Solubility of Nitrogen in Liquid Nickel-Based Alloys

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The solubility of nitrogen in liquid binary nickel-based alloys (Ni-Co, Ni-Fe, and Ni-Cr) and ternary Ni-Cr-Co alloys was measured by the Sieverts' method between 1550 °C and 1750 °C. Solubility data and standard free energies and enthalpies of solution of nitrogen in the alloys are presented and interaction parameters are discussed. The validity of Sieverts' law at 1600 °C and pressures up to 1 atm was also confirmed.

I. INTRODUCTION

INTEREST in studying the dissolution of nitrogen in liquid metals follows first from the need to obtain experimental data, but also from a desire to understand the physical chemistry principles of the interaction of nitrogen with metallic metals. A number of these studies[1–13] have been concerned with the solubility of nitrogen in the liquid state of pure nickel and nickel-based alloys, which are used in chemical and thermal industries. To understand the behavior of nitrogen in these alloys, it is necessary to have reliable fundamental data pertaining to the solubility and thermodynamics of nitrogen, and, in an effort to extend our knowledge in these areas, this investigation of the thermodynamics of nitrogen solubility in the liquid state was undertaken. The behavior of nitrogen in pure liquid nickel has been described in a previous article.[14] Attention here is focused on the alloying elements chromium, cobalt, and iron, all of which are present in industrial materials used in nuclear reactors and jet-engine turbines; the article reports the validity of Sieverts' law and the thermodynamic properties of these liquid nickel-based alloys.

II. APPARATUS AND EXPERIMENTAL PROCEDURE

The details of the experimental apparatus and procedures have been given previously,[14] and only aspects relevant to the present results are given here. This investigation was made using a constant-volume Sieverts' apparatus, shown in Figure 3 of a previous article.[14]

The metallic-raw-materials specifications from manufacturer's data were as follows.

Nickel: 0.0003 pct Cu, 0.0004 pct Al, 0.0005 pct Si, and 0.0003 pct N

Cobalt: 0.0003 pct Cu, 0.0003 pct Zn, and no nitrogen detected

Iron: 0.003 pct Ni, 0.003 pct C, 0.0007 pct S, and 0.0002 pct N

Chromium: 0.01 pct Fe, 0.005 pct Ni, 0.001 pct Si, and 0.0005 pct N

Recrystallized alumina crucibles (99.80 pct Al_2O_3) were used throughout the investigation, with no evidence of a crucible-melt reaction. Argon, hydrogen, and nitrogen gases were of maximum purities: 99.998, 99.995, and 99.999 pct, respectively. Melt temperatures were measured with an optical pyrometer, and the temperature scale was calibrated against the melting points of five pure metals.

The method by which the nitrogen solubility in pure nickel alloys was determined[14] was also followed in these studies, and changes in alloy composition were obtained in a series of runs in which additional alloying metal was added from a sealed storage arm which is a part of the reaction chamber. The compositions of the alloys studied is indicated in the appropriate figure (Figures 1 through 4) and in Table II.

The solubility of nitrogen varies considerably over the range of alloys examined in this work, and the accuracy of the technique has been established through studies on liquid pure nickel.[14] A series of 15 measurements established a solubility of 0.0020 wt pct with a standard deviation of ±0.0002 wt pct, and this is considered to be the limit of precision of the experiments. In measurements on alloys, further errors may arise due to, for example, the technique of alloy addition, mixing in the melt, evaporation of material, and other factors not pertinent to measurements on pure nickel. These variations are quantified by showing, on the relevant graphs of results in the following sections, the data points for all experiments in a repeated series.

III. EXPERIMENTAL RESULTS AND DISCUSSION

There are two types of nickel alloys that were subjected to investigation. These are the binary alloys of nickel with Fe, Co, or Cr and the ternary alloys of nickel with Co and Cr.

A. *Effect of Pressure*

The effect of nitrogen pressure on the solubility of nitrogen was carried out on nickel-based alloys to examine the validity of Sieverts' law at pressures up to 1 atm. Plots of the solubility data at 1600 °C as a function of the square root of the nitrogen pressure for the Ni-Co, Ni-Fe, Ni-Cr, and Ni-Cr-Co alloys are presented in Figures 1 through 4. As it was assumed that the initial concentration of nitrogen in the melt is negligible,[14] the origin is taken as an additional point in each figure. Due to the problem of metal volatilization, experiments at very low pressure were avoided. From these figures, it is obvious that for each alloy system, the solubility follows a linear relationship with the square root of pressure, indicating the validity of Sieverts' law for a nitrogen solution in these alloy systems within the range of

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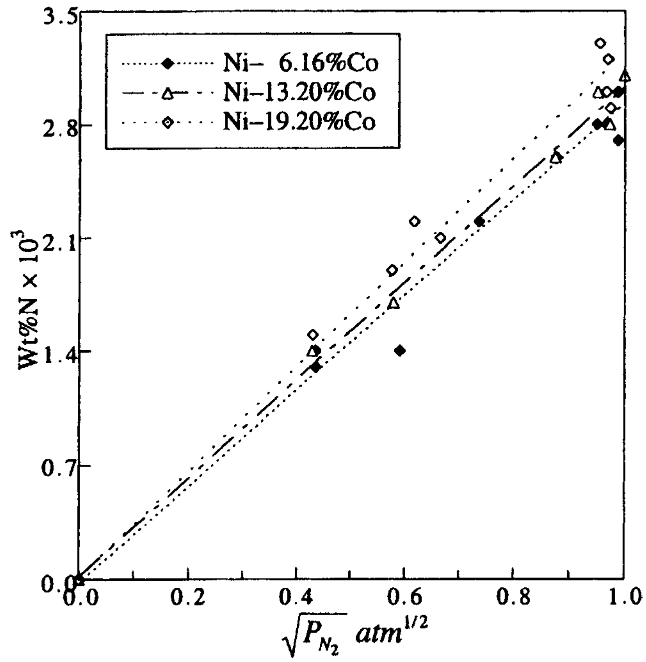

Fig. 1—Effect of pressure on the solubility of nitrogen in Ni-Co alloys at 1600 °C.

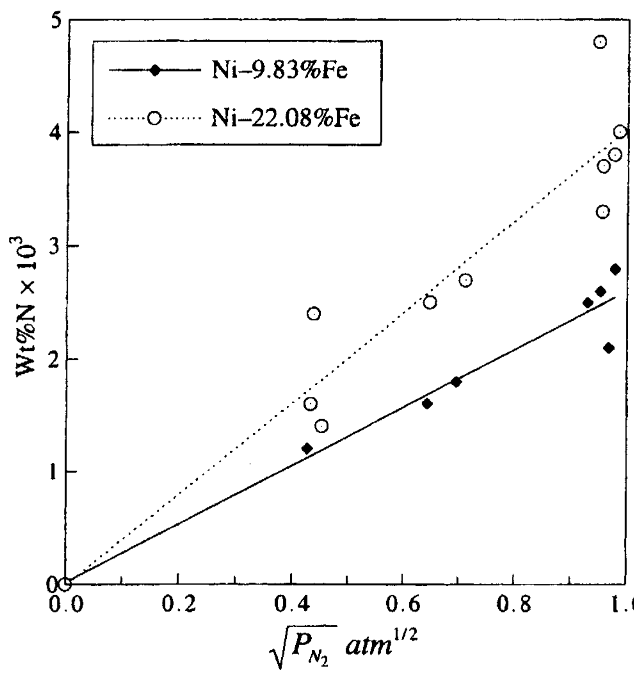

Fig. 2—Effect of pressure on the solubility of nitrogen in Ni-Fe alloys at 1600 °C.

