Solubility of Nitrogen in Liquid Ni, Ni–Nb, Ni–Cr–Nb, Ni–Fe–Nb, and Ni–Cr–Fe–Nb Systems

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By means of sampling methods, we have determined the solubility of nitrogen in liquid Ni, Ni–Nb, Ni–Cr–Nb, Ni–Fe–Nb, and Ni–18Cr–5.2Nb systems within the temperature range from 1 773 K to 1 873 K and with the niobium content from 5 to 20 mass%. It has been found that Sieverts’ formalism successfully describes the solubility of nitrogen in all these liquid alloys up to 7 atm of the nitrogen partial pressure. Niobium addition increases the nitrogen solubility and its effect to increase nitrogen solubility is only second to chromium. Furthermore, we have derived the enthalpy and entropy of dissolution of nitrogen in these liquid alloys, determining the first order interaction parameter, \( a_{NN, Ni–Nb} \), = \(-0.0785\), up to 20 mass% Nb in nickel between nitrogen and niobium. In addition, the effects of alloying elements on the activity coefficient of nitrogen have been further investigated and the second order cross-interaction parameters between nitrogen and chromium or iron with niobium at 1 873 K have been determined as \( f_{Cr, Nb}^{Ni–Nb} = 0.0256 \) and \( f_{Fe, Nb}^{Ni–Nb} = 0.0115 \).

KEY WORDS: niobium; nitrogen solubility; interaction parameter; liquid nickel-based alloys.

1. Introduction

Nickel-based superalloys are one of the most commonly used high temperature materials.1,2) These alloys have been extensively employed in the aeronautical and nuclear engineering industries and they must meet increasingly stringent requirements in terms of reliability and mechanical properties.3–5) It is well known that some impurity elements (i.e., nitrogen, oxygen, sulfur, etc.) are detrimental to the mechanical properties of nickel-based superalloys. Therefore, it is essential to strictly control the impurity level in smelting process. In particular, a small amount of nitrogen can be very deleterious.3–6) Therefore, residual concentration of this element must be perfectly controlled.5,6) The achievement of extremely low nitrogen levels requires the knowledge of thermodynamic data for nitrogen solubility in liquid pure nickel and nickel-based alloys. Its importance is not only for fundamental researches but also for industrial and economic reasons. Although the thermodynamics of nitrogen solubility in nickel-based alloys is very important, there was almost no direct studies at this aspect.

It is well-known that the thermodynamics of nitrogen solubility in binary and ternary liquid iron-based alloys was the subject of extensive theoretical and experimental investigations in the sixties and seventies of the last century.6–9) For instance, a considerable background of knowledge has been built up on the nitrogen chemical behavior in liquid iron and iron-based alloys. The solubility of nitrogen in liquid iron and binary iron-base alloys was determined by Maekawa et al.10) and Pehlke et al.11) Likewise, some studies have been conducted for the solubility of nitrogen in liquid ternary and quaternary iron-base alloys.12–18) Anson et al.19) even measured the solubility of nitrogen in molten duplex stainless steel. Ishii et al.21) summed up the effect of alloying elements on the solubility of nitrogen in liquid iron.

However, little is known regarding nitrogen in liquid pure nickel or nickel-based alloys. Nitrogen solubility in liquid pure nickel was determined in several studies.23–29) Wada and Pehlke30) were the first to experimentally report the nitrogen solubility in Ni–Cr alloys, and determined the first and second order interaction parameters between nitrogen and chromium in liquid nickel. Subsequently, the behaviors of nitrogen in liquid binary alloy Ni–Mn, Ni–Fe, Ni–Co, Ni–Mo, and Ni–W alloys were further investigated.25,30,31) However, up to date no literature has been found concerning the solubility of nitrogen in liquid nickel-based alloys containing niobium. It is clear that niobium is an important strengthening element for nickel-based superalloys, because it usually segregates in \( \gamma' \) phase, \( \gamma'' \) phase, \( \delta \) phase and MC carbides.32–34) In similarity to several other transition metals in groups IV B and V B, niobium was also demonstrated to be a strong nitride forming element. Nevertheless, the lack of suitable thermochemical data renders the calculations of the nitrogen concentration difficult when niobium is alloyed in nickel-based alloys.

