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Solubility of nitrogen in liquid Fe-10Ti and Fe-25Ti alloys

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ABSTRACT

Purpose: of the study was to determine the physicochemical characteristics of thermodynamic equilibrium in the liquid metal-gas system, where the liquid metal was a liquid Fe-Ti alloy, and the reaction gas was always a mixture of nitrogen and argon with preset chemical composition.
Design/methodology/approach: In the experimental studies, the levitation metal melting technique was used, which enabled, on the one hand, the liquid metal-gas thermodynamic system appropriate to the purpose to be fabricated and, on the other hand, precise measurements to be carried out within a wide nitrogen partial pressure range from 0.0005 to 0.070 atm and in the appropriate range of metal temperature variations (1973-2273 K). The solidification of a 1 g-mass sample at a rate higher than 1000 K/s assured the complete nitrogen fixation in the solidified sample compared to the liquid-state sample.
Findings: It has been established in the study by experimentally measuring the nitrogen concentration in the liquid Fe-Ti alloy with varying titanium contents under hyperbaric conditions that the solubility of nitrogen in liquid Fe-Ti alloys increases with increasing partial pressure of nitrogen in the gaseous phase, and with increasing liquid metal temperature and titanium content of the metal.
Research limitations/implications: The study has found that when the intensive parameters increase above the critical values, the non-metallic phase forming on the levitating metal drop surface is a titanium nitride film, as demonstrated by X-ray analysis. Such samples were eliminated from the characteristics of nitrogen solubility in the homogeneous metallic phase.
Practical implications: The collected data on the thermodynamic quantities of the liquid Fe-Ti-N alloy has enriched the autonomous thermodynamic database containing information about liquid alloys of iron with nitrogen, which is being built at Czestochowa University of Technology.
Originality/value: The developed formulas seem to be valuable, because - as the relevant literature indicates - the Fe-Ti system has not been examined so far under such extreme thermodynamic conditions.
Keywords: Titanium; Iron alloys; Alloy nitrogen; Experimental tests; Liquid alloy-gaseous phase system equilibrium

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1. Introduction

Alloy nitrogen containing steels, so called HNS (High Nitrogen Steels), due to their good mechanical properties (such as the yield point, tensile strength, embrittlement temperature, service fatigue strength, the critical stress intensity parameter value, ductility) and enhanced resistance to corrosion (e.g. pitting corrosion, crevice corrosion, stress corrosion, corrosion fatigue, …), find application in various branches of the economy. Examples include the transport, power engineering, the defence industry, etc. One of the strongly nitride-forming elements occurring in alloy steels is titanium. Iron alloys of complex chemical composition are currently studied in a wide liquid metal temperature range and at gaseous phase pressures considerably exceeding 0.1 MPa. It is particularly essential to consider the effect of nitrogen on its activity coefficient, which was first noted in study [1].

Basic research on the use of nitrogen as an alloy element in iron alloys has been conducted at the Department of Extraction and Recycling of Metals of the Czestochowa University of Technology for a dozen or so years. The primary goal of this research has been to develop an autonomic database of thermodynamic data related to the solubility of nitrogen in liquid metals and their binary alloys with iron.

2. Original investigation

The basic purpose of the study was to determine the physicochemical characteristics of thermodynamic equilibrium in the liquid metal-gas system, where the liquid metal was a liquid Fe-Ti alloy, and the reaction gas was always a mixture of nitrogen and argon with preset chemical composition.

In order that such characteristics might be reliable, it was necessary to create conditions in which, aside from the interactions between the nitrogen and a given metal in the Fe-Ti alloy, a self-interaction of the nitrogen in the liquid metal will reveal itself to such an extent that it could be measured with an appropriate experimental technique. In a liquid metal–gas system, the self-interaction of a gaseous element will be visible at relatively high concentrations of that element in the liquid metal. If it is known that the equilibrium nitrogen concentration in liquid metal is strongly influenced by the partial pressure of nitrogen in the gaseous phase, then, of course, such tests will be best suited to the formulated goal, in which the range of variation will extend within an appropriately wide interval.