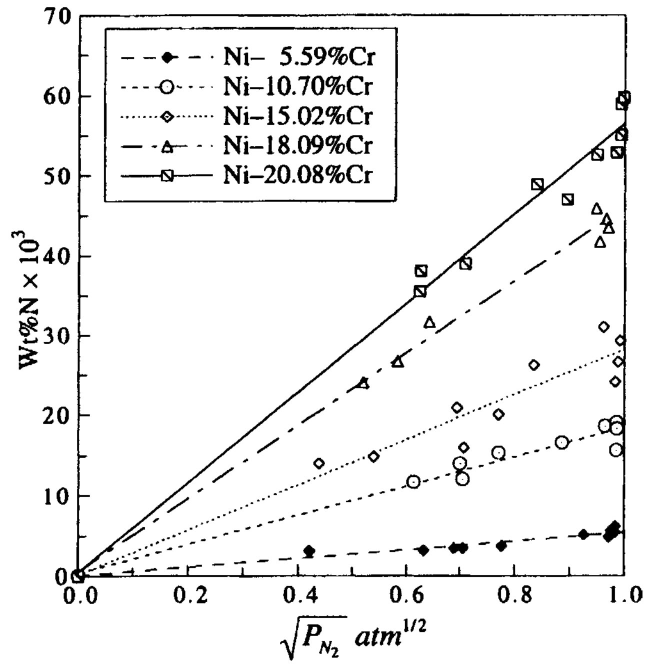

Fig. 3—Effect of pressure on the solubility of nitrogen in Ni-Cr alloys at 1600 °C.

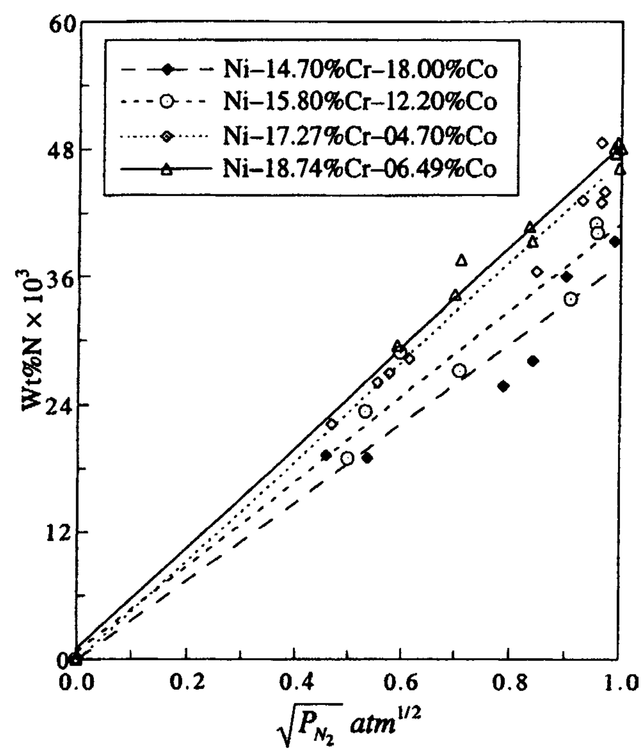

Fig. 4—Effect of pressure on the solubility of nitrogen in Ni-Cr-Co alloys at 1600 °C.

the experimental conditions of pressures up to 1 atm and at 1600 °C.

Fedorchenko *et al.*[1] examined the validity of Sieverts' law at 1600 °C for three concentrations of chromium in nickel: 2.00, 16.80, and 21.80 pct, as shown in Figure 5. In this figure, the curves indicate that the solubility of nitrogen in these alloys obeyed Sieverts' law. Furthermore, these curves indicate that the effect of pressure on the solubility of nitrogen increased with increasing chromium concentration, as is indicated by comparing the slopes of the curves shown in Figure 6. Similar results on the validity of Sieverts' law and on the pressure effect on the solubility were obtained in this study for five concentrations of chromium: 5.59, 10.70, 15.02, 18.95, and 20.08 pct, as illustrated in Figures 3 and 6. In Figure 6, the slope of each curve in Figures 3 and 5 for the present study and that of Fedorchenko *et al.*[1] are plotted against the percentage of chromium. Both studies

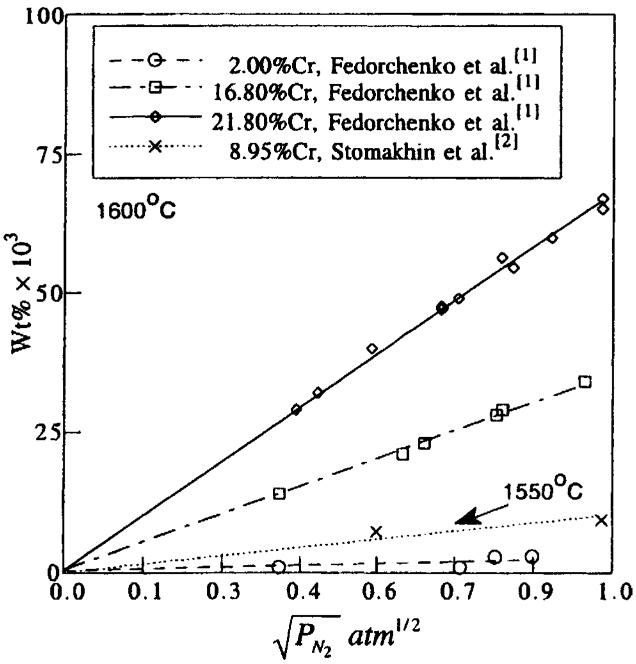

Fig. 5—Vadility of Sieverts' law for nitrogen at 1600 °C in liquid Ni-Cr alloys.

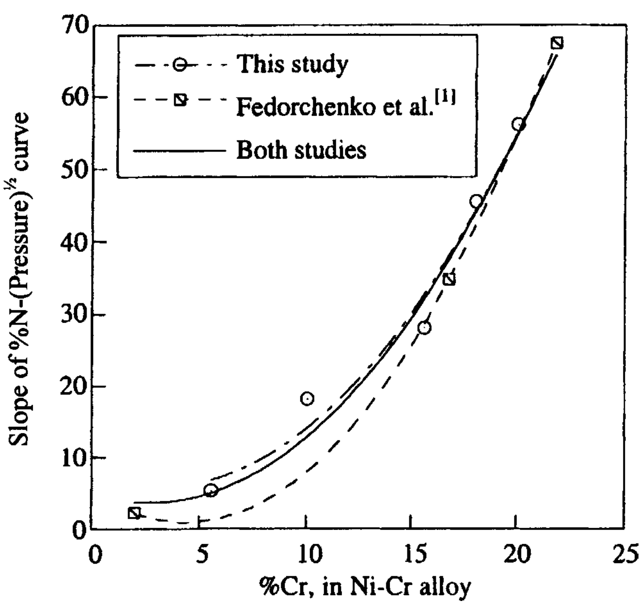

Fig. 6—Slope variation of pct N $-$ $\sqrt{P_N}$ curves plotted in Figs. 4 and 6 for Ni-Cr alloys.

report sharp increases in the pct N $- \sqrt{P_{N_2}}$ slope with increasing chromium concentration. Combining the data of both investigations (plotted as the full line in Figure 6), the effect of pressure on the solubility of nitrogen in Ni-Cr alloys as a function of chromium content can be represented as a best-fit curve by

$$\text{Slope} = 4.074 + (-0.8 \times \text{pct Cr}) + 0.167 \times (\text{pct Cr})^2 \qquad [1]$$

The validity of Sieverts' law at 1550 °C was also considered by Stomakhin *et al.*[2] for a Ni-Cr alloy containing 8.95 pct Cr. The results are shown in Figure 5, which indicate that the solubility of nitrogen in Ni-8.95 pct Cr at 1550 °C obeys Sieverts' law.