The object of this work is to study the influence of
niobium content on the equilibrium nitrogen solubility in the liquid state under elevated nitrogen partial pressure, to observe the validity of Sieverts’ law for binary, ternary and quaternary nickel-based alloys, and to determine the enthalpy and entropy of dissolution of nitrogen and the interaction parameters. These obtained thermodynamic data would lay a foundation to build a thermodynamic model for elucidation of the nitrogen solubility in liquid nickel-based superalloys.

2. Experimental Procedure

The sampling method was used in this study to measure the nitrogen solubility in liquid pure nickel and nickel-based alloys. In terms of the previous investigations of nitrogen solubility in liquid pure nickel, Ni–Cr and iron-based alloys under high pressure, we have developed a special high pressure induction furnace at our laboratory, as shown in Fig. 1.

The master alloys were prepared in a 5 kg vacuum induction melting furnace to reduce the initial dissolved gas content and the burning loss of alloying elements. The raw materials were electrolytic nickel, electrolytic chromium, electrolytic iron, and electron beam niobium. The purities of these metallic raw materials were compiled in Table 1. The master alloys were processed into specimens. Then, in each experiment, 120 g of specimen was contained in an MgO (Φ50 mm × 40 mm × 60 mm) ceramic crucible and melted by using a 6.7 kHz and 35 kW induction power supply. In order to minimize any contamination risk, ultra-high purity argon (99.999 mass% pure) and nitrogen gases (99.99 mass% pure) were used. Before melting the metallic charge, the reaction chamber with the metal specimen was heated slowly and held under vacuum conditions to remove adsorbed gases. However, after melting the charge, extended periods under vacuum conditions were avoided to prevent evaporation of niobium, the error caused by vaporization from the melt was expected to be the greatest for niobium-containing alloys. The niobium vapor may react with nitrogen gas forming nitride or the nitrogen may be absorbed on the niobium deposition. To prevent these errors, no vacuum degassing was done in the molten state. Subsequently, the melting chamber was filled with ultrahigh purity nitrogen so as to give the desired pressure. The pressure in the system was measured and controlled by an IFM PG2453 pressure sensor. Temperature was measured by immersing a thermocouple contained in a protective alumina sheath in the melt. After reaching a desired value, the temperature was controlled by a Shimaden FP93 PID brainpower temperature controller, which could offer accurate temperature controlling within ±1 K. At the end of a run, the melt was cooled rapidly by turning off the induction coil and increasing overall flow velocity of cooling water, meanwhile, high pressure was exerted on the melt during solidification, which was eight times higher than saturation pressure.35) Table 2 showed an overview of the investigated alloy systems, where Ni-5Nb meant the alloy contains 5 mass% niobium. Moreover, a series of preliminary experiments were performed in order to determine the optimum holding time to confirm equilibrium with the gas phase. The starting time (t = 0) was defined as the time point where the metallic charge was completely molten, and sampling was performed at the seven holding times: 10, 30, 60, 90, 120, 150, and 180 min.

Specimens were processed into Φ4 mm × 30 mm bars, the subsequent chemical analysis for nitrogen content was carried out by means of the gas extraction method with a LECO TCH-600T oxygen-nitrogen-hydrogen analysis instrument with a precision of 0.025 ppm or 0.3% RSD. The reproducibility of the chemical analyses was good.