It was assumed that thus obtained thermodynamic data would provide a contribution to the construction of a thermodynamic model serving for the determination of nitrogen solubility in high-nitrogen steels and alloys which, as per the international nomenclature, are referred to, respectively, as HNS (High Nitrogen Steels) and HNA (High Nitrogen Alloys).

2.1. The scope of experimental tests

Within experimental tests, the nitrogen concentrations in the liquid Fe-N-Ti ternary alloy were determined under thermodynamic equilibrium conditions. The range of variation of thermodynamic factors, i.e. gaseous phase nitrogen pressure, liquid metal temperature and alloy element contents, are given in Table 1.

Table 1.
A summary of iron-titanium liquid alloy experimental test results

No	Nitrogen partial pressure, [atm]	Alloy temperature, [K]	Ti content, [wt%]
1.	0.001-0.0100	1873-2073	10
2.	0.0005-0.0250	1873-2073	25

2.2. Apparatus and testing methodology

The levitation metal melting method was employed for the tests. The method allows the elimination of the ceramic crucible, whereby the reaction system is a liquid metal-gas diphase system. This creates exceptionally advantageous conditions for contactless temperature measurement, as the ever occurring - though in minimal quantities - oxides collect in the lower part of the drop, thereby exposing the liquid metal in an area sufficient for taking a precise measurement. The eddy currents induced by the variable electromagnetic field in the metal, after rapidly melting it, also very quickly homogenize the forming liquid metal solution with nitrogen, thus allowing the thermodynamic equilibrium to be attained equally quickly. By changing electromagnetic field intensities, the temperature of the metal drop can be changed, which offers the possibility of taking measurements within a very wide ΔT range of up to several hundred degrees. Shutting down the high-frequency current supply of the inductor causes a small-mass sample to fall down by gravity, which can then cool down - e.g. in a copper mould - at a very high cooling rate. In these conditions, the nitrogen fixed in the solidified metal largely corresponds to the nitrogen dissolved in the metal drop, therefore the concentration, as determined by the chemical analysis of the sample, can be identified with the equilibrium concentration for the liquid state.

A detailed description of the test stand is provided, e.g., in reference [2].

Immediately before the experiment, a technical vacuum was created in the experimental setup which was subsequently filled three times with a test class Ar-N_2 mixture, each time attaining a pressure of 15 atm. After completion of above-mentioned activities, the oxygen and moisture contents of the working gas in the reactor were identical to those of the high-purity mixtures contained in the cylinders.

The experiment proper involved the melting of a metal sample (m=1±0.1g;) in a state of suspension in an electromagnetic field in an appropriate reaction gas at a pressure slightly higher than 1 atm, and then rapid filling of the metal reactor body with the same working gas until the preset nitrogen pressure level had been attained, with heating the liquid metal up to the proper temperature. In this state, the specimen was held for a duration of 180 s, which, based on studies [3-4], was considered satisfactory for the liquid metal-gaseous phase system to attain the thermodynamic equilibrium in the conditions of the experiment. After the levitation coil power supply had been switched off, a sample of a mass of approx. 1 g fell down by gravity into a copper testing mould. The metal solidified and crystallized under the conditions of cooling at a rate of 10^3 - 10^4 K×s^{-1}, [5]. The nitrogen content of the nitrogen-saturated titanium and iron-titanium alloy in micro-ingots was determined using a Leco TC-336 apparatus.

2.3. Selection of experimental test conditions

When conducting study [2] it was found that a new non-metallic phase formed on the surface of the drop under specific conditions. This phase was identified - a film of vanadium nitrides occurred on the sample surface. Also the study on the solubility of nitrogen in liquid Fe-Ti alloys found a similar phenomenon to have occurred, as shown in Figure 1.

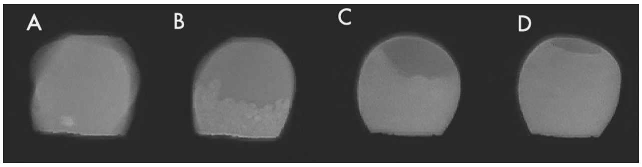

Fig. 1. A view of a new phase building up on the surface of the Fe-Ti sample during its saturation with nitrogen

Figure 1 clearly shows areas that could be identified as a new phase.