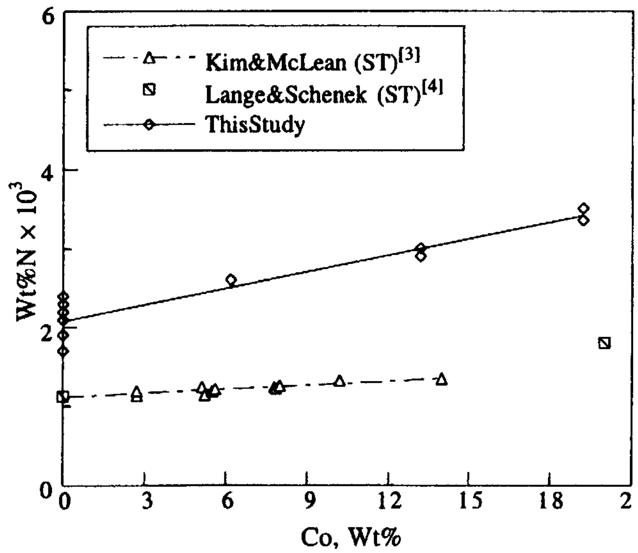

Fig. 7—Solubility of nitrogen in Ni-Co alloys at 1600 °C and 1 atm pressure.

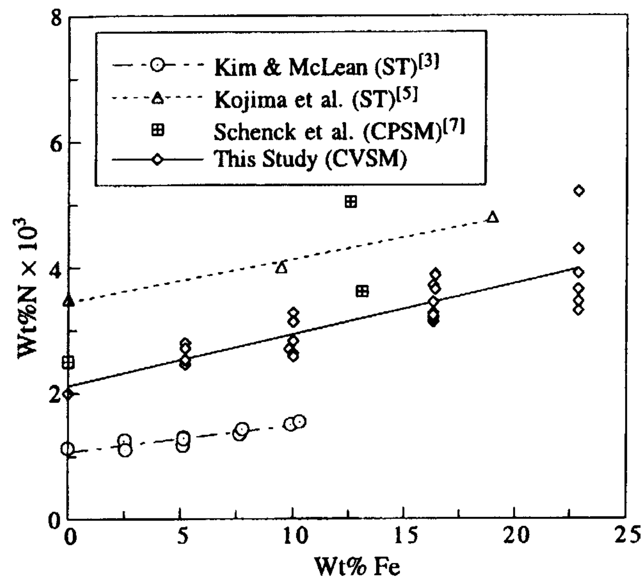

Fig. 8—Solubility of nitrogen in Ni-Fe alloys at 1600 °C and 1 atm pressure.

B. *Effect of Alloying Elements*

1. *Solubility of nitrogen*

Several experiments were made to determine the solubility of nitrogen in binary and ternary nickel-based alloys as a function of the concentration of alloying elements. The experimental data on the solubility are plotted in Figures 7 through 10.

The results for Ni-Co binary alloys are presented in Figure 7 along with the data of Kim and McLean[3] and Lange and Schenck.[4] The results of the present work show an increase in solubility with the addition of cobalt, as indicated by the full line in this figure. In contrast, the results reported by Kim and McLean,[3] who implemented a sampling technique

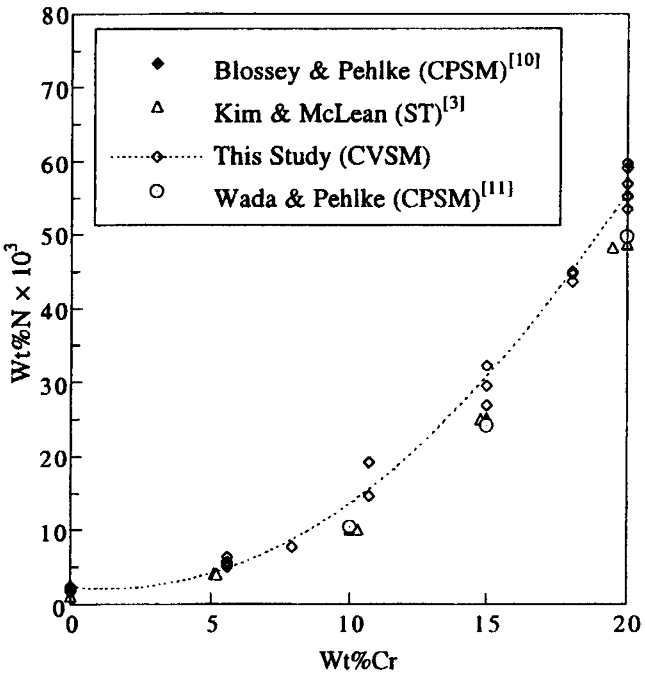

Fig. 9—Solubility of nitrogen in Ni-Cr alloys at 1600 °C and 1 atm pressure.

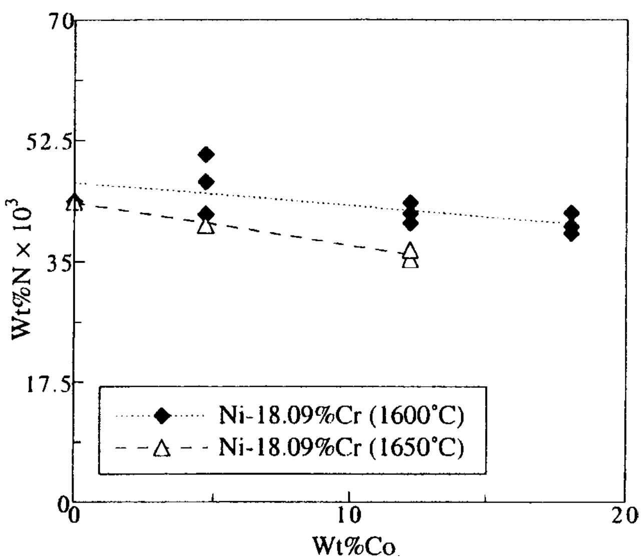

Fig. 10—Solubility of nitrogen in Ni-Cr alloys as a function of cobalt concentration at two temperature levels.

