, in particular iron alloys, in the broad range of nitrogen concentrations is justifiable.

The main purpose of the present work is to develop an explicit form of the function expressing the concentration relationship of the activity coefficient of nitrogen through the solution constituent interaction and self-interaction parameters, as proposed by Wagner and Lupis and by Elliott.


For the measurement of the solubility of gaseous elements in liquid metals, the following basic methods were applied:
1) method of measuring the absolute quantity of absorbed gas (Sieverts’ method),
2) sample freezing method,
3) method of levitation melting in a magnetic field.

The basis of all methods is the achievement of thermodynamic equilibrium between the liquid metal and the gaseous phase at a specific temperature and pressure. The differences lie in the methods of determining the equilibrium concentration of gas in metal.

The method of the direct measurement of the quantity of absorbed gas was first applied by Sieverts.7) According to this method, the determination of the quantity of absorbed gas is done by measuring the decrease in gas volume—in an air-tight reaction system—while maintaining constant pressure (the isobaric variant), or measuring the decrease in gas pressure, while maintaining constant system volume (the isochoric variant). The isobaric variant is developed primarily in works by Chipman8) and Pehlke et al.9) Whereas the isochoric variant has been developed by Yavovsky9) and Morozov.10)

The advantages of Sieverts’ method include: The capability to directly measure the quantity of absorbed gas, the capability to directly monitor the phenomenon of gas absorption or release and the moment of thermodynamic equilibrium settlement.

The main drawbacks of the method include the necessity of determining the hot volume and the dependence of the results on the number of sublimates of metal examined and also the lack of possibilities of carrying out tests under the conditions of high pressure or very high temperatures.

According to the sample freezing method, the equilibrium gas content of metal is determined by an indirect method by taking samples and then freezing them, or by quick chilling of the whole mass of metal examined, followed by the chemical analysis of the sample. The basic condition of the correctness of results in the sample freezing method turns out to be the certainty of the establishment of the initial equilibrium concentration of gas in metal at the experiment temperature in the subsequently frozen sample to be subjected to chemical analysis.

The levitation melting (LM) method may be comparable with the sample freezing method, but owing to its unique features (the elimination of the ceramic crucible, an unlimited temperature range, the elimination of errors resulting from the inhomogeneous chemical composition of metal, that are possible in the sample freezing method) it is more appropriate to regard it as a separate method. The small mass of metal, its intensive circulation inside the drop, the high magnitude of specific surface contacting the gaseous phase, all create conditions for fast saturation of the liquid metal with the gaseous element. A combined process of metal casting to a small mould and chilling it to the solidification temperature, and the solidification itself, take place practically instantly, which promotes a complete fixing of nitrogen in the metal that melted at the experiment temperature. The results obtained by the LM method are independent of the size of sublimates and the interaction of the metal examined with the crucible material, therefore this method is applicable in the widest temperature range, which, by itself, enhances the accuracy of the measurement results of gaseous element solubility.

Taking into account the experience gained from the use of the 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 work12) and its upgraded version enabling the digital recording of measurement monitoring is described in work.13) A schematic diagram of the testing stand is shown in Fig. 1.

The proper experiment involved the melting of a metal sample in a state of suspension in an electromagnetic field in an appropriate reaction gas at a pressure slightly higher than 1 atm, and rapid filling the metal reactor body with the identical working gas until the preset nitrogen pressure level was attained, while heating the liquid metal up to the appropriate temperature.

In this state, the specimen was held for a time of 180 s, which, based on works,12,13) was considered sufficient for the liquid metal–gaseous phase system to reach the thermodynamic equilibrium under the experiment conditions. After the power supply of the levitation coil had been switched off, a sample of a mass of approx. 1 g dropped by gravity to a copper testing mould. The metal solidified under the cooling conditions at a cooling rate of $10^{-5}$ K·s$^{-1}$.14,15)

3. Theoretical Principles and Definitions

The phenomenon of dissolution of two-atom molecules of gaseous nitrogen in liquid metal, under the assumption of thermodynamic equilibrium existing between nitrogen in the gaseous phase and in solution, is described in detail, e.g. in the author’s works.16,17)

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

\[ \lg f_N = e_N^{(N)} [\% N] + e_N^{(X)} [\% X] + r_N^{(N)} [\% N]^2 + r_N^{(X)} [\% X]^2 \]

