

Nitrogen Solution and Titanium Nitride Precipitation in Liquid Fe-Cr-Ni Alloys

HARUE WADA AND ROBERT D. PEHLKE

The solubility of nitrogen in liquid Fe-Cr, Fe-Ni, Ni-Cr, and Fe-Cr-Ni alloys up to 20 wt pct Ni and 40 wt pct Cr was measured by the Sieverts' method. The first and second order interactions in iron between nitrogen and chromium, and nitrogen and nickel were determined. Chromium increases the nitrogen solubility at lower chromium concentrations but the second order interaction term which is of the opposite sign becomes significant at higher chromium levels and compensates partly for the effect of the first order interaction term. Nickel decreases the nitrogen solubility in iron. Titanium nitride formation in liquid Fe-Cr, Fe-Ni, and Fe-Cr-Ni alloys also was investigated. The first and second order interactions between titanium and chromium or nickel were determined at 1600°C. Chromium increases the solubility product of TiN, principally by decreasing the activity of nitrogen in the melt. Nickel decreases the solubility product of TiN by increasing the activities of nitrogen and titanium.

CONTROLLING nitrogen contents at an optimum level is important for developing desirable properties in alloy steels. An appropriate level of nitrogen often shows a beneficial effect in stabilizing austenite and strengthening these steels. In other instances, nitrogen is regarded as a harmful impurity, so that its content is maintained at a low level or it is stabilized by addition of strong nitride-forming elements such as titanium. In the latter case, precipitation of nitride or carbo-nitride in processing and heat treatment of steel reduces soluble nitrogen in the matrix and removes its adverse effects. Because fine nitride or carbo-nitride precipitates often improve the mechanical properties of steels, intentional additions of nitrogen and a nitride forming element or elements are sometimes employed to obtain these precipitation effects.

A considerable amount of work has been carried out on the solubility of nitrogen in pure iron and dilute iron alloys. The published data on nitrogen solubility in dilute iron alloys have been reviewed by Pehlke and Elliott.¹ Humbert and Elliott² measured the nitrogen solubility in binary and ternary alloys of the entire Fe-Cr-Ni system. Also, the nitrogen solubility in liquid Fe-Ni or Fe-Cr alloys has been measured by Pehlke and Elliott,¹ Saito, *et al.*,³ Schenck, *et al.*,⁴ Blosssey and Pehlke,⁵ Wada, *et al.*,⁶ and Kojima, *et al.*⁷ These studies cover the concentration range from dilute solution to pure Ni or Cr. However, few measurements have been made of nitrogen solubility in multi-component iron alloys with relatively high alloy contents.⁸⁻¹⁰ Gunji, *et al.*¹¹ measured the nitrogen solubility in liquid multicomponent alloys by the quenching method in the composition range up to 25 wt pct Cr and 15 wt pct Ni.

Titanium nitride precipitation in liquid pure iron has been investigated by Evans and Pehlke,¹² and Rao and Parlee.¹³ Frage, *et al.*¹⁴ proposed an equation represent-

ing the solubility product of titanium nitride as a function of titanium concentration. However, direct measurements of the solubility limits for titanium nitride precipitation have not been made in liquid binary or ternary Fe-Ni-Cr alloys.

The object of the present work was to determine the effects of alloying elements and temperature on nitrogen solubility and the solubility product of titanium nitride over a wide concentration range in binary or ternary Fe-Cr-Ni alloys. Experiments were carried out in the temperature range 1450 to 1800°C.

EXPERIMENTAL METHOD

Apparatus

The Sieverts' method was used for measuring nitrogen solubility and nitride formation in this work.^{5,8,9,10,12} The apparatus is shown schematically in Fig. 1.

Materials

The purities and sources of the metallic materials used in this work are summarized in Table I.