3. Results

Figure 2 compiles the results for the variation of nitrogen content with time in liquid Ni-20Nb, Ni-20Cr-10Nb, and Ni-20Fe-10Nb alloys. Nitrogen contents increase with time and increase rapidly within the first 30 minutes, and then reach a saturated value after 90 minutes for the three alloys. Kobayashi et al.21) and Kowanda’s35) studies indicated that the time to reach equilibrium has little relation to the

![Fig. 1. Schematic diagram of experimental apparatus.](image)

| Table 1. Purity of metallic raw materials. |
|------------------------------------------|
| Material                        | Purity (mass%) |
|-----------------------------------|----------------|
| Electrolytic nickel               | 99.99         |
| Electrolytic iron                | 99.9          |
| Electrolytic chromium            | 99.99         |
| Electron beam niobium            | 99.99         |

| Table 2. Investigated alloy systems. |
|--------------------------------------|
| Alloy system | Ni  | Ni–Nb | Ni–Cr–Nb | Ni–Fe–Nb | Ni–Cr–Fe–Nb |
|--------------|-----|-------|----------|----------|-------------|
| Pure nickel  | Ni–5Nb   | Ni–10Cr–5Nb | Ni–10Fe–5Nb | Ni–10Cr–Fe–5Nb |
| Ni–10Nb     | Ni–10Cr–10Nb | Ni–10Fe–10Nb | Ni–15Nb     | Ni–20Cr–5Nb | Ni–20Fe–5Nb |
| Ni–15Nb     | Ni–20Cr–10Nb | Ni–20Fe–5Nb  | Ni–20Nb     | Ni–20Cr–10Nb | Ni–20Fe–10Nb |
nitrogen partial pressure. Meanwhile, in our experiment the melt was strongly stirred by electromagnetic forces, being favorable for nitrogen mass transfer in liquid phase so as to shortening the equilibrium time. Finally, the holding time was set to be 150 min to ensure that all of the alloy systems reach their equilibriums over a wide range of temperature and nitrogen partial pressure.

Dissolution of nitrogen in molten alloy can be expressed as follow,

$$\frac{1}{2} N_2(g) = [N] \quad \text{........................................ (1)}$$

Following Eq. (1), the equilibrium constant $K$ of this reaction can be further expressed as,

$$K = \frac{a_N}{\sqrt{p_{N_2}}} = f_N \cdot \left(\text{mass}\% N\right) \quad \text{...... (2)}$$

where $a_N$ and $f_N$ are the activity and the activity coefficient of nitrogen in the liquid alloy, respectively, mass% $N$ is nitrogen dissolution in weight percent, and $p_{N_2}$ is the partial pressure of nitrogen in the gas phase. The standard state is the hypothetical 1 mass% dissolution of nitrogen in pure nickel and the reference state is a dissolution with nitrogen at infinite dilution.

If the nitrogen solubility obeys Sieverts’ law for all alloys, the amount of dissolved nitrogen is directly proportional to the square of root of nitrogen partial pressure:

$$\text{mass}\% N = K_S \sqrt{p_{N_2}} \quad \text{......... (3)}$$

where $K_S$ is the Sieverts’ constant and represents the nitrogen concentration at 1 atm nitrogen partial pressure.36)

**Figure 2.** Variation of nitrogen content with time.

**Figure 3.** Solubility of nitrogen vs. pressure for liquid Ni–Nb alloys at 1873 K. (Online version in color.)

**Table 3.** Sieverts’ constant $K_S$ and the square of Pearson’s correlation coefficient $r^2$.

| Alloy            | $K_S$  | $r^2$ | Alloy            | $K_S$  | $r^2$ |
|------------------|--------|-------|------------------|--------|-------|
| Ni-5Nb           | 0.0021 | 0.99  | Ni-20Cr-10Nb     | 0.1583 | 0.99  |
| Ni-10Nb          | 0.0116 | 0.99  | Ni-10Fe-5Nb      | 0.0050 | 0.99  |
| Ni-15Nb          | 0.0203 | 0.99  | Ni-10Fe-10Nb     | 0.0141 | 0.99  |
| Ni-20Nb          | 0.0476 | 0.97  | Ni-20Fe-5Nb      | 0.0095 | 0.99  |
| Ni-10Cr-5Nb      | 0.0200 | 0.99  | Ni-20Fe-10Nb     | 0.0224 | 0.99  |
| Ni-10Cr-10Nb     | 0.0366 | 0.99  | Ni-18Cr-17Fe-5.2Nb | 0.1684 | 0.99  |
| Ni-20Cr-5Nb      | 0.0906 | 0.99  |