After grouping the polynomial components, we get:

\[ \lg f_N = \lg f_N^{(X)} + \lg f_N^{(N)} \quad (2) \]

where

\[ \lg f_N^{(X)} = e_N^{(X)} [\% X] + r_N^{(X)} [\% X]^2 \quad (3) \]

\[ \lg f_N^{(N)} = e_N^{(N)} [\% N] + r_N^{(N)} [\% N]^2 + r_N^{(X)} [\% X] \quad (4) \]

If we assume that

\[ e_N^{(N)} = e_N^{(N)} + r_N^{(N)} [\% N] + r_N^{(N)} [\% X] \quad (5) \]

Equation (1) will take on the form as below

\[ \lg f_N = \lg f_N^{(X)} + E_N^{(N)} [\% N] \quad (6) \]

At a constant temperature and constant concentration of the component X in the Fe–N–X alloy, the activity and solubility of nitrogen depend exclusively on its concentration, and we can write

\[ \lg [\% N] = \lg K_N^{(Fe)} - \lg f_N^{(X)} - E_N^{(N)} [\% N] \quad (7) \]

It is obvious that, under similar conditions, Eq. (5) for M–N alloys (for example Fe–N, Cr–N, V–N, etc.) reduces to the following form:

\[ E_N^{(N)} = e_N^{(N)} + r_N^{(N)} [\% N] \quad (8) \]

and, as a consequence, Eq. (7) also takes on a simplified form Eq. (9)

\[ \lg [\% N] = \lg K_N^{(M)} - E_N^{(N)} [\% N] \quad (9) \]

4. Solubility of Nitrogen in Liquid Metals

4.1. Iron

Elementary studies on the solubility of nitrogen in liquid iron under pressures higher than atmospheric pressure were carried out within the author’s work.18) The testing stand used in the tests is shown in Fig. 1 above. The test conditions are given in Table 1.

From the thermodynamic point of view it is obvious that, during the self-cooling of the saturated liquid Fe–N solution, the formation of the ferrite solid phase δ should cause the process of nitrogen desorption from the liquid phase to the micro-bubble nuclei to proceed. Depending on the desorption reaction driving force (i.e., the magnitude of the difference in equilibrium concentrations between the liquid metal and the ferrite δ) and the self-cooling rate, the micro-bubbles will grow and become visible as blisters in the microstructure image. In the case of low self-cooling rates, they may surface before the metal solidifies. This phenomenon has been confirmed in the author’s studies, e.g., by micro-ingot structure images and by the measurements of micro-ingot apparent density, which is described in detail in work.18) It was determined that, at the self-cooling rates that were applied in the author's studies (103 K/s), nitrogen bubbles in the Fe–N alloy micro-ingot attained sizes possible to be identified in microstructure images, if the liquid iron was saturated at the pressure \( P_{\text{sat}} \), higher than approx. 0.2 MPa.

As the Fe–N–O alloy micro-ingot macrostructure indicates, the gas micro-bubble growth process during solidification has been completely eliminated in this case.18) As is discussed in detail in monograph,12) the results of the studies on the Fe–N system have only allowed the determination of the temperature relationship of the equilibrium constant of the reaction of nitrogen dissolution in liquid iron, according to the following equation:

\[ \log K_{N(Fe)} = - \frac{664 \pm 60}{T} - 0.999 \pm 0.030 \quad (10) \]

Equation (10) has been derived based on the experimentally measured apparent value of the constant \( K_{N(Fe)} \), which, when nitrogen concentration [%N]→0, approaches its actual value. At a constant temperature of 1 873 K, the value of the equilibrium constant is contained in the range from 0.0441 to 0.0445 with a probability of 0.95.

Whereas, the same results provide the grounds for the statement that it is not possible to describe the nitrogen–nitrogen self-interaction in liquid iron, and therefore the self-interaction parameter cannot be determined.

The next step in the search for possibilities of the quantitative definition of the nitrogen–nitrogen self-interaction in liquid iron was to undertake an investigation into the solubility of nitrogen in iron with a specific oxygen content assuring the inhibition of gas micro-bubble growth during metal solidification so that a solid, bubble-free micro-ingot macrostructure be obtained. In that case, the nitrogen, as determined by the chemical analysis of such a micro-ingot, is equivalent to its content of liquid metal.