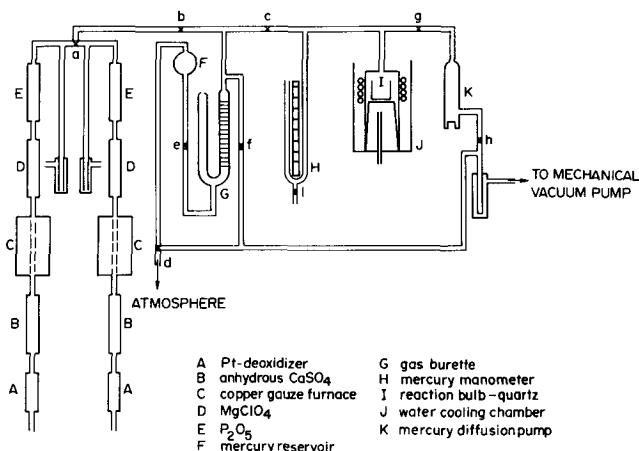


Fig. 1—Schematic diagram of Sieverts' apparatus.

HARUE WADA is Research Associate and ROBERT D. PEHLKE is Professor and Chairman, Department of Materials and Metallurgical Engineering, The University of Michigan, Ann Arbor, MI 48109.

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Table I. Purity of Metallic Materials

Material	Purity, Wt Pct	Source
Ferrovac-E Iron	99.97	Crucible Steel—Syracuse Div.
	0.00015 N ₂	Colt Industries
	0.0012 O ₂	Syracuse, N.Y.
Chromium	99.9	Ventron Co.
	0.003 N ₂	Alfa Products
	0.08 O ₂	Danvers, Mass.
Nickel	99.97	Williams & Co.
Titanium	99.7	Ventron Co.
	max 0.05 N ₂	Alfa Products Danvers, Mass.

High purity argon gas (minimum purity: 99.996 pct) was used for hot volume measurements in the system. A high purity oxygen free nitrogen gas (minimum purity: 99.99 pct, maximum oxygen: 0.5 ppm) was used for the equilibrations. These gases were further purified by passing through a catalytic Pt-deoxidizer, anhydrous CaSO₄, copper gauze furnace heated to 420°C, MgClO₄ and P₂O₅ to remove oxygen and water vapor.

Experimental Procedure

The experimental procedure was essentially the same as that described by Evans and Pehlke.¹⁵ From 50 to 100 g of charge materials, pure iron, pure chromium and pure nickel, were placed in a 32 mm ID high purity recrystallized alumina crucible (Coors, AD998) which was surrounded by a 36 mm ID recrystallized alumina crucible for thermal shielding. The inner and outer crucibles were covered with alumina lids, and an alumina insulating disc was placed between the two crucibles. A pure titanium disc was stored in the arm of the Sieverts' bulb. The hot volume of the system was measured using argon gas for each run. The hot volume ranged from 58 to 61 cm³ at 1600°C and 750 mm Hg argon gas pressure and was found to decrease linearly with decreasing pressure, with increasing temperature and with increasing charge weight. After the hot volume was measured the pure titanium disc was dropped into the melt from its storage place using a magnetic push rod. Titanium additions were very small (maximum addition of 0.238 g) and therefore the effect of titanium additions on the hot volume could be neglected.

The melt temperature was measured with a Leeds and Northrup disappearing filament type optical pyrometer. The pyrometer and sighting system were calibrated against the melting points of pure iron and pure nickel.¹⁶ Emissivity changes with composition were regarded as negligible. Considering measurement error, the effects of slight vaporization, and emissivity changes, it was determined that the accuracy of temperature measurement of the melts was within ± 10°C.

X-ray diffraction analysis was carried out to identify the nitride precipitated during equilibration. The nitride was extracted from the solidified ingot by the ester-halogen technique (Beeghly method),^{17,18} and then X-ray powder diffraction photographs of dried

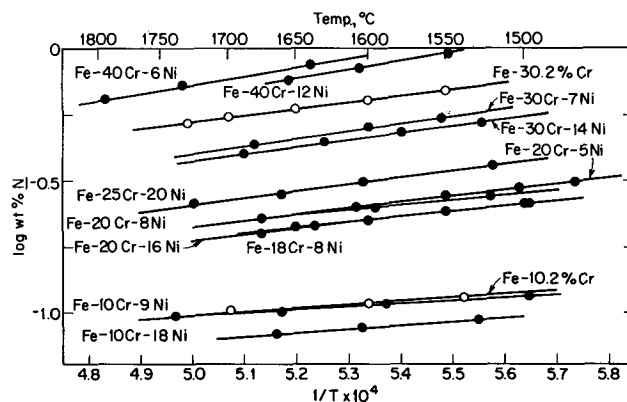


Fig. 2—Nitrogen solubility in Fe-Cr and Fe-Cr-Ni alloys.