It was assumed a priori in the study that, as the extensive parameters (mainly the gaseous phase parameters and temperature) increased above the critical values, the non-metallic phase forming on the surface of the levitating metal drop was a vanadium nitride film. The correctness of this assumption was demonstrated using X-ray analysis.

The examination was made on a Rigaku-Denki X-ray diffractometer using filtered cobalt radiation and a scintillation counter.

When a non-metallic phase occurs, the system loses the homogeneous properties and becomes a heterophase system, i.e. the gaseous phase–liquid metal binary system changes to a ternary system of gaseous phase–liquid metal–vanadium nitrides. For obvious reasons, the examination results are untrue with respect to the homogeneous system and therefore must be rejected. This phenomenon, which could be predicted on the ground of the theory of liquid metallic solutions, required the use of a testing methodology that was developed during the study on the Fe-N-V and V-N alloys. Namely, the vision monitoring of the metal drop view with digital image recording was employed. Thus, any samples, on which titanium nitrides started to appear, could be eliminated.

2.4. A summary of the test results

Three series of experiments were carried out. The solubility of nitrogen in liquid Fe-Ti alloys has been examined, and the results are given in Table 2.

Table 2.
The conditions and results of the tests of nitrogen solubility in the liquid iron-titanium alloy

No	Ti, [%wt]	T, [K]	P_{N2}, [atm]	[%N], [%wt]
1.	10.0	2173	0.00010	0.0200
2.	10.0	2173	0.00010	0.0206
3.	10.0	2173	0.00010	0.0199
4.	10.0	2073	0.00100	0.0340
5.	10.0	2073	0.00100	0.0341
6.	10.0	2073	0.00100	0.0332
7.	10.0	2173	0.00150	0.0390
8.	10.0	2173	0.00150	0.0392
9.	10.0	2173	0.00150	0.0384
10.	10.0	2173	0.00030	0.0370
11.	10.0	2173	0.00030	0.0371
12.	10.0	2173	0.00030	0.0375
13.	10.0	1973	0.00150	0.0251
14.	10.0	1973	0.00150	0.0240
15.	10.0	1973	0.00150	0.0243
16.	10.0	1973	0.00010	0.0148
17.	10.0	1973	0.00010	0.0147
18.	10.0	1973	0.00010	0.0150
19.	25.0	2073	0.00100	0.0490
20.	25.0	2073	0.00100	0.0489
21.	25.0	2073	0.00100	0.0485
22.	25.0	2073	0.03000	0.1500
23.	25.0	2073	0.03000	0.1349
24.	25.0	2073	0.03000	0.1587
25.	25.0	2173	0.00050	0.0620
26.	25.0	2173	0.00050	0.0609
27.	25.0	2173	0.00050	0.0625
28.	25.0	2173	0.00200	0.0690
29.	25.0	2173	0.00200	0.0698
30.	25.0	2173	0.00200	0.0692
31.	25.0	2173	0.02500	0.1600
32.	25.0	2173	0.02500	0.1644
33.	25.0	2173	0.02500	0.1645
34.	25.0	1973	0.00250	0.0420
35.	25.0	1973	0.00250	0.0430
36.	25.0	1973	0.00250	0.0430
37.	25.0	1973	0.02500	0.1100
38.	25.0	1973	0.02500	0.1083
39.	25.0	1973	0.02500	0.1102

3. Discussion of the results

3.1. General relationships for nitrogen dissolution in the liquid metal—gaseous phase system

A detailed description of these relationships is provided in our monograph [6]. Currently, the most widespread method for quantitative determination of the nitrogen activity coefficient is the one relying on the description of experimental data. This description brings about an explicit form of the function expressing the concentration activity coefficient relationship through the interaction parameters as proposed by Wagner and Lupis and Elliott, as well as the nitrogen self-interaction parameters.