Assuming the nitrogen–nitrogen self-interaction at a given temperature, the following equation is true for the liquid Fe–N–O solution:

\[ \log [\% N] = \log K^{(O)} - \log [\% O] - e_N^{(N)} [\% N] \quad (11) \]

Under the conditions of the author’s studies, oxygen concentration in the Fe–N–O alloy was contained in the range of 0.175–0.217 wt%. Bearing in mind a potential reduction of calculation accuracy for this reason, it was assumed:

\[ \log K_{N(Fe)} - e_N^{(O)} [\% O] = \text{const.} \quad (12) \]

Expression (11) together with assumption (12) allowed the determination of the \( e_N^{(N)} \) parameter value at a given liquid metal temperature, and ultimately its temperature characteristics in the form of the following relationship:

\[ e_N^{(N)} = \frac{386 \pm 118}{T} - 0.158 \pm 0.058 \quad (13) \]

It is difficult at this point to verify the calculated values of the parameter \( e_N^{(N)} \), as well as its functional dependence on

<table>
<thead>
<tr>
<th>No.</th>
<th>Type of</th>
<th>( P_{\text{sat}} ) MPa</th>
<th>Temperature, K</th>
<th>Constituent content, wt-%</th>
<th>( C )</th>
<th>( O )</th>
<th>( S )</th>
<th>( N )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Fe</td>
<td>0.1–3.2</td>
<td>1903–2203</td>
<td>(&lt;0.003)</td>
<td>(&lt;0.0005)</td>
<td>(&lt;0.0005)</td>
<td>(&lt;0.0007)</td>
<td></td>
</tr>
<tr>
<td>2.</td>
<td>Fe–O</td>
<td>0.1–2.6</td>
<td>1903–2203</td>
<td>(&lt;0.009)</td>
<td>(&lt;0.017)</td>
<td>(&lt;0.001)</td>
<td>(&lt;0.0007)</td>
<td></td>
</tr>
</tbody>
</table>
temperature, as there are no evidence for their existence in relevant literature.

4.2. Chromium

Nitrogen saturation was carried out at temperatures of 1 870, 1 950, 2 050 and 2 150°C and in the range of nitrogen partial pressure from 0.1 to 2.5 MPa.

Figure 2 shows the results of the author’s own research carried out in the pressure range from 0.1 to 2.5 MPa and data calculated by the inter- and extrapolation of other authors’ results to the temperatures of the author’s own tests. As is seen, the latter ones relate to the pressures \( P_N < 0.1 \) MPa and their purpose was to enrich the author’s own data set. Unfortunately, it was impossible to use the literature data, as is shown in the distribution of the measurement points, therefore those data were neglected and only the author’s own test results were used for further calculations. The following relationship of the equilibrium constant \( K_{N(Cr)} \) versus temperature was obtained:

\[
\lg K_{N(Cr)} = \frac{7 135 \pm 67}{T} - 2.09\
\]

Taking into account Eqs. (8) and (9) and the distribution of experimental points in Fig. 2 it can be seen that the Cr–N solution clearly deviates from Sieverts’ law. The nitrogen solubility in liquid chromium, \( f_{N(N)} \), can be calculated using the self-interaction parameter \( \varepsilon^{(N)} \), whose temperature relationship has the following form:

\[
\varepsilon^{(N)} = \frac{386 \pm 32}{T} - 0.043\
\]

4.3. Nickel and Cobalt

In experimental tests, nitrogen concentrations in liquid Ni–N and Co–N binary alloys were determined under the conditions of thermodynamic equilibrium for three temperatures: 1 773, 1 873 and 1 973 K, by varying nitrogen pressure within the reaction chamber from 0.1 to 4.0 MPa. These tests are described in detail in work.21

For all liquid metal temperatures, the relationships of the square root of \( \frac{P}{\sqrt{N}} \) vs. \( \frac{1}{T} \) can be calculated using the self-interaction parameter \( \varepsilon^{(N)} \), whose temperature relationship has the following form:

\[
\ellg K_{N(Ni)} = \frac{-2 800 \pm 45}{T} - 1.57 \pm 0.02 \]........(16)

\[
\ellg K_{N(Co)} = \frac{-2 589 \pm 138}{T} - 1.14 \pm 0.07 \]........(17)

4.4. Vanadium

The analysis of the available literature shows that the experimental data on the solubility of nitrogen in liquid vanadium are fragmentary and only concern references.22–24 Nevertheless, they have been used for compilation in subsequent works. The authors of work23 investigated the solubility of nitrogen in liquid vanadium at a temperature of 2 203 K. Work24 reports data on nitrogen solubility in liquid vanadium at 2 223 K. The authors of work25 tested the solubility of nitrogen in liquid vanadium at 2 273 K.

Argon–nitrogen gas mixtures with a nitrogen fraction of, respectively, 0.1; 0.2; 0.3; 2; 5 and 6 vol% were used in the own tests. The lowest nitrogen partial pressure, at which experiments were conducted, was 0.003 atm. In the testing conditions (temperatures of 2 173, 2 273 and 2 373 K), a homogeneous solution of nitrogen in liquid vanadium was obtained.