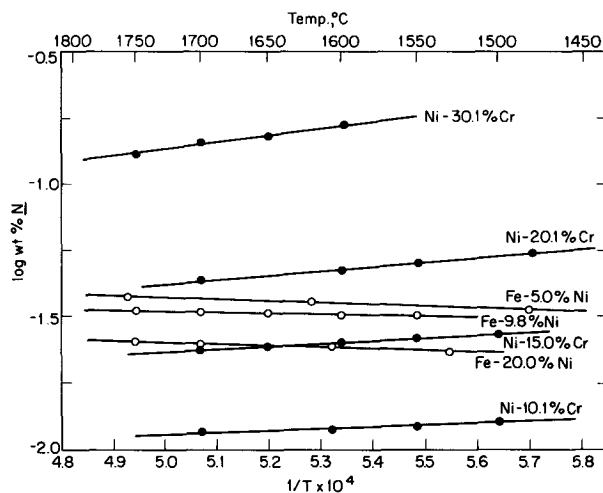


Fig. 3—Nitrogen solubility in Fe-Ni and Cr-Ni alloys.

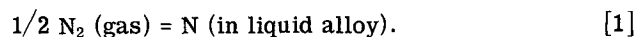
extracted residues were taken using a Guinier-type camera.

EXPERIMENTAL RESULTS AND DISCUSSION

Solubility of Nitrogen

The experimental results of measurements of the nitrogen solubility in Fe-Cr, Fe-Ni, Ni-Cr, and Fe-Cr-Ni alloys under one atmosphere nitrogen pressure are shown in Figs. 2 and 3. The reported solubility includes the initial nitrogen contents of alloying materials as given in Table I. Solid lines representing $\log(\text{wt pct N})$ as a function of inverse temperature were determined by linear regression analysis. No departure from Sieverts' Law was observed in the composition range studied in this work. The Fe-Cr and Fe-Cr-Ni alloys show higher solubilities for nitrogen than Fe-Ni and Ni-Cr alloys. Chromium markedly increases the nitrogen solubility in Fe-Cr, Fe-Cr-Ni and Ni-Cr alloys. Temperature dependence of the nitrogen solubility is negative in Fe-Cr, Ni-Cr and Fe-Cr-Ni alloys and positive in Fe-Ni alloys.

Fe-Cr-Ni Alloys. The solution of nitrogen in liquid iron alloys is generally written as



The free energy of solution of half a mole of nitrogen in the hypothetical 1 wt pct solution of nitrogen in the alloy is

$$\Delta G_N^a = -RT \ln \frac{(\text{wt pct N})_{\text{alloy}}}{\sqrt{P_{N_2}}} = \Delta H_N^a - T\Delta S_N^a \quad [2]$$

where ΔH_N^a and ΔS_N^a are the heat and the entropy of solution, respectively, referred to 1 atmosphere nitrogen pressure and an infinitely dilute hypothetical 1 wt pct N solution in the given alloy. ΔH_N^a can be determined from the temperature coefficient of nitrogen solubility by the equation:

$$\frac{d(\Delta G_N^a/T)}{d(1/T)} = \Delta H_N^a = -R \left[\frac{d(\ln(\text{wt pct N})_{\text{alloy}})}{d(1/T)} \right] P_{N_2} \quad [3]$$

The effects of alloying elements i, j, \dots ($= \text{Cr}, \text{Ni}, \dots$) on the heat and the entropy of solution of nitrogen in alloys are written as¹⁹

$$\begin{aligned} \Delta H_N^a &= \Delta H_N^c + \sum h_N^i (\text{pct } i) + \sum l_N^i (\text{pct } i)^2 + \sum_{i \neq j} l_N^{ij} \\ &\quad \times (\text{pct } i) (\text{pct } j) \\ \Delta S_N^a &= \Delta S_N^c + \sum s_N^i (\text{pct } i) + \sum p_N^i (\text{pct } i)^2 + \sum_{i \neq j} p_N^{ij} \\ &\quad \times (\text{pct } i) (\text{pct } j) \end{aligned} \quad [4]$$

where ΔH_N^c and ΔS_N^c represent the heat and the entropy of solution of nitrogen, respectively, in the hypothetical 1 wt pct N solution in iron, and