and studied the solubility of nitrogen in nickel-cobalt alloys up to 12.5 pct Co, show less of an increase in the solubility with a cobalt addition, and the solubility values are lower than that of the present work. Lange and Schenck,[4] who also used a sampling technique, reported values of nitrogen solubility in nickel containing up to 20 wt pct cobalt similar to those of Kim and McLean.[3]

The effect of iron content on the solubility of nitrogen in Ni-Fe alloys at 1600 °C is illustrated together with the reported data of four other investigators in Figure 8. From the figure, it is seen that the effect of iron on solubility is stronger than that found in the Ni-Co system, and Ni-Fe alloys dissolve more nitrogen than that dissolved by Ni-Co alloys. This behavior was also noticed by Kim and McLean,[3] but their results are again much lower than that found in this work and, in spite of the similarity in the experimental technique being used by them and Kojima *et al.*,[5] the latter authors reported much higher solubility values, as seen in Figure 8. Schenck and Frohberg[7] also studied the solubility of nitrogen in Fe-Ni alloys using a similar technique to that applied in this study, but a different method (the constant-pressure Sieverts' method (CPSM)) and reported two values of nitrogen solubility in nickel containing around 13 pct Fe. One of these values is in good agreement with those reported by the present study, but the other one is much higher than those reported by both this study and other investigators. This difference could be due to experimental errors, which include pressure monitoring during the course of the experiment. All investigators who implemented the CPSM used mercury manometers to control the pressure within the reaction system and reported an error in pressure readings between 2 and 4 mm Hg,[8,9] which would have a clear effect on the equilibrium solubility. The precision of pressure measurements in the present constant-volume Sieverts' method (CVSM) experiments is superior (±0.0005 atm) and, combined with calibration of the hot volume for each experiment, gives greater precision in the data.

Figure 9 summarizes the effect of chromium additions on the solubility of nitrogen in Ni-Cr alloys at 1600 °C. The results of nitrogen solubility and the technique being implemented to determine it in three other studies by Blossey and Pehlke,[10] Wada and Pehlke,[11] and Kim and McLean[3] are also presented in Figure 9. As shown graphically, chromium additions have a remarkable effect on increasing the nitrogen content in Ni-Cr alloys. The solubility determined by this work is in reasonable agreement with these other studies. The difference between the various techniques of measurement is much less obvious in Ni-Cr alloys, since the solubility levels are much higher than in other binary alloys and errors due to nitrogen loss or inaccurate pressure measurements are less significant. In general, the results indicated that an increase in chromium content up to 10 wt pct has a small effect on nitrogen solubility, but above that level, the effect is increasingly large.

The effect of cobalt concentration on the solubility of nitrogen in a Ni-18.09 pct Cr alloy was examined at two temperatures. The weight percent of cobalt in the alloy is plotted against the equilibrium solubility in Figure 10. The results show that the nitrogen solubility decreased with the addition of cobalt. As is obvious from Figure 9, chromium sharply increased the nitrogen content in nickel and, as the addition of cobalt to the Ni-Cr alloy decreases overall the percentage of chromium, so the solubility in Ni-Cr apparently decreased with the addition of cobalt, as shown in Figure 10. Experiments performed at higher temperatures produced samples with lower nitrogen concentrations, as shown in Figure 10.

The first-order interaction parameter for the effect of an alloying element on the solubility of nitrogen in nickel can be represented by Eq. [2]:

$$e_{N}^{i} = \frac{\partial \log f_{N}}{\partial \text{ pct } i} \qquad [2]$$

The previous equation is valid when the relationship between log f_N and pct i is linear, but when the data deviate from linearity, second-order terms should be included.

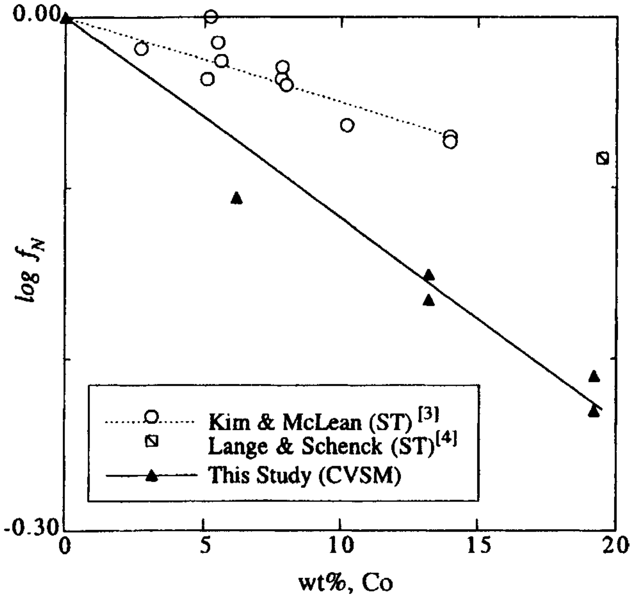

Fig. 11—The influence of cobalt on the logarithm of the activity coefficient of nitrogen in liquid pure nickel at 1600 °C and 1 atm pressure.

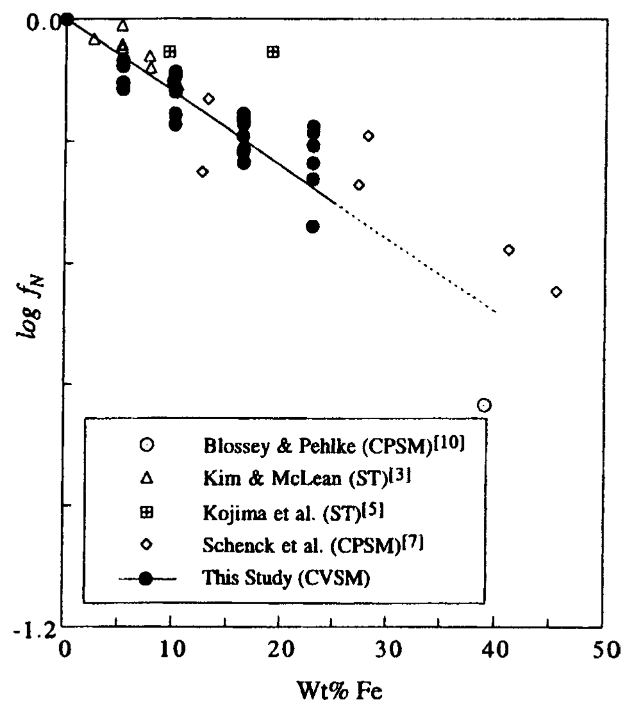

Fig. 12—The influence of iron on the logarithm of the activity coefficient of nitrogen in liquid pure nickel at 1600 °C and 1 atm pressure.