Figure 3 shows the influence of niobium on the nitrogen solubility in liquid nickel-based alloys up to 7 atm of nitrogen partial pressure at 1873 K. The validity of Sieverts’ law is confirmed by means of the liner regression analysis using the square of the Pearson’s correlation coefficient $r^2$.30) The validity of Sieverts’ law is approved, if $+0.97 \leq r^2 \leq +1.00$ in **Table 3**. The curves in Fig. 3 indicate that the nitrogen solubility lines show no departure from Sieverts’ law, and the solubility of nitrogen increases with increasing the niobium content. However, our results reveal that the linear correlation coefficient decreases with increasing the niobium content, and this tendency is more pronounced with higher niobium contents. The similar experimental phenomena were observed in liquid Ni–Cr alloys.29)

The experimental result of the nitrogen solubility in liquid Ni–Nb is compiled as functions of temperature in **Figure 4**. Temperature dependence of the nitrogen solubility is negative in liquid Ni–Nb alloys, while the solubility of nitrogen in pure nickel increases with increasing temperature.23,27,37) This fact demonstrates that the addition of niobium changes temperature dependence of the nitrogen solubility, and niobium in liquid nickel shifts the nitrogen dissolution reaction towards an exothermic process. This behavior was similarly observed for chromium in liquid nickel.38)

**Figures 5 and 6** show the solubility of nitrogen in ternary and quaternary alloys, indicating two-fold facts. In the first, the nitrogen concentration is remarkably increased along with increasing the chromium, niobium and iron contents, and, in the second, the adherence of nitrogen experimental data to the regression lines reveals that Sieverts’ law also holds for all of those investigated alloys over the studied pressures.

**Figure 7** shows the experimental results of the temperature dependence of the solubility of nitrogen measurements at the nitrogen partial pressure of 1 atm in liquid Ni, Ni–Cr–Nb, Ni–Fe–Nb, and Ni–18Cr–17Fe–5.2Nb alloys, respectively. The solid lines are determined by regression analysis. It can be observed that niobium increases the nitrogen solubility in all these alloys. Apparently, the nitrogen content...
solubility increases with decreasing temperature in both Ni–Cr–Nb and Ni–Cr–Fe–Nb alloys, but increases with increasing temperature in pure nickel. Nevertheless, the tendency is complex in Ni–Fe–Nb alloys in which the temperature dependency of nitrogen solubility is converted from positive to negative with increasing niobium content. It needs to be emphasized that Abdulrahman et al. [31] also observed that the nitrogen solubility increases with increasing temperature in Ni–Fe alloys. This fact further reveals that the niobium addition changes the temperature dependency of nitrogen solubility in Ni–Fe–Nb alloys.

4. Discussion

The free energy of the dissolution of a half mole of nitrogen in the hypothetical 1 mass% dissolution of nitrogen is:

\[
\Delta G_N^{\text{alloy}} = \Delta H_N^{\text{alloy}} - T \cdot \Delta S_N^{\text{alloy}} = -RT \ln \left( \frac{(\text{mass}\% \text{N})_{\text{alloy}}}{P_N} \right) \quad \text{... (4)}
\]

where \(\Delta H_N^{\text{alloy}}\) and \(\Delta S_N^{\text{alloy}}\) are the enthalpy and the entropy of nitrogen dissolution in liquid nickel-based alloys, respectively. \(\Delta H_N^{\text{alloy}}\) can be determined from the temperature coefficient of nitrogen solubility as reads,

\[
\frac{d(\Delta G_N^{\text{alloy}}/T)}{d(1/T)} = \Delta H_N^{\text{alloy}} = -R \left[ \frac{d(\text{mass}\% \text{N})_{\text{alloy}}}{d(1/T)} \right]_{\text{pcm}} \quad \text{... (5)}
\]