$$\begin{aligned} h_N^i &= \partial(\Delta H_N^a - \Delta H_N^c) / \partial(\text{pct } i), \\ l_N^i &= 1/2 [\partial^2(\Delta H_N^a - \Delta H_N^c) / \partial(\text{pct } i)^2], \\ l_N^{ij} &= [\partial^2(\Delta H_N^a - \Delta H_N^c) / \partial(\text{pct } i) \partial(\text{pct } j)], \\ s_N^i &= \partial(\Delta S_N^a - \Delta S_N^c) / \partial(\text{pct } i), \\ p_N^i &= 1/2 [\partial^2(\Delta S_N^a - \Delta S_N^c) / \partial(\text{pct } i)^2], \\ p_N^{ij} &= [\partial^2(\Delta S_N^a - \Delta S_N^c) / \partial(\text{pct } i) \partial(\text{pct } j)]. \end{aligned}$$

The standard free energy change for nitrogen solution in pure iron is

$$\Delta G_N^c = \Delta H_N^c - T\Delta S_N^c \quad [5]$$

The nitrogen solubility obeyed Sieverts' Law in this work; therefore the activity coefficient of nitrogen due to the presence of the alloying elements is

$$\begin{aligned} \log f_N &= \frac{1}{19.155 T} (\Delta G_N^a - \Delta G_N^c) \\ &= \frac{1}{19.155 T} [(\Delta H_N^a - \Delta H_N^c) - T(\Delta S_N^a - \Delta S_N^c)] \\ &= \sum e_N^i (\text{pct } i) + 1/2 \sum e_N^{ii} (\text{pct } i)^2 \\ &\quad + \sum e_N^{ij} (\text{pct } i) (\text{pct } j), \quad (\text{Ref. 20}) \end{aligned} \quad [6]$$

where e_N^i, e_N^j represent the interaction parameters between nitrogen and the alloying elements $i, \text{ or } j$.

From Eqs. [4] and [6], the first and second order interaction parameters are written as a function of temperature:

$$\begin{aligned} e_N^i &= \frac{1}{19.155} (h_N^i/T - s_N^i) \\ e_N^{ii} &= \frac{2}{19.155} (l_N^i/T - p_N^i) \\ e_N^{ij} &= \frac{1}{19.155} (l_N^{ij}/T - p_N^{ij}). \end{aligned} \quad [7]$$

Table II. Experimental Results, Heat and Entropy of Solution of Nitrogen

Wt Pct Fe	Wt Pct Ni	Wt Pct Cr	$-\Delta H_N^a$, J/g-atom N	$-\Delta S_N^a$, J/K, g-atom N
89.8	0	10.2	23,890	31.28
69.8	0	30.2	47,990	29.35
90.2	9.8	0	-6,660	25.08
80.0	20.0	0	-10,970	25.20
81.0	9.0	10.0	21,270	30.02
72.0	8.0	20.0	38,570	32.20
63.0	7.0	30.0	53,960	34.54
54.0	6.0	40.0	60,840	32.99
72.0	18.0	10.0	27,530	34.96
64.0	16.0	20.0	41,590	34.67
56.0	14.0	30.0	51,020	33.66
48.0	12.0	40.0	60,620	33.70
74.0	8.0	18.0	39,230	33.41
75.0	5.0	20.0	46,060	36.01
55.0	20.0	25.0	48,730	35.71
0	89.9	10.1	11,800	43.08
0	85.0	15.0	19,930	41.32
0	79.9	20.1	31,240	42.04
0	69.9	30.1	49,010	41.11

The heat and entropy of solution of nitrogen in liquid Fe-Cr, Fe-Ni and Fe-Cr-Ni alloys were determined using Eqs. [2] and [3] and are summarized in Table II.