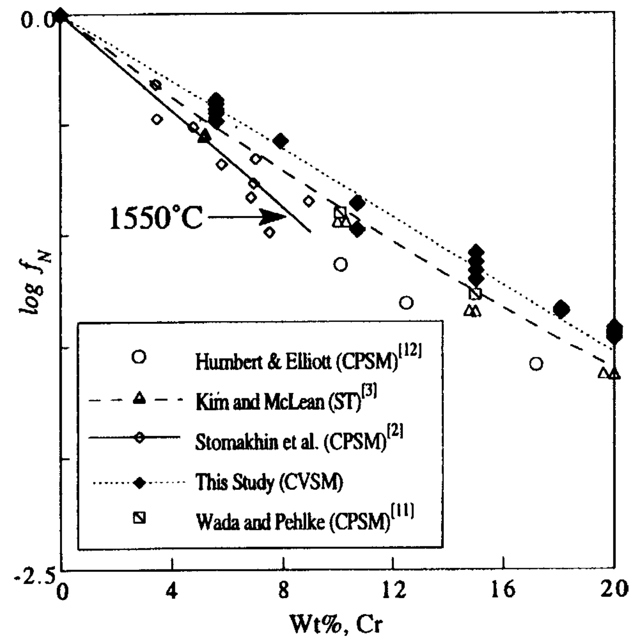

Fig. 13—The influence of chromium on the logarithm of the activity coefficient of nitrogen in liquid pure nickel and 1600 °C at 1 atm pressure.

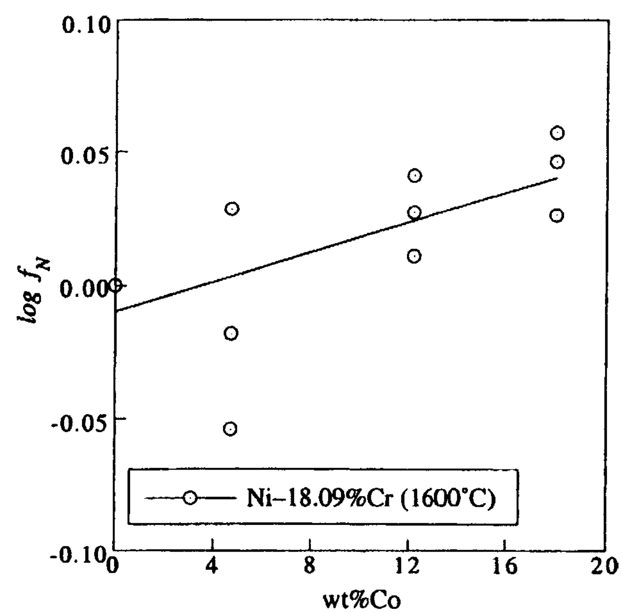

Fig. 14—The influence of cobalt on the logarithm of the activity coefficient of nitrogen in liquid Ni-Cr at 1600 °C and 1 atm pressure.

The common logarithm of activity coefficients for the binary and ternary alloy groups were calculated from Eqs. [3] and [4].

$$\log f_{\mathrm{N}} = \log K^{o} - \log K^{1} \qquad [3]$$

$$\log f_{\mathrm{N}} = \log K^{1} - \log K^{u} \qquad [4]$$

where K^{o}, K^{1}, and K^{u} are the equilibrium constants for the reaction 1/2N ↔ N (dissolved in liquid metal) for liquid pure nickel and binary and ternary alloys, respectively. The values are graphically presented in Figures 11 through 14 against the weight percent of the alloying elements (cobalt, iron, and chromium, respectively), along with the available results from the literature.

For the alloys of Ni-Co, presented in Figure 11, values of the logarithm of the nitrogen activity coefficient decrease with increasing cobalt concentration. The result obtained can be represented by the following relation:

$$\log f_{\mathrm{N}} = -0.0118 \text{ (wt pct Co)} \qquad [5]$$

The results reported by Kim and McLean[3] were shown to follow the relationship

$$\log f_{\mathrm{N}} = -0.005 \text{ (wt pct Co)} \qquad [6]$$

Kim and McLean,[3] as well as the present work, show a linear reduction of the activity coefficient of nitrogen with the addition of cobalt, but the difference is in the value of the interaction parameter (e_N^{Co}), which is represented by the slopes of the lines. In the present work, the value is found to be equal to -0.0118, while that published by Kim and McLean[3] is smaller and equal to -0.005. These investigators[3] show a small effect of cobalt additions on the solubility of nitrogen in liquid nickel, while the present results indicate a stronger effect.

The effect of iron on the activity coefficient of nitrogen for the present work is seen in Figure 12 together with the results of Blossey and Pehlke,[10] Schenck *et al.*,[7] Kojima *et al.*,[5] and Kim and McLean.[3] The results of the present investigation are in very good agreement with other authors. The variation of ($\log f_N$) with wt pct Fe in the present work is indicated by the bold line and extended by the dotted line for comparison. From this figure, ($\log f_N$) decreases with increasing iron content according to the following equation:

$$\log f_N = -0.0144 \text{ (wt pct Fe)} \qquad [7]$$

The results published by Kim and McLean[3] and those of Schenck *et al.*[7] also show a similar trend, and most of their data are located very near the line representing the present work. However, they reported the following relationship:

$$\log f_N = -0.012 \text{ (wt pct Fe)} \qquad [8]$$

Thus, there is little difference between the results of the present work and those of Kim and McLean.[3] In contrast, Blossey and Pehlke[10] and Kojima *et al.*[5] give higher negative and positive effects of iron on the interaction parameter, respectively. From this review, it may be concluded that the results of the present study are well located within the results of the other studies.

For Ni-Cr alloys, the effect of chromium additions on the activity coefficient of nitrogen is illustrated in Figure 13. It was found that the effect is much stronger than that indicated in the previous alloys of Ni-Co and Ni-Fe and yields the following relationship:

$$\log f_N = -0.0766 \text{ (wt pct Cr)} \qquad [9]$$

It appears from this equation that the effect of chromium on the activity coefficient of nitrogen is almost 6 times stronger than cobalt and iron.

The figure also shows the results of Kim and McLean[3] and Wada and Pehlke.[11] The present experimental results on the variation of the activity coefficient with chromium concentration are in reasonable agreement with those of other investigators. Kim & McLean[3] give a value of -0.097 for the interaction coefficient up to 10 wt pct Cr. Above this concentration, the relation becomes curvilinear. The present results show a linear relationship with a slope of -0.0766 up to almost the same chromium concentrations. This value is in reasonable agreement with that found by Kim and McLean and also with Fedorchenko *et al.*,[1] who published a value of -0.098, while Humbert and Elliott[12] show a more negative value of -0.130.

The ternary-alloy results on the variation of the logarithm of the activity coefficient of nitrogen with weight percent cobalt for Ni-18.09 pct Cr-Co at 1600 °C are plotted in Figure 14. The slope of this plot yields the first-order interaction

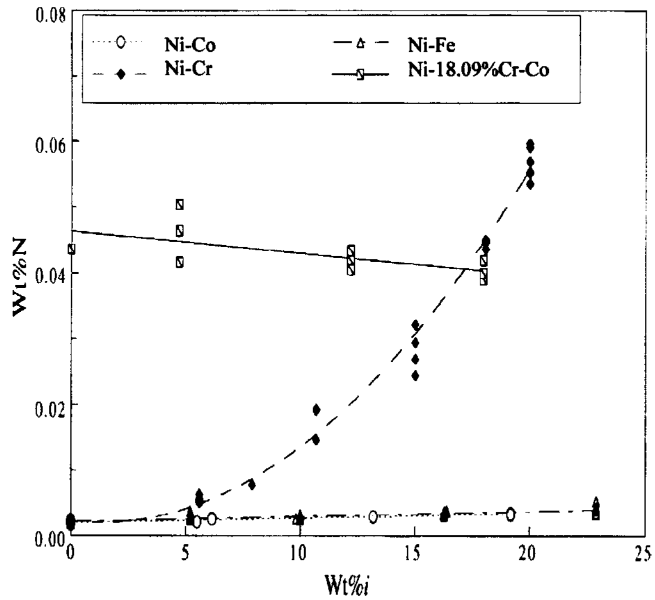

Fig. 15—Summary of the effect of alloying elements on the equilibrium solubility of nitrogen in nickel.