4.1. Solubility of Nitrogen in Liquid Pure Nickel

The standard Gibbs free energy of nitrogen dissolution in liquid pure nickel is:

\[
\Delta G_N^0 = \Delta H_N^0 - T \Delta S_N^0 \quad \text{... (6)}
\]

and also

\[
\Delta H_N^0 - T \Delta S_N^0 = -RT \ln K \quad \text{... (7)}
\]

where \(\Delta G_N^0\), \(\Delta H_N^0\) and \(\Delta S_N^0\) are the standard Gibbs free energy, enthalpy and entropy of nitrogen dissolution in liquid nickel, respectively. With converting the natural loga-
rithms into common logarithms and taking a specific value of the gas constant (R = 8.3145 J/(K·mol)), Eq. (7) can be further expressed in the particular form, as follows,

$$\log K = \frac{-\Delta H_N^0}{19.145} \times \frac{1}{T} + \frac{\Delta S_N^0}{19.145} \quad \cdots (8)$$

Figure 7 compiles the influence of temperature on the solubility of nitrogen in liquid pure nickel. Note that the logarithm of the solubility of nitrogen is plotted against the reciprocal temperature. The value enables the determination of the effect of temperature on $\log(\text{mass}\%N)$ in the following relationship as follows,

$$\log(\text{mass}\%N) = -1.198 \frac{T}{T_0} - 2.18 \quad \cdots (9)$$

Therefore, by combining Eq. (2), Eqs. (8) and (9), the change of the standard Gibbs free energy in pure liquid nickel can be written as below,

$$\Delta G_{N(Ni)}^{0} = 22.9 + 41.7 \times 10^{-3} T \text{ kJ/mol} \quad \cdots (10)$$

Furthermore, Fig. 8 summarizes the experimental values of the free energy ($\Delta G_N^0$) of nitrogen dissolution in liquid pure nickel as compared with other previously published data. It shows that the reported values at 1873 K range from 55 kJ/mol to 110 kJ/mol. In our current studies, the value of $\Delta G_N^0$ has been determined to be 101 kJ/mol at 1873 K, which is in good agreement with those reported values by Abdullrahman et al., Fedorchenko et al., Kim et al., Stomakhin et al. and Blossey et al.

But Wada et al. reported a much lower value. The previously reported solubility of nitrogen in liquid pure nickel at 1873 K and 1 atm nitrogen partial pressure is compiled in Fig. 9 in which the distribution of these experimental data shows the nitrogen solubility in a range from 0.0009 mass% to 0.0020 mass% upon different experimental measurements. In our current studies, we have determined that the solubility of nitrogen is 0.0013 mass% in liquid pure nickel at 1873 K and 1 atm nitrogen partial pressure. However, the solubility of nitrogen in liquid pure nickel at 1873 K and 1 atm nitrogen partial pressure was determined to be 0.0018 mass% by Herrera-Trejo et al., 0.0011 mass% by Kim et al., 0.0012 mass% by both Pehlke et al. and Kowanda et al., 0.0020 mass% - the maximum reported value by Abdullrahman et al., 0.0009 mass% - the smallest value by Siwka. Note that the disagreements among these studies may be related to the limitations of the different experimental methods and relatively low solubility of nitrogen in nickel.

### 4.2. Ni–Nb Alloys

According to the experiment results in Figs. 3, 5 and 6 in which the nitrogen solubility obeys Sieverts’ law, mass% N is thus proportional to $\sqrt{p_1}$, and the activity coefficient of nitrogen can be expressed as follows, by considering the presence of the alloying elements.

$$\log f_N = \frac{1}{19.145T} \times (\Delta H_N^{\text{alloy}} - \Delta H_N^0) \times \left(1 - \frac{T}{T_H}ight)$$

where $\Delta H_N^{\text{alloy}}$ and $\Delta H_N^0$ represent the first and the second order enthalpy of nitrogen dissolution in liquid pure nickel and liquid nickel-based alloys, respectively. $f_N$ can be expressed as:

$$f_N = \left(\frac{\text{mass}\% N(\text{in pure nickel})}{\text{mass}\% N(\text{in alloy})}\right)_{p_1,T} \quad \cdots (12)$$

$$\log f_N = \log(\text{mass}\% N)_{\text{pure nickel}} - \log(\text{mass}\% N)_{\text{alloy}} \quad \cdots (13)$$

Note that the standard Gibbs free energy of nitrogen dissolution in liquid pure nickel can be calculated through Eq. (10). The experimental results, enthalpy and entropy of dissolution of nitrogen and the logarithm of activity coefficient of
nitrogen at 1 873 K are summarized in Table 4.