Investigation into the solubility of nitrogen in liquid V–N alloy, carried out with the application of levitation melting techniques, have shown that, under specific conditions, a new non-metallic phase appears on the drop surface.25 This phenomenon, which could be predicted on the basis of the theory of liquid metallic solutions, forced the modification of the research methodology applied before. Namely, the vision monitoring of the metal drop view with digital image recording was introduced. Thus, all samples, on which vanadium nitrides started to appear, could be eliminated.

The identified phenomenon of vanadium nitride release had not been noticed in previous studies. Therefore, results obtained therein might have been burdened with great errors, and thermodynamic characteristics developed on their basis did not reflect the properties of the liquid V–N system.

Figure 3 shows the relationship of \( \ellg[\%N] \sqrt{P_N} \) versus nitrogen content in the liquid V–N solution. The slope of the straight line corresponds to the empiric parameter \( E_N^{(V)} \) (with the minus sign), while the abscissa corresponds to the value of \( \ellg K_{N(V)} \) for \( P_N = 0 \).

According to the Eq. (9) on the basis of the determined
values of the equilibrium constant \( \lg K_{\text{N(V)}} \) for particular temperatures, its temperature relationship has been derived as follows:

\[
\lg K_{\text{N(V)}} = \frac{15,083 \pm 4,361}{T} - 5.27 \pm 1.92 \quad \ldots (18)
\]

5. Solubility of Nitrogen in Liquid Fe–X Alloys

Within the author’s own thermodynamic studies, liquid binary alloys of iron with nitrogen were dealt with, where X denotes the following alloy-forming elements: Cr, Mo, Ni, V, Si and C. The testing conditions are shown in Table 2. To develop the thermodynamic characteristics of the Fe–Mn–N alloy, data on nitrogen solubility, as measured under the conditions of the high partial pressure \( P_{\text{N}_2} \), available in work\(^3\) and in work\(^{27}\) were used.

5.1. Fe–Cr–N Alloy

Figure 4 illustrates graphically variations in the activity coefficient \( f_N \) as a function of nitrogen concentration in the Fe–Cr–N alloy under own research conditions. The values of the coefficient \( f_N \) were determined using the following equation:

\[
\lg f_N = \lg K_{\text{Fe(N)}(\text{Cr})} - \lg \left( \frac{\%N}{\sqrt{P_{\text{N}_2}}} \right) \quad \ldots (19)
\]

Figure 4 clearly indicates that the activity coefficient of nitrogen, \( f_N \), in the liquid Fe–Cr–N alloy depends distinctly on its nitrogen concentration, though this might not be visible at lower nitrogen concentrations. Therefore, when developing quantitative thermodynamic characteristics of the alloy in question, various interactions between nitrogen and chromium, as well as between the nitrogen itself, should be allowed for.

For computational purposes with the original literature data and with the author’s own research results, Eq. (7) was transformed to the following form:

\[
\lg K_{\text{Fe(N)}} = \lg \left( \frac{\%N}{\sqrt{P_{\text{N}_2}}} \right)^{\lambda} \quad \ldots (20)
\]

The form of Eq. (20) allowed the experimental data to be processed using a simple linear statistical model. The computation results are shown in Figs. 5 and 6. When analyzing the distribution of values of the experimental coefficient \( E_N^{(\text{Fe})} \) and its random dispersions, we can see that they clearly depend on the experimental method applied in research.

In the case of the crucible metal melting method, the dependence of the coefficient \( E_N^{(\text{Fe})} \) on chromium concentration in the Fe–Cr–N is not explicit. Explicit features can be noticed with respect to the results of tests, where levitation metal melting was used. In this case, the results of studies on Fe–N and Cr–N alloys are confirmed, namely that the magnitude of nitrogen–nitrogen self-interaction in the latter alloy is greater than in the former alloy. The facts stated here find their grounds, if we take into consideration the differences in metal cooling rates, which are achieved in particular testing methods. If a metal is melted by the crucible method, the cooling rates of the sample after saturating it with nitrogen are so low that the nitrogen fixing coefficient, as measured by the ratio of the liquid state equilib-

![Fig. 4. Effect of nitrogen concentration in the Fe–Cr–N alloy on the nitrogen activity coefficient.](image-url)
rimum concentration to the nitrogen content of the micro-ingot, will be much greater than unity. This difference will be the greatest in Fe–Cr–N alloys of a low chromium content, where the effects of iron will become pronounced. It is most probably for this reason that works\(^{3,28,29}\) obtained results, according to which the nitrogen-nitrogen self-interaction in low chromium-content Fe–Cr–N alloys is greater than even in the Cr–N alloy.