The standard free energy of solution of nitrogen in liquid pure iron was computed from experimental measurements by Pehlke and Elliott,¹ Humbert and Elliott,² Turnock and Pehlke⁸ and Gomersall, McLean and Ward²¹ as

$$\Delta G_N^c = (4720 \pm 1050) + (23.40 \pm 0.59) T \quad \text{J/g-atom N.} \quad [8]$$

Then the heat and the entropy of solution of nitrogen in Fe-Cr-Ni alloys summarized in Table II are computed by regression analysis as

$$\begin{aligned} \Delta H_N^a &= 4720 - 3140 (\text{pct Cr}) + 32.11 (\text{pct Cr})^2 \\ &\quad + 160 (\text{pct Ni}) - 35.13 (\text{pct Ni})^2 \\ &\quad + 30.69 (\text{pct Cr}) (\text{pct Ni}) \quad \text{J/g-atom N} \\ \Delta S_N^a &= -23.40 - 0.80 (\text{pct Cr}) + 0.0113 (\text{pct Cr})^2 \\ &\quad - 0.0360 (\text{pct Ni}) - 0.0201 (\text{pct Ni})^2 \\ &\quad + 0.0180 (\text{pct Cr}) (\text{pct Ni}) \quad \text{J/K, g-atom N.} \quad [9] \end{aligned}$$

The excess enthalpy and entropy are determined from Eqs. [4] and [9] as:

$$\begin{aligned} h_N^{\text{Cr}} &= -3140 (\pm 250) \quad \text{J/g-atom N} \\ h_N^{\text{Ni}} &= 160 (\pm 540) \\ l_N^{\text{CrCr}} &= 32.11 (\pm 5.10) \\ l_N^{\text{NiNi}} &= -35.13 (\pm 25.86) \\ l_N^{\text{CrNi}} &= 30.69 (\pm 11.67) \\ s_N^{\text{Cr}} &= -0.80 (\pm 0.59) \quad \text{J/K, g-atom N} \\ s_N^{\text{Ni}} &= -0.0360 (\pm 0.304) \\ p_N^{\text{CrCr}} &= 0.0113 (\pm 0.0028) \end{aligned}$$

$$p_N^{NiNi} = -0.0201 (\pm 0.0142)$$

$$p_N^{CrNi} = 0.0180 (\pm 0.0065).$$

Then the first and second order interaction parameters are determined as

$$e_N^{Cr} = -164/T + 0.0415$$

$$e_N^{Ni} = 8.33/T + 0.0019$$

$$e_N^{CrCr} = 3.35/T - 0.0012$$

$$e_N^{NiNi} = -3.67/T + 0.0021$$

$$e_N^{CrNi} = 1.60/T - 0.0009. \quad [10]$$

Values for the various interaction parameters obtained in the present study are summarized in Table III and compared with the results of previous investigations at 1600°C.

Combining Eqs. [6], [8] and [10], the nitrogen solubility in liquid Fe-Cr-Ni alloys at 1 atm nitrogen pressure is given by the following expression

$$\begin{aligned} \log(\text{wt pct N}) &= \log(\text{wt pct N})_{Fe} - \log f_N \\ &= (-247/T - 1.22) - (-164/T + 0.0415) \\ &\quad \times (\text{pct Cr}) - (8.33/T + 0.0019) (\text{pct Ni}) \\ &\quad - 1/2 (3.35/T - 0.0012) (\text{pct Cr})^2 \\ &\quad - 1/2 (-3.67/T + 0.0021) (\text{pct Ni})^2 \\ &\quad - (1.60/T - 0.0009) (\text{pct Cr}) (\text{pct Ni}). \end{aligned} \quad [11]$$

At 1600°C, the nitrogen solubility is

$$\begin{aligned} \log(\text{wt pct N}) &= -1.352 + 0.046 (\text{pct Cr}) - 0.00032 \\ &\quad \times (\text{pct Cr})^2 - 0.0063 (\text{pct Ni}) \\ &\quad - 0.00007 (\text{pct Ni})^2 + 0.00008 (\text{pct Cr}) \\ &\quad \times (\text{pct Ni}). \end{aligned} \quad [12]$$

The first order interaction term of chromium predicts

an increase in the nitrogen solubility; however, the second order term of opposite sign becomes significant at higher chromium levels. For instance, the second order term reaches about 20 pct of the first order term at 30 pct Cr. Therefore, the second order term should not be neglected in describing nitrogen behavior in high chromium alloys. Nickel decreases the nitrogen solubility, and its effect is much smaller than that of chromium. The effects of nickel are about 7 pct and 16 pct of the effects of chromium in Fe-18 pct Cr-8 pct Ni and Fe-25 pct Cr-20 pct Ni alloys, respectively. The effects of the cross interaction term are 2 pct and 4 pct, respectively, of that of chromium in these alloys.