Note that the logarithm of Eq. (2) can be expressed as,

$$\log K = \log \frac{f_N}{p_N} = \log f_N + \log (\text{mass}\% N) - \frac{1}{2} \log p_N.$$

........................................ (14)

thus

$$\log (\text{mass}\% N) - \frac{1}{2} \log p_N = \log K - \log f_N.$$

........................................ (15)

$$\log K = \left[ e_{NNi}^{\text{Nb}} (\text{mass}\% \text{Nb}) + e_{Ni}^{\text{Nb}} (\text{mass}\% \text{Nb})^2 \right]$$

........................................ (16)

Figure 10 compiles the resulting $\log (\text{mass}\% N) - 1/2 \log p_N$ versus mass% Nb curve. The activity of nitrogen and the first order interaction parameter are ascertained by means of regression analysis of the curve according to the Wagner formalism. The result of regression analysis indicates that the first order interaction parameter is determined as,

$$e_{NNi}^{\text{Nb}} (1 873 K) = -0.0785.$$

At 1 873 K, the value of intercept is,

$$\log K = -2.92.$$

The value of log K reveals the solubility of nitrogen in pure nickel (with Nb mass% = 0) as 0.0012 mass% at 1 873 K, which is in good agreement with our currently measured value.

The first order interaction parameter $e_{Ni}^{\text{Nb}}$ can be calculated from the value of $e_{NNi}^{\text{Nb}}$ using the following relationship:\(^{10}\)

$$e_{Ni}^{\text{Nb}} (1 873 K) =$$

$$\frac{M_{\text{Nb}}}{M_{\text{N}}} \frac{M_{\text{Ni}}}{M_{\text{N}}} \times 0.434 \times 10^{-2} \times \frac{M_{\text{Ni}} - M_{\text{Nb}}}{M_{\text{N}}} = -0.5450.$$

........................................ (18)

where both $M_{\text{Nb}}$ and $M_{\text{N}}$ are the atomic masses of niobium and nitrogen, respectively.

### 4.3. Ni–Cr–Nb and Ni–Fe–Nb Alloys

From Eq. (11), the activity coefficients of nitrogen in Ni–Cr–Nb and Ni–Fe–Nb alloys can be expressed as follows.

For Ni–Cr–Nb alloys:

$$\log (\text{mass}\% N) = \log f_{Ni}^{(Ni-Cr-Nb)} + e_{Ni}^{Cr} (\text{mass}\% Cr) (\text{mass}\% N).$$

........................................ (21)

For Ni–Fe–Nb alloys:

$$\log (\text{mass}\% N) = \log f_{Ni}^{(Ni-Fe-Nb)} + e_{Ni}^{Fe} (\text{mass}\% Fe) (\text{mass}\% N).$$

........................................ (22)

The effects of chromium and iron on nitrogen solubility in liquid nickel can be represented in terms of their influence on the corresponding activity coefficients. According to the Wagner and Chipman’s formalism,\(^{40}\) the logarithm of the activity coefficients of nitrogen in liquid Ni–Cr and Ni–Fe alloys, $\log f_{Ni}^{(Ni-Cr)}$ and $\log f_{Ni}^{(Ni-Fe)}$, are given by:

$$\log f_{Ni}^{(Ni-Cr)} = e_{Ni}^{Cr} (\text{mass}\% Cr) + e_{Ni}^{Cr} (\text{mass}\% Cr)^2$$

........................................ (23)

$$\log f_{Ni}^{(Ni-Fe)} = e_{Ni}^{Fe} (\text{mass}\% Fe) + e_{Ni}^{Fe} (\text{mass}\% Fe)^2$$