Due to the above considerations, in further computations for developing the relationship of the coefficient \(E^{(N)}_N\) in relation to chromium content—a summary of the author’s own data (levitation metal melting).

Fig. 5. Distribution of experimental values of the coefficient \(E^{(N)}_N\) in relation to chromium content—a summary of the author’s own data (levitation metal melting).

Fig. 6. Distribution of experimental values of the coefficient \(E^{(N)}_N\) in relation to chromium content—a summary of the author’s own data (levitation metal melting).


<table>
<thead>
<tr>
<th>Temperature</th>
<th>(E^{(N)}_N) (E^{(N)}_N) (E^{(N)}_N)</th>
<th>(E^{(N)}_N) (E^{(N)}_N) (E^{(N)}_N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1973</td>
<td>0.038</td>
<td>3.84e+11.0</td>
</tr>
<tr>
<td>2073</td>
<td>0.028</td>
<td>3.52e+1.27</td>
</tr>
<tr>
<td>2173</td>
<td>0.020</td>
<td>3.40e+0.33</td>
</tr>
</tbody>
</table>

The coefficients of Eq. (22) are essentially the parameters of nitrogen–nitrogen–chromium and nitrogen–nitrogen–chromium–chromium self-interactions, respectively, \(e^{(N)}_N\) and \(e^{(N,N,Cr)}_N\). The values of these parameters for particular temperatures are given in Table 3. After determining the self-interaction parameters, the 1st order \(e^{(N)}_N\) and the 2nd order \(e^{(N,Cr,Cr)}_N\) interaction parameters were determined using the transformed general relationship (6). Having measurement results available at three considerably differing temperatures (each by 100 K), their temperature relationships were developed.

In Figs. 7(a) through 7(c), the experimental data are represented graphically with points, and the computational data (respectively, at extreme nitrogen partial pressures that were applied in the tests on the Fe–Cr–N alloy, and which amounted to \(P_{N_{\min}}=0.1\) MPa and \(P_{N_{\max}}=2.6\) MPa) are denoted with solid lines. The number of experimental points at a given chromium content of alloy is denoted with the symbol “n”. This symbol defines the number of changes in \(P_{N}\), that were applied in experiments—with \(\%[\text{Cr}]\) const. and \(T=\) const. As is indicated by Fig. 7, the computation results are in equally good agreement with the experimental data at all testing temperatures, in the whole range of chromium content variations and in the entire range of variation of nitrogen solubility in the liquid Fe–Cr alloy.

5.2. Fe–Mo–N Alloy

When analyzing the results of the studies on the liquid Fe–Mo–N alloy it was found that the activity coefficient, similarly as in the Fe–Cr–N alloy, depended on the nitrogen concentration of the alloy concerned, which is illustrated as
5.3. Fe–Ni–N Alloy

In the studies on the liquid Fe–Ni–N alloy, no effect of nitrogen on its activity coefficient was found. Hence, on the basis of the test results, only the interaction parameters $e^{(N)}_{N}(Ni)$ and $r^{(N)}_{N}(Ni)$ were determined.

5.4. Fe–V–N Alloy

As work\textsuperscript{13) reports, when analyzing the results of studies on the liquid Fe–V–N alloy it was found that, similarly as for the Fe–Cr–N and Fe–Mo–N alloys, the nitrogen activity coefficient, $f_{N}$, depended on the concentration of nitrogen in the alloy in question, the examples of which are shown graphically in Fig. 9. Considering the fact that vanadium in iron alloys increases nitrogen solubility in those alloys even stronger than chromium does, similarly as for the Fe–Cr–N alloy, the measurements results were processed mathematically, first transforming Eq. (7) to the following form:

\[
\lg K_{N(Fe)} - \lg [\%N] = \lg f_{N}^{(V)} + E_{N}^{(N)} [\%N] \quad \ldots \quad (23)
\]

As described in detail in work\textsuperscript{13), the use of Eq. (23) and the linear approximation relationship in the original mathematical processing of experimental data brought about the values of the experimental coefficient $E_{N}^{(N)}$ (the effect of vanadium concentration on the values of $E_{N}^{(N)}$—Fig. 10) and the values of the activity coefficient $f_{N}^{(V)}$.