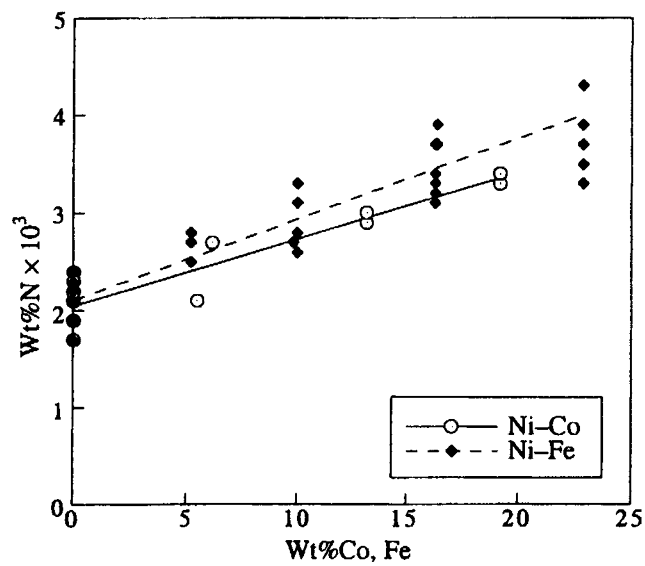

Fig. 16—Magnified scale (Fig. 16) of the effect of cobalt and iron on the solubility of nitrogen in pure nickel.

parameter e_N^{Co}, which is equal to 0.0035. This value suggests that the activity of nitrogen in this alloy increases with increasing cobalt concentration, and so the solubility of nitrogen decreased, as illustrated in Figure 14.

This effect may be further clarified in Figures 15 through 17. The first two figures represent the variation of nitrogen solubility with additions of alloying elements. The results show a sharp increase in solubility with chromium, while cobalt and iron exhibited a small increase. For the latter two elements, a magnified scale is shown in Figure 16, which indicates that there is little difference in effect between the iron and cobalt. Figure 17 presents the variation of the logarithm of the activity coefficient of nitrogen with the concentrations of Cr, Co, and Fe. In the nickel ternary alloy, cobalt behaves in a different way from that seen in Ni-Co binary

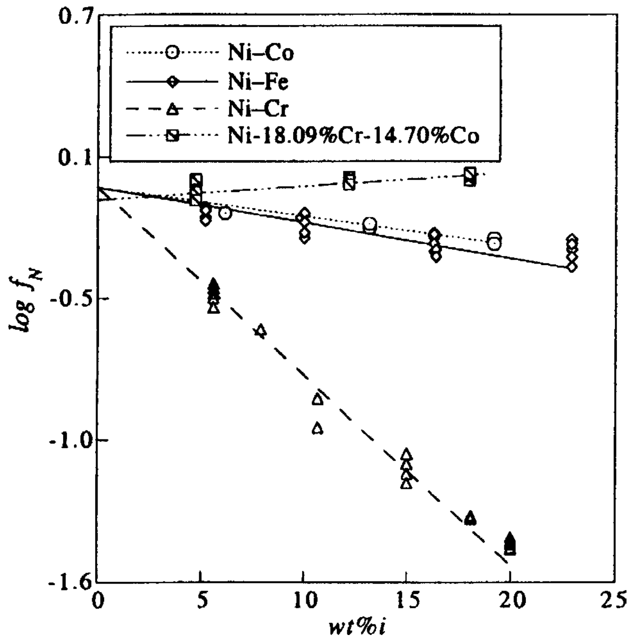

Fig. 17—Review on the influence of alloying element additions on the logarithm of the activity coefficient of nitrogen.

Table I. First-Order Interaction Parameters in Liquid Pure Nickel at 1600 °C

Authors	e_N^i Co	e_N^i Fe	e_N^i Cr	Concentration of Co, Cr, and Fe (Wt Pct)
Blossey and Pehlke[10]	−0.0054	—	—	dilute
Fedorchenko *et al.*[1]	—	—	−0.098	10
Humbert and Elliott[12]	—	−0.015	−0.13	—
Kim and McLean[3]	−0.005			<80
		−0.012		0 to 15
			−0.097	0 to 10
Wada and Pehlke[11]	—	—	−0.101	0 to 20
This study	−0.0118			0 to 20
		−0.0144		0 to 22
			−0.0766	0 to 20

alloys. As is pointed out by this study and the literature, nitrogen dissolves to a greater extent in nickel with the addition of chromium than with cobalt. Therefore, the addition of cobalt to nickel containing a higher percentage of chromium (18 wt pct) reduces the effect of chromium on nitrogen solubility and, consequently, increases the activity. This means that the value of e_N^i is more positive.

The effect of the alloying elements Co, Cr, and Fe on the solubility of nitrogen found by the present study is compared with earlier studies[1,3,10–12] in Table I. In this table, the values of the first-order interaction parameters e_N^{Co}, e_N^{Cr}, and e_N^{Fe} for the binary alloys Ni-Co, Ni-Cr, and Ni-Fe, respectively, are listed. In the case of Ni-Co alloys, the value of e_N^{Co} reported by Blossey and Pehlke[10] and Kim and McLean[3] is −0.005, which is more positive than that found by the present study (−0.0118). Humbert and Elliott[12] and Kim and McLean[3] found values of e_N^{Fe} of −0.015 and −0.012, respectively, and both authors are in good agreement with the value of $e_N^{Fe} = -0.0144$ found by the present work. Ni-Cr alloys were found to dissolve much more nitrogen than the Ni-Co and the Ni-Fe binary alloys, as shown in Figure 15, because Cr interacts much more strongly with nitrogen than iron and cobalt. This is shown by the value of e_N^{Cr} which is equal to −0.0766, as compared with −0.0144 and −0.0118 for Fe and Co, respectively. The data of Fedorchenko *et al.*[1] and Kim and McLean[3] agree quite reasonably with the present investigation, and they reported values of e_N^{Cr} of −0.098 and −0.097, respectively. In contrast, Humbert and Elliott[12] reported a value of −0.13, and Wada and Pehlke[11] reported a value of −0.101. All authors of the earlier studies and the present work agree that the interaction between Cr and nitrogen is stronger than that between nitrogen and iron, which is similar to that of nitrogen with Co. Comparing the effect of these elements on the solubility of nitrogen with their atomic number, plotted in Figure 18, it may be noticed that the lower the atomic number (fewer 3d electrons than nickel) of the element, the greater is the effect on nitrogen solubility.