........ (24)

Based on relative data,\(^{30,38}\) the logarithm of the activity coefficients of nitrogen in liquid Ni–Cr and Ni–Fe alloys, $\log f_{Ni}^{(Ni-Cr)}$ and $\log f_{Ni}^{(Ni-Fe)}$ are,

$$\log f_{Ni}^{(Ni-Cr)} =$$

$$-0.0856 (\text{mass}\% Cr) + 5 \times 10^{-4} \times (\text{mass}\% Cr)^2.$$

........ (25)

### Table 4. Experimental results, the enthalpy and entropy of dissolution of nitrogen and logarithm of activity coefficient of nitrogen at 1 873 K.

| Alloy system     | Mass% Nb | $-\log f_{Ni,1873 K}$ | $\Delta H_{\text{sol}}^{\text{molv}}, \text{J/mol}$ | $\Delta S_{\text{sol}}^{\text{molv}}, \text{J/mol}$ |
|------------------|----------|------------------------|--------------------------------------------------|--------------------------------------------------|
| Ni–Nb            | 5        | 0.1303                 | 36 249                                           | 68.53                                             |
|                  | 10       | 0.6136                 | 17 874                                           | 49.46                                             |
|                  | 15       | 1.0018                 | 33 747                                           | 50.51                                             |
|                  | 20       | 1.3085                 | 37 282                                           | 46.52                                             |
| Ni-10Cr-Nb       | 5        | 1.0211                 | 40 186                                           | 53.58                                             |
|                  | 10       | 1.3221                 | 60 128                                           | 58.46                                             |
| Ni-20Cr-Nb       | 5        | 1.7733                 | 14 478                                           | 25.45                                             |
|                  | 10       | 1.8635                 | 40 347                                           | 37.54                                             |
| Ni-10Fe-Nb       | 5        | 0.4228                 | -81 904                                          | -0.15                                             |
|                  | 10       | 0.9816                 | -83 813                                          | -11.87                                            |
| Ni-20Fe-Nb       | 5        | 0.9604                 | -46 129                                          | -6.91                                             |
|                  | 10       | 1.0486                 | 10 843                                           | 37.38                                             |
| Ni-18Cr-17Fe-5.2Nb | 5.2    | 1.9381                 | 45 338                                           | 38.77                                             |

![Fig. 10](image) Log(%N)−1/2 log pN vs. the niobium content at 1 873 K.
\[
\log f_{(Ni-Fe)} = -0.0163(\text{mass\% Fe}) - 2 \times 10^{-4} \times (\text{mass\% Fe})^2 \quad \text{(24)}
\]

The logarithm of the activity coefficients of nitrogen in liquid Ni–Fe–Nb and Ni–Cr–Nb alloys at 1873 K can be expressed by the following equation, respectively.

\[
\log f_{(Ni-Cr-Nb, 1873 K)} = -0.0163(\text{mass\% Fe}) - 2 \times 10^{-4} \times (\text{mass\% Fe})^2 \\
-0.0785 \times (\text{mass\% Nb}) + r_{(Ni-Nb)}^{Cr, Nb}(\text{mass\% Fe})(\text{mass\% Nb}) \\
\quad \text{........................................ (25)}
\]

\[
\log f_{(Ni-Cr-Nb, 1873 K)} = -0.0856(\text{mass\% Cr}) + 5 \times 10^{-4} \times (\text{mass\% Cr})^2 \\
-0.0785 \times (\text{mass\% Nb}) + r_{(Ni-Nb)}^{Fe, Nb}(\text{mass\% Cr})(\text{mass\% Nb}) \\
\quad \text{........................................ (26)}
\]

where \(r_{(Ni-Nb)}^{Cr, Nb}\) and \(r_{(Ni-Nb)}^{Fe, Nb}\) are the first order interaction parameters of chromium and iron at 1873 K, respectively. The experiment results for the activity coefficient of nitrogen are analyzed by the regression analysis. The second order cross interaction parameters between nitrogen, and chromium or iron and niobium can be thus determined as,

\[
\begin{align*}
&e_{(Ni-Nb)}^{Cr, Nb} = 0.0256 \pm 0.0041 \\
&e_{(Ni-Nb)}^{Fe, Nb} = 0.0115 \pm 0.0019
\end{align*}
\]