Chipman and Corrigan¹⁹ proposed the following equation for predicting the nitrogen solubility at any temperature in any liquid iron alloy in terms of the first order interaction parameters at 1600°C:

$$\begin{aligned} \log(\text{wt pct N}) &= -188/T - 1.25 - (3280/T - 0.75) \\ &\quad \times \sum_j e_{N,1600^\circ C}^j (\text{pct } j). \end{aligned} \quad [13]$$

Blossey and Pehlke⁵ proposed an equation for nitrogen solubility near 1600°C in iron alloys containing up to 10 pct Ni and 20 pct Cr of the form:

$$\begin{aligned} \log(\text{wt pct N}) &= -1.348 + 0.0518 (\text{pct Cr}) - 0.000541 \\ &\quad \times (\text{pct Cr})^2 - 0.011 (\text{pct Ni}) \\ &\quad + 0.000252 (\text{pct Cr}) (\text{pct Ni}) \\ &\quad - (350 - 135 (\text{pct Cr}))(1/T - 1/1873). \end{aligned} \quad [14]$$

Figure 4 shows the predicted nitrogen solubility in three base commercial alloys calculated by Eqs. [11], [13] and [14] and the experimental results obtained in this study. $e_{N,1600^\circ C}^{Cr} = -0.045$ and $e_{N,1600^\circ C}^{Ni} = 0.01$ were used for the calculation by Eq. [13]. Eq. [11] represents the experimental results more accurately over the wide temperature range for these base commercial alloys.

Ni-Cr Alloys. Nitrogen solubility in liquid Ni-Cr

Table III. Interaction Parameters for Fe-Cr-Ni Nitrogen Solutions

	Present Study	Pehlke and Elliott ¹	Blossey and Pehlke ⁵	Turnock and Pehlke ⁸	Gunji, <i>et al</i> ¹¹
e_N^{Cr*}	-0.046	-0.045	-0.052	-0.047	-0.041
e_N^{Ni*}	0.0063	0.010	0.011	0.011	0.011
$e_N^{Cr,Cr*}$	0.00063		0.00108	0.00035	0.00003
$e_N^{Ni,Ni*}$	0.00014				
$e_N^{Cr,Ni*}$	-0.00008		-0.00025	-0.00041	0.0002
$h_N^{Cr}(J)$	-3140 ± 250	-2930 ± 210			
$h_N^{Ni}(J)$	160 ± 540	419 ± 167			
$z_N^{Cr}(J)$	32 ± 5				
$z_N^{Ni}(J)$	-35 ± 26				
$z_N^{Cr,Ni}(J)$	31 ± 12				
s_N^{Cr}	-8.0				
s_N^{Ni}	-0.0360				
p_N^{Cr}	0.0113				
p_N^{Ni}	-0.0201				
$p_N^{Cr,Ni}$	0.0180				
$e_N^{Cr*}(\text{in Ni})$	-0.101	-0.13†			
$e_N^{Cr,Cr*}(\text{in Ni})$	0.0021				

*Values at 1600°C.

†Humbert and Elliott².

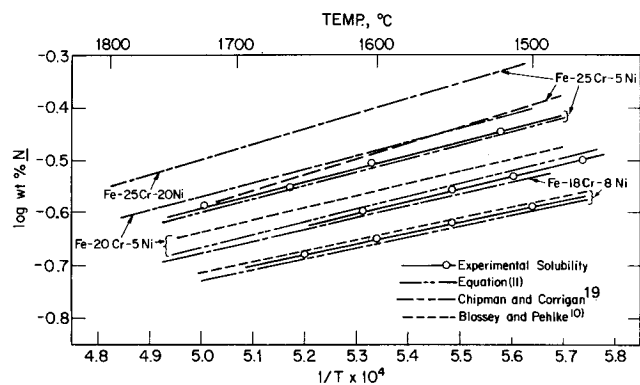


Fig. 4—Predicting nitrogen solubility in commercial base alloys.