At a constant temperature and a constant concentration of component X in the Fe-N-X alloy, the activity and solubility of nitrogen may depend solely on the nitrogen concentration; so, for this alloy, and assuming that nitrogen obeys the law of ideal gases and considering Equation (1), we can write:

$$\lg \frac{[\%N]}{\sqrt{P_{N_2}}} = \lg K_{N(Ni)} - \lg f_N^{(X)} - E_N^{(N)} \cdot [\%N] \quad (1)$$

In the study, the extremely strong influence of titanium on the solubility of nitrogen in the iron alloys examined requires a very detailed analysis of the suitability of the presented interpretation of test results. Therefore, a simplified formula of mathematical description of the measurements results was adopted using multiple regression analytical equations.

So far, the maximum titanium content of the titanium alloys under examination has been 0.77 wt%. Within this study, experimental tests on the solubility of nitrogen in Fe-Ti alloys with higher and much higher titanium contents were carried out. Therefore, it is not possible to directly verify the our own results with literature results on the ground of classic theories describing diluted solutions through expressing the activity coefficient by the methods of Wagner and Lupis and Elliott.

3.2. Solubility of nitrogen in liquid Fe-Ti alloys

The analysis of data was made and the analytical nitrogen solubility relationships were developed for individual alloys examined, as dependent on the gaseous phase nitrogen pressure and liquid metal temperature, using multiple regression.
A general notation of the employed regression function was as follows:

$$z=a_0+a_1x+a_2y \quad (2)$$

where: z - [N], %; $x - \sqrt{P_{N_2}}, \left[\sqrt{atm}\right]; y - \frac{1}{T}, \left[\frac{1}{K}\right]$

With the use of the developed relationships it is possible to calculate the nitrogen content of individual liquid alloys under experimentally preset thermodynamic conditions.
The values of coefficients a_0, a_1, a_2, along with the statistical measures of the relationships as expressed by a general equation in the form of (2) respectively for a given Fe-Ti alloy, are summarized in Table 3.

The analysis of the results clearly shows that the nitrogen content of the Fe-Ti alloy increases with the increase in gaseous phase nitrogen partial pressure and with the increase in liquid metal temperature. It can also be noticed that the nitrogen partial pressure stronger increases the nitrogen content of iron-titanium alloys than temperature does.

Table 3.
A summary of processing of results by multiple regression

No	Ti $[\%]_{wt.}$	Coefficient Name	Coefficient Value	Standard error
1	10.0	a_0	0.154	0.0257
		a_1	0.462	0.0906
		a_2	-285.5	53.9
2	25.0	a_0	0.466	0.0380
		a_1	0.716	0.0267
		a_2	-915.9	80.3

4. Conclusions

The solubility of nitrogen in the liquid Fe-Ti alloy with varying titanium contents was measured experimentally in the study. The use of the levitation metal melting method enabled precise measurements to be carried out. The original investigation was carried out while considering contemporary views on the methodology of this type of tests. To quantitatively describe the results of our investigation, a mathematical statistics method, and specifically multiple regression, was employed.

It was found in the study that when the intensive parameters increased above the critical values, the non-metallic phase forming on the levitating metal drop surface was a titanium nitride film, as demonstrated by X-ray analysis. The beginning of film formation was identified optically using computerized image recording. Such samples were removed from the solubility characteristics, whereby any errors resulting from melting in ceramic crucibles were eliminated, and only this melting has been used so far in literature on the subject. The research methodology developed within the study, which assures the thermodynamic equilibrium state of the homogeneous liquid metal phase system to be attained, can be regarded as original.

The nitrogen solubility in liquid Fe-Ti alloys increases with the increase in gaseous phase nitrogen partial pressure and with the increase in liquid metal temperature. The developed formulas seem to be valuable, because - as can be noted in the literature on the subject - the Fe-Ti has not been previously examined under such extreme conditions. Hence, the determination of the relationship between nitrogen solubility in the iron-titanium alloy and gaseous phase nitrogen partial pressure and liquid metal temperature for the first time can be recognized as the research effect of this study.

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