4.4 Discussions of Nitrogen Solubility

Figure 11 summarizes the interpolated nitrogen concentrations at 1873 K and 1 atm nitrogen partial pressure for Cr, Nb, Fe, and Co elements in liquid nickel. The solubility of nitrogen nonlinearly increases with increasing the contents of chromium and niobium. In the binary Ni-X systems (X=Cr, Nb, Fe, Co), the effects of the alloying elements on the nitrogen solubility can be evaluated by the nitrogen content vs. the alloying element content (in mass\%) at 1873 K and 1 atm nitrogen partial pressure as shown in Fig. 11, and the affecting degree rank of elements has a close relationship with their positions in the periodic table.

The position of elements in the periodic system depends on their electron structure. The volume of reception or removal of electrons by an alloying element, however, is directly combined with the transition of electrons between the gaseous component and the solvent and can be impeditive (decreasing the solubility of nitrogen) or promotive (increasing the solubility).\(^{42}\) It is obvious that Cr, Fe and Nb increase the solubility of nitrogen, and chromium exhibits the highest increase of nitrogen solubility. Meanwhile, the effect of niobium is only slightly lower than that of chromium. With respect to the effects of both Cr and Nb, it can be seen that both of Fe and Co evidences a slight increase of nitrogen solubility with increasing their contents in Fig. 11, thereby indicating a sharp contrast between Cr (or Nb) and Fe (or Co). Kowanda \textit{et al.}\(^{30}\) indicated that the effect of alloying elements on the solubility of nitrogen significantly decreases with increasing group number, while the effect slightly decreases with increasing their atomic numbers in the same group of the periodic table. In addition, the similar results can be obtained through a comparison of their interaction parameters.\(^{31,38}\) Therefore, the sequence of the increasing effects on nitrogen solubility has been determined as Cr>Nb>Fe>Co.

5. Conclusions

The solubility of nitrogen in liquid Ni, Ni–Nb, Ni–Cr–Nb, Ni–Fe–Nb and Ni–Cr–Fe–Nb systems is measured by the sampling method in the temperature range from 1773 K to 1873 K under different partial nitrogen pressures. The following conclusions are summarized as follows,

1) The validity of Sieverts’ law is demonstrated for a nitrogen dissolution in binary alloys (Ni–Nb), ternary alloys (Ni–Cr–Nb, Ni–Fe–Nb), and quaternary alloy (Ni–18Cr–17Fe–5.2Nb) at 1873 K and nitrogen pressures up to 7 atm.

2) Niobium-alloying addition increases the solubility of nitrogen in all alloys and the rising of temperature reduces the solubility of nitrogen in liquid Ni–Nb, Ni–Cr–Nb, and Ni–Cr–Fe–Nb alloys. This fact can be attributed to the exothermic reaction of nitrogen dissolution. However, the tendency is complex in Ni–Fe–Nb alloys in which the temperature dependency of nitrogen solubility shows a transfer from positive to negative with increasing niobium content.

3) The solubility of nitrogen in liquid pure nickel at 1873 K and 1 atm nitrogen partial pressure is measured to be 0.0013 mass\%. The standard Gibbs free energy of nitrogen dissolution in pure liquid nickel is derived to 101 kJ/mol.

4) The effect of niobium content on nitrogen behavior can be described by the first order interaction parameters \(E_{(Ni-Nb)}^{(Cr-Nb)}\). In addition, we have determined the second order cross interaction parameters between nitrogen, and chromium (or iron) with niobium at 1873 K.

5) Niobium addition apparently increases nitrogen solubility and its effect is only slightly lower than that of chromium. In the binary Ni-X systems (X=Cr, Nb, Fe, Co), the sequence of the increasing effects on nitrogen solubility can be specified as Cr>Nb>Fe>Co.
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