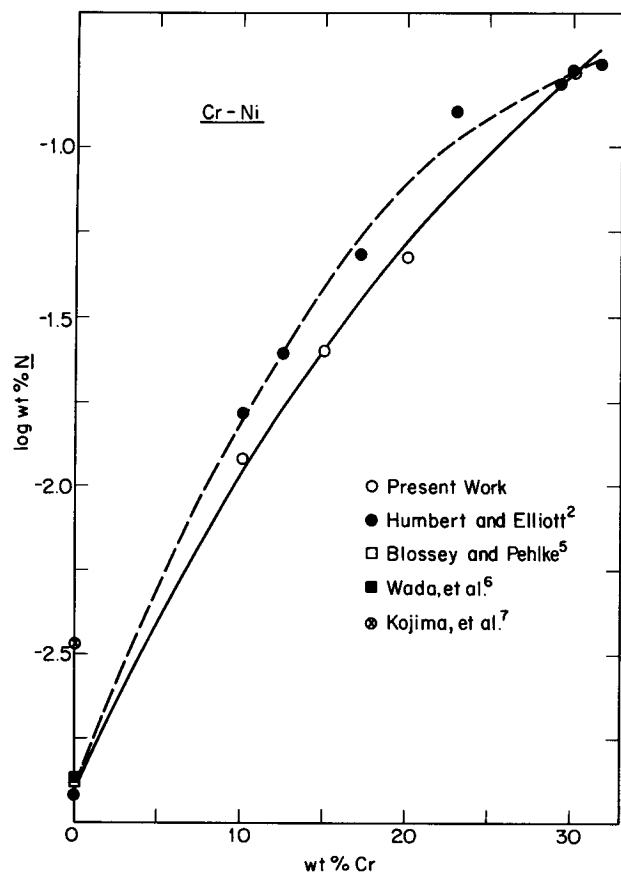


Fig. 5—Nitrogen solubility in Cr-Ni alloys at 1600°C.

alloys at 1600°C is shown in Fig. 5 as a function of chromium concentration and compared with previous results. The heat and entropy of nitrogen solution in Ni-Cr alloys were determined from the solubility lines and are summarized in Table II. The heat of solution of nitrogen in liquid pure nickel was reported as 44,800 J/g-atom N by Blossey and Pehlke,⁵ and 28,050 J/g-atom N by Wada *et al.*⁶ On the other hand, the heat of solution of nitrogen in liquid chromium was reported as -49,820 (Ref. 6), -53,590 (Ref. 3) and -108,860 J/g-atom N (Ref. 2). Therefore, it is reasonable to expect that Ni-Cr alloys will show a negative heat of solution, even at 10 wt pct Cr.

Humbert and Elliott² also reported the heat of solution in Ni-Cr alloys. However, it is difficult to

determine the effect of temperature on the interaction parameters, because of scattering of available data.

The solid line of Fig. 5 represents the present experimental results as

$$\log (\text{wt pct N}) = -2.883 + 0.101 (\text{pct Cr}) - 0.0011 (\text{pct Cr})^2. \quad [15]$$

From Eq. [15], the first and second order interactions between nitrogen and chromium in liquid nickel are determined as e_N^{Cr} (in Ni) = -0.101 and $e_{\text{CrCr}}^{\text{Cr}}$ (in Ni) = 0.0021 at 1600°C. These values are summarized in Table III, and compared with previous result.

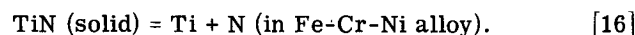
Titanium Nitride Formation

The solubility product of titanium nitride in Fe-Cr, Fe-Ni and Fe-Cr-Ni liquid alloys was measured by the Sieverts' method. Figure 6 shows an example of "the break point"^{15,22} of the solubility curve for a melt containing 30 wt pct Cr and 0.284 wt pct Ti. The wt pct Ti and wt pct N associated with the nitride formation points for each experimental melt are summarized in Table IV.

The lattice spacing determined by X-ray diffraction for titanium nitride extracted from solidified ingots was in good agreement with the ASTM standard pattern for stoichiometric TiN.

In Figs. 7 and 8, the logarithm of the solubility products of TiN are plotted against reciprocal temperature for Fe-Cr, Fe-Ni and Fe-Cr-Ni alloys. Solid lines represent linear regression analyses of $\log ((\text{wt pct Ti})(\text{wt pct N}))$ as a function of $1/T$. Chromium increases the solubility product of TiN while nickel decreases the solubility product.