2. *Solubility dependence of temperature*

In order to determine the effect of melt temperature on the equilibrium solubility of nitrogen in nickel-based alloys, studies were carried out over a range of temperatures from 1550 °C to 1750 °C. The results obtained at 1 atm pressure for the Ni-Co, Ni-Fe, Ni-Cr, and Ni-Cr-Co alloys are plotted in Figures 19 through 22 according to the integrated form of the Van't Hoff relationship:

$$\log \text{pct N} = \frac{-\Delta H_N^\circ}{2.303\ RT} + \frac{\Delta S_N^\circ}{2.303\ R} \qquad [10]$$

According to the previous equation, a plot of log pct N against the reciprocal melt temperature should give a linear relationship, and this is shown in Figure 19 through 22. The solubility dependence on temperature as a function of alloying elements is explained in the following sections.

a. *Ni-Co*

The experimental results for each alloy are shown in Figure 19, in which the data are represented on linear curves which indicate that the solubility of nitrogen increased slightly with increasing temperature, but also that the solubility dependence on temperature for the examined alloys is similar and small.

The standard enthalpy change for the nitrogen solution in each of the studied alloys was calculated by substitution of the slope value for each line in Eq. [10]. The values are listed in Table II. These values are positive, thus indicating that the solution reaction of nitrogen in the alloy system Ni-Co is endothermic. The temperature coefficient in each studied alloy was computed by substituting the value of the standard enthalpy change in Eq. [11]. The coefficients are listed in Table II.

$$\frac{\partial \text{ pct N}}{\partial T} = \frac{\Delta H_N^\circ \times \text{pct N}}{R(T)^2} \qquad [11]$$

b. *Ni-Fe*

In a similar way to that in the previous alloy (Ni-Co), the influence of temperature on the equilibrium solubility of nitrogen was determined for four concentrations of iron: 5.20, 10.0, 16.3, and 22.08 wt pct in nickel. The experimental results are presented in Figure 20. It is clear from this figure

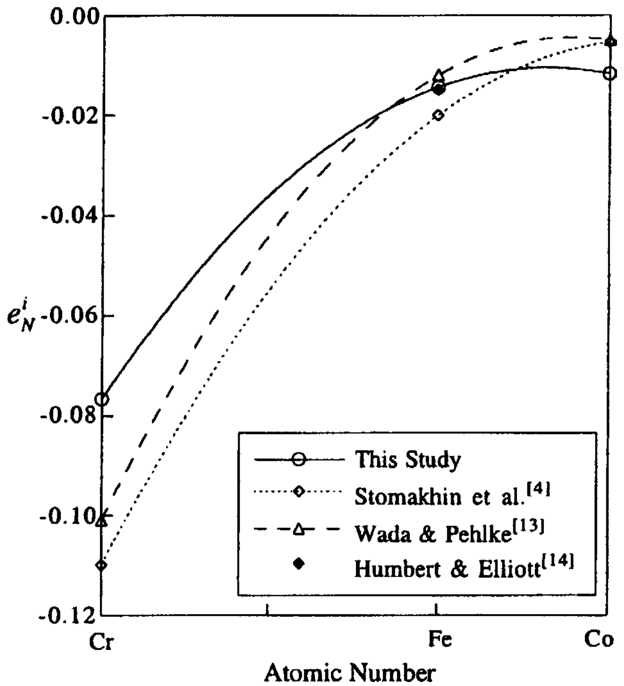

Fig. 18—First-order interaction parameters (e_N^i) as a function of atomic number.

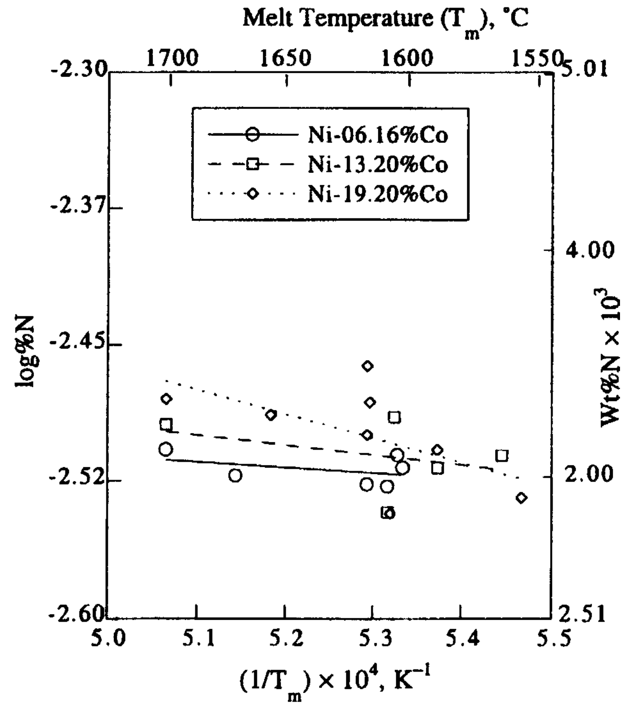

Fig. 19—Temperature dependence of nitrogen solubility in Ni-Co alloys.

Table II. Thermodynamic Data for Nitrogen Solution in Pure Liquid Nickel and Nickel Alloys at 1600 °C

Composition (Wt Pct)				$\left(\frac{\partial \text{ pct N}}{\partial\ °\text{C}}\right) \times 10^6$	Thermodynamic Parameters (kJ/mole)	
Ni	Co	Fe	Cr	(Wt Pct/°C)	ΔG_N^0	ΔH_N^0
100.0	—	—	—	1.64	96.555	17.652
93.84	6.16	—	—	1.05	91.943	8.620
86.80	13.20	—	—	1.43	90.094	18.786
80.08	19.20	—	—	3.70	89.880	25.271
94.80	—	5.20	—	3.29	91.842	25.982
90.00	—	9.83	—	4.22	91.135	31.530
83.70	—	16.30	—	6.75	89.257	43.848
77.92	—	22.08	—	13.0	91.073	89.956
94.41	—	—	5.59	−7.67	80.864	−32.928
89.30	—	—	10.70	−14.28	65.274	−22.217
85.00	—	—	15.02	−22.20	55.145	17.878
81.91	—	—	18.09	−26.4	48.517	−13.003
80.00	—	—	20.08	−10.30	48.580	−5.435
74.85	6.49	—	18.74	−22.8	44.772	−10.782
78.03	4.70	—	17.27	−84.6	46.065	−46.316
72.10	12.20	—	15.80	−48.6	47.442	−28.340
67.30	18.00	—	14.70	4.46	47.513	2.483

that the solubility increases with increasing temperature, and the effect of temperature for the first three alloys is almost the same and is somewhat lower than that in the alloy containing 22.08 wt pct Fe. This behavior is similar to that seen in Figure 19, where the solubility dependence of temperature in Ni-19.20 wt pct Co showed a similar behavior.