The distribution of points in Fig. 10 indicates that the effect of vanadium in the Fe–V–N alloy on the value of $E_{N}^{(N)}$ is curvilinear. For this reason, Eq. (5) was expanded to the following form:

\[
E_{N}^{(N)} = e_{N}^{(N,V)} + [\%V] \cdot f_{N}^{(N)} [\%N] \cdot \frac{[\%V]}{[\%N]} \quad \ldots \quad (24)
\]

Taking into account the parameter $e_{N}^{(N)}$ determined previously, Eq. (24) was transformed to the following form, convenient from the point of view of the processing of experimental test results:

\[
E_{N}^{(N)} - e_{N}^{(N)} \frac{[\%V]}{[\%N]} \quad \ldots \quad (25)
\]

The coefficients of Eq. (25), being essentially the self-interaction coefficients of the 2nd and the 3rd order, were used for deriving their values at given testing temperatures and for developing their temperature relationships.

Experimental results relating the activity coefficient $f_{N}^{(N)}$ testify about strong influence of vanadium concentration in the Fe–V–N alloy on its value. Also in this case the rela-
tionship is curvilinear, and for this reason, with respect to vanadium, Eq. (3) was transformed to a form allowing the processing of the test results with the linear regression function model, namely:

$$\frac{\lg r_{N}^{(V)}}{[\%V]} = e_{N}^{(V)} + r_{N}^{(V)} \cdot [\%V] \quad \text{(26)}$$

Here again, the coefficients of Eq. (26), being essentially the interaction coefficients of the 1st and the 2nd order, were used for deriving their values at given testing temperatures and for developing their temperature estimations.

5.5. Fe–Si–N Alloy

In this case, when analyzing the experimental data, no effect of nitrogen concentration on the value of the nitrogen activity coefficient was found. A further analysis of the nitrogen activity coefficient values showed that the effect of silicon concentration is rectilinear. Respective calculations can be found in work.\textsuperscript{36} As a result, a temperature relationship of the nitrogen and silicon 1st order interaction parameter was developed.

5.6. Fe–C–N Alloy

The iron–carbon system is a basis for steel metallurgy. The majority of steels contain carbon, hence detailed data on nitrogen solubility are essential in order to precisely predict the solubility of nitrogen in more complex alloys, all the more so because carbon strongly influence the activity of nitrogen in liquid iron.

In previous works, the effect of carbon on the activity coefficient of nitrogen in liquid iron used to be described using the interaction parameter of the 1st order, \(e_{N}^{(C)}\). Later on, in particular in work,\textsuperscript{37} applying a broad range of carbon concentrations up to the saturation concentration, it was demonstrated that, for the Fe–C system, the relationship \(\lg e_{N}^{(C)}\sim[C]\) should be nonlinear, the values of the 1st order parameter were overestimated due to the neglecting of this nonlinearity and were only useful for a very rough estimation of nitrogen solubility in Fe–C alloys, and not applicable to carbon-containing multi-constituent alloys. Using the temperature relationship of the equilibrium constant in the liquid Fe–N alloy, previously developed in work,\textsuperscript{38} the following equation for the calculation of nitrogen solubility in the liquid Fe–C alloy was ultimately proposed in work:\textsuperscript{39}

$$\lg \%N = \log_{10} \left( \frac{P_{N_i}}{T} \right) - 0.995 \left( \frac{100}{T} + 0.045 \right) \cdot [\%C]$$

$$\left( \frac{90}{T} - 0.036 \right) \cdot [\%C]^2 \quad \text{(27)}$$

A detailed discussion of this problem, along with an in-depth analysis of literature data, is provided in monograph.\textsuperscript{17} It was also pointed out in that monograph that the existing literature data were related to partial nitrogen pressures of \(P_{N_i} \leq 0.1\) MPa, and thus are applicable to relatively low nitrogen contents of the Fe–C alloy. As a consequence, they could be little precise to be used in multi-constituent iron alloys with high nitrogen content, i.e. high-nitrogen steels. In order to verify this hypothesis, measurements of nitrogen solubility in the Fe–C alloy were carried out, the results of which are reported in the author’s work.\textsuperscript{30} The basic difference between the tests presented in relevant literature and the author’s own tests concerns the nitrogen partial pressure in the gaseous phase, as a consequence of which much higher nitrogen contents (as shown in Table 2, the \(P_{N_i}\) was varied in the range from 0.097 to 1.78 MPa) were obtained in the author’s tests. It was assumed that, at considerably higher nitrogen concentrations in the Fe–C–N alloy, the nitrogen activity coefficient would be determined in a precise manner. Considering the temperature relationships of the interaction parameters of the 1st order, \(e_{N}^{(C)}\), and the 2nd order, \(r_{N}^{(C)}\), as determined in work,\textsuperscript{38} and the temperature relationships of the self-interaction parameter of the 1st order, \(e_{N}^{(N)}\)—relationship (13), and the temperature relationship of the equilibrium constant for the liquid iron–nitrogen gaseous phase—relationship (10), as determined in the previous monograph,\textsuperscript{39} the following equation is proposed for the calculation of nitrogen solubility in the liquid Fe–C alloy:

$$\lg \%N = \log_{10} \left( \frac{P_{N_i}}{T} \right) - 0.999 \left( \frac{386}{T} - 0.158 \right) \cdot [\%N]$$

$$- \left( \frac{280}{T} - 0.053 \right) \cdot [\%C] - \left( \frac{74}{T} - 0.047 \right) \cdot [\%C]^2$$

$$\text{.......................(28)}$$

5.7. Fe–Mn–N Alloy

To develop the thermodynamic characteristics, data on nitrogen solubility, as measured under the conditions of high partial pressure \(P_{N_i}\), available in work—(metal melting in a crucible) and in work—(levitation metal melting), were used. As it was presented in detail in earlier work\textsuperscript{39} for the averaged temperature equal to 1896 K, yielded the following value of the mixed self-interaction parameter:

$$r_{N}^{(N,Mn)} = (3.4 \pm 1.3) \cdot 10^{-3} \quad \text{(29)}$$

In order to calculate the nitrogen activity coefficient, in addition to the parameter described by Eq. (29), it is recommended to use the interaction parameters \(e_{N}^{(Mn)}\) and \(r_{N}^{(Mn)}\) determined by the authors of work,\textsuperscript{40} whose temperature relationships are as follows:

$$e_{N}^{(Mn)} = - \frac{73}{T} + 0.022 \quad \text{(30)}$$

$$r_{N}^{(Mn)} = \frac{0.8}{T} - 3.8 \cdot 10^{-4} \quad \text{(31)}$$

In the case of the Fe–Mn–N alloy, further studies are needed, in spite of the essential difficulties associated with the intensive evaporation of the element in question at its high contents of iron alloys.
6. Solubility of Nitrogen in Liquid Ternary Iron Alloys with Chromium

A particular interest in two-phase HNS steels can be observed recently. In such steels, elements that often exist besides chromium are vanadium and molybdenum, occurring either separately or together. Therefore, tests were carried out with the aim of determining the joint interactions between nitrogen, chromium and the elements in question. In order to process the results of experiments with these liquid alloys, Eq. (1) needed to be extended by adding the mixed interaction parameters.

The value of the member \( \lg f_N \) is determined directly from the experimental data, whereas the term \( \lg f_N \) from the experimental and computational data based on the interaction parameters determined in the studies on binary and ternary solutions, as below:

\[
\lg f_N = e_N^{(C)} \cdot [\%Cr] + e_N^{(X)} \cdot [\%X] + \ldots
\]

After combining Eq. (36) with Eq. (34) and dividing both sides by ([%Cr] · [%X]), we obtain the following form of the equation, which is convenient for the processing of the results of the studies on quaternary alloys:

\[
\lg f_N = e_N^{(C)} + e_N^{(X)} \cdot [\%X] + \ldots
\]

After grouping the components of polynomial (32) by known (the determined interaction parameters in binary and ternary solutions) and unknown interaction parameters (the mixed parameters in quaternary solutions), as below:

\[
\lg f_N = e_N^{(C)} + e_N^{(X)} \cdot [\%X] + \ldots
\]

At the end of this paper, we give the following form of the equation, which is convenient for the processing of the results of the studies on quaternary alloys:

\[
\lg f_N = e_N^{(C)} + e_N^{(X)} \cdot [\%X] + \ldots
\]

Table 4 defines the conditions and experimental results of the studies on nitrogen solubility in the liquid iron alloy with chromium and vanadium, while Table 5—with chromium and molybdenum.

Using Eqs. (32), (10)—the standard condition of the activity coefficient \( f_N \), determined experimentally, and finally Eq. (37) in combination with the linear approximation statistical model, the values of the interaction parameters \( r_N^{(C,X)} \) and \( r_N^{(N,X)} \) for vanadium and molybdenum, and their temperature relationships, were determined.

7. Summary

The facts quoted in the introduction and the review of the author's studies on the solutions of nitrogen in metals and iron alloys seem to provide grounds for putting forward an argument for the necessity of considering in the thermodynamic description of these alloys not only the parameters of interaction of nitrogen with the constituents of a particular solution, but also the parameters of self-interaction of nitrogen with nitrogen and nitrogen with other elements.

The results of the author's studies on the liquid solutions of Fe–N, Fe–N–O, Cr–N, Fe–Cr–N, Fe–C–N, Fe–Si–N, Fe–Ni–N, Fe–Mo–N, Fe–V–N, Fe–Cr–Mo–N and Fe–Cr–V–N, concerning the effect of chemical composition and the temperature of liquid alloys, and nitrogen partial pressure on nitrogen solubility have enabled a unique thermodynamic database to be created, whose main elements are given in Table 6. Using the data provided in Table 6, the model thermodynamic equation for the calculation of nitrogen solubility in high-nitrogen steels of variable chemical composition, smelted in wide ranges of temperature and nitrogen partial pressure in the working gas, can be easily set. For such calculation, the equation has the following form:

\[
\lg [\%N] = \frac{1}{2} \log P_N - \frac{664}{T} - 0.999 - \log f_N \ldots \ldots (38)
\]

In the case of the presence of manganese in the steel, in the calculation of \( \log f_N \) the interaction parameters, as described by Eqs. (30) and (31), should be used complementarily.

In order to determine the consistency of the calculated values of the activity coefficient \( f_N \) with the experimental values in quantitative terms, the whole collection of data from own studies, extended by the values obtained from the studies on the Cr–N alloy, extrapolated to the conditions of the studies on other alloys, have been processed mathemati-
cally and represented in the $\lg f_N$ vs $\lg f_{\text{cal}}$ coordinate system. The calculation results are shown graphically in Fig. 11. The distribution of measurement points relative to the ideal fitting curve of the mathematical model (38) shows good consistence between calculational and experimental values within a whole, very wide range of variation of the activity coefficient $f_N$.

REFERENCES

3) A. Satir-Kolorz, H. K. Feichtinger and M. O. Speidel: Giesereiforschung, 41 (1989), No. 4, 149.

Table 6. Thermodynamical data.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>$\lg K_{\text{N(X)}}$</th>
<th>Interaction parameters</th>
<th>Self-interaction parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>$f_N^i$</td>
<td>$f_N^{j,i}$</td>
<td>$f_N^{i,i}$</td>
<td>$f_N^{j,j}$</td>
</tr>
<tr>
<td>Fe-N</td>
<td>-664</td>
<td>-0.999</td>
<td>386</td>
</tr>
<tr>
<td>Cr-N</td>
<td>7135</td>
<td>-2.09</td>
<td>386</td>
</tr>
<tr>
<td>V-N</td>
<td>15083</td>
<td>-5.27</td>
<td>-</td>
</tr>
<tr>
<td>Ni-N</td>
<td>2800</td>
<td>-1.57</td>
<td>-</td>
</tr>
<tr>
<td>Co-N</td>
<td>2589</td>
<td>-1.14</td>
<td>-</td>
</tr>
<tr>
<td>Fe-Cr-N</td>
<td>-171</td>
<td>+0.043</td>
<td>0.7</td>
</tr>
<tr>
<td>Fe-Mn-N</td>
<td>-73</td>
<td>+0.07</td>
<td>6.2</td>
</tr>
<tr>
<td>Fe-Mo-N</td>
<td>-77</td>
<td>+0.0257</td>
<td>0.32</td>
</tr>
<tr>
<td>Fe-V-N</td>
<td>-424</td>
<td>+0.1</td>
<td>6.1</td>
</tr>
<tr>
<td>Fe-Ni-N</td>
<td>173</td>
<td>-0.00012</td>
<td>0.206</td>
</tr>
<tr>
<td>Fe-Si-N</td>
<td>79.2</td>
<td>+0.0104</td>
<td>-</td>
</tr>
<tr>
<td>Fe-C</td>
<td>280</td>
<td>-0.053</td>
<td>74</td>
</tr>
<tr>
<td>Fe-Ni-Mn</td>
<td>$f_{\text{Ni-(Mo)}}$</td>
<td>-0.60</td>
<td>-1.9 $\times$ 10^{-4}</td>
</tr>
<tr>
<td>Fe-Cr-V-N</td>
<td>$f_{\text{Cr-(V)}}$</td>
<td>-1.51</td>
<td>-4.2 $\times$ 10^{-4}</td>
</tr>
</tbody>
</table>

Fig. 11. Comparison of the calculated values of the coefficient $f_N$ against the experimental data.