According to the Van't Hoff equation, a linear fit for the data of each alloy was taken, and the standard enthalpy change of the nitrogen solution was calculated and is listed in Table II.

c. *Ni-Cr*

In this system, the solubility of nitrogen was also determined as a function of temperature between 1500 °C and 1750 °C. The chromium addition was up to 20 wt pct in five separate alloys 5.59, 10.70, 15.02, 18.09, and 20.08 wt pct Cr). The results are shown in Figure 21. It was found by this study that the solubility decreased with increasing temperature in all Ni-Cr alloys. The calculated values of the temperature coefficients are found to be negative, as shown in Table II. The slope of each curve in Figure 21 was taken,

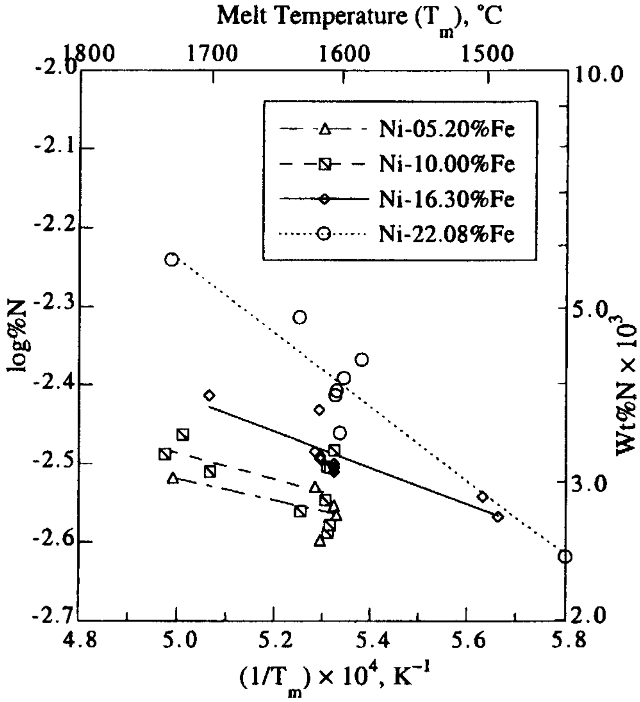

Fig. 20—Temperature dependence of nitrogen solubility in nickel-iron alloys.

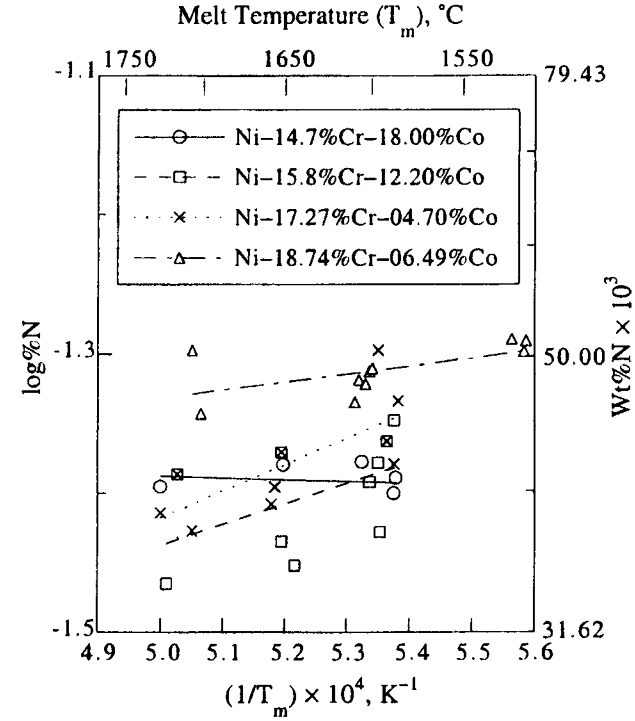

Fig. 22—Temperature dependence of nitrogen solubility in Ni-Cr-Co alloys.

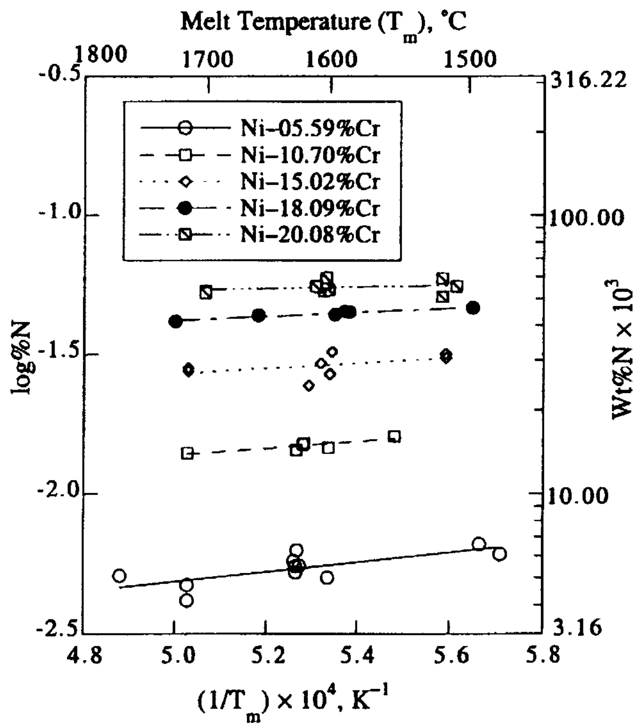

Fig. 21—Temperature dependence of nitrogen solubility in Ni-Cr alloys.

and the standard enthalpies of the nitrogen solution were determined.

d. *Ni-Cr-Co*

This system was evaluated based on four alloys. The alloy compositions are listed in Table II. These alloys were made by adding a known weight of cobalt into the initial two ingots of Ni-Cr having 20.0 and 18.09 wt pct Cr. The data for the solubility of nitrogen in Ni-Cr alloys containing 6.49, 4.70, and 12.2 wt pct of cobalt are presented in Figure 22, which shows a negative temperature dependence of nitrogen solubility. The temperature coefficients are negative and equal to -22.8×10^{-6}, -84.6×10^{-6}, and -48.6×10^{-6} wt pct/°C, respectively. In the case of the fourth alloy, Ni-14.7 wt pct Cr-18.0 wt pct Co, represented by the bold line, the change in solubility with temperature is positive and the temperature coefficient is 4.46×10^{-6} wt pct/°C. These differences can be attributed to the concentration of chromium and cobalt in the alloy. When the chromium content in the first three alloys is higher than that of cobalt, the variation with temperature is negative, while in the fourth alloy, the percentage of chromium is less than cobalt; therefore, the temperature dependence becomes positive. The standard enthalpy changes for nitrogen solution were calculated and are given in Table II. The results show negative values for the first three alloys and positive values for the fourth one.

IV. CONCLUSIONS

1. The solubility of nitrogen in liquid pure nickel was found to increase with individual additions of chromium, iron, and cobalt. Their effect on the activity coefficient of nitrogen was determined and may be summarized by the following equations:

$$\log f_N = -0.0766 \text{ (wt pct Cr)}$$
$$\log f_N = -0.0144 \text{ (wt pct Fe)}$$
$$\log f_N = -0.0118 \text{ (wt pct Co)}$$

2. The validity of Sieverts' law was demonstrated for a nitrogen solution in nickel binary alloys (Ni-Cr, Ni-Fe,

and Ni-Co) and ternary alloys (Ni-Cr-Co) at 1600 °C and 1 atm pressure.

3. The solubility of nitrogen in all binary nickel alloys, except Ni-Cr, shows an endothermic reaction. Therefore, the nitrogen solubility in these alloys increased with increasing melt temperature, while in the case of Ni-Cr alloys, the solubility increased with decreasing melt temperature, as the reaction is exothermic.
4. There is a relation between the atomic number and the interaction parameter e_N^i, for the studied alloying elements.

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