The precipitation of titanium nitride in liquid iron alloys is controlled by concentrations of nitrogen, titanium and other alloying elements and temperature. The reaction for TiN formation in Fe-Cr-Ni alloys is



The equilibrium constant K for this reaction is expressed as

$$K = a_{\text{N}} a_{\text{Ti}} = f_{\text{N}} (\text{wt pct N}) f_{\text{Ti}} (\text{wt pct Ti}). \quad [17]$$

Because Sieverts' Law holds true in the relation between the nitrogen gas pressure and the solubility of nitrogen, e_N^{N} is zero; therefore,

$$\begin{aligned} \log K = & \log K'_{\text{Fe-Cr-Ni}} + \sum_{i=\text{Cr, Ni, Ti}} e_N^i (\text{pct } i) \\ & + \sum_{i=\text{Cr, Ni, Ti, N}} e_{\text{Ti}}^i (\text{pct } i) + 1/2 \sum_{i=\text{Cr, Ni}} e_{\text{N}}^{ii} (\text{pct } i)^2 + 1/2 \sum_{i=\text{Cr, Ni}} e_{\text{Ti}}^{ii} (\text{pct } i)^2 \\ & + (e_{\text{CrNi}}^{\text{CrNi}} + e_{\text{TiNi}}^{\text{CrNi}}) (\text{pct Cr}) (\text{pct Ni}) \end{aligned} \quad [18]$$

where K' is the solubility product of TiN in an Fe-Cr-Ni melt, and (wt pct N) and (wt pct Ti) are the concentrations of nitrogen and titanium at the break point in an Fe-Cr-Ni melt, respectively. Because the titanium concentration was much lower than that of chromium or nickel in this study, the second order interaction

terms with respect to titanium, e_{N}^{TiTi} (wt pct Ti)² or e_{Ti}^{TiTi} (wt pct Ti)² can be neglected in Eq. [18].

The solubility product of TiN in liquid pure iron can be written as

$$\log K = \log K'_{Fe} + e_{N}^{Ti} (\text{pct Ti})_{Fe} + e_{Ti}^{Ti} (\text{pct Ti})_{Fe} + e_{Ti}^{N} (\text{pct N})_{Fe} \quad [19]$$

where K'_{Fe} is the solubility product of TiN in pure iron and (pct Ti)_{Fe} and (pct N)_{Fe} are the weight percentages of titanium and nitrogen associated with the break points in pure iron. The values of K in Eqs. [18] and [19] are identical at the same temperature.

A value of $\log K_{1600^{\circ}\text{C}} = -2.55$ was obtained by substituting the experimental data of (pct N)_{Fe} and (pct Ti)_{Fe}, $e_{Ti}^{N} = -1.81$ and $e_{N}^{Ti} = -0.53$ obtained by Evans and Pehlke,¹² and $e_{Ni}^{Ti} = 0.053$ determined by Furu-

kawa and Kato,²³ into Eq. [19]. Furukawa and Kato measured the activity of titanium in Fe-Ti alloys by mass-spectrometry and compared the results with previous works²⁴⁻²⁶ at 1600°C. Substituting the values of $\log K$, e_{N}^{Ti} , e_{Ti}^{N} , e_{Ti}^{Ti} and of e_{N}^{Cr} , e_{Ni}^{Ni} , e_{CrCr}^{Cr} , e_{NiNi}^{Ni} and e_{CrNi}^{CrNi} given in Table III into Eq. [18], the following equation can be derived:

Table IV. Summary of Experimental Results on Titanium Nitride Precipitation

Alloy	Wt Pct Cr	Wt Pct Ni	Wt Pct Ti	Wt Pct N at Break	Temperature, °C			
Fe-Cr	10.0		0.115	0.064	1600			
				0.117	1700			
				0.142	0.059	1630		
				0.172	0.046	1600		
				0.304	0.035	1650		
					0.050	1700		
					0.110	1800		
					0.120	1800		
				20.0		0.212	0.030	1550
							0.100	1650
	0.220	1755						
	0.337	0.020	1550					
		0.051	1650					
		0.032	1600					
		0.085	1700					
		0.170	1782					
	30.0		0.144				0.076	1552
							0.144	1612
				0.262	1679			
				0.284	0.077	1650		
				0.158	1700			
Fe-Ni				5.0		0.072	0.0098	1450
							0.0210	1525
							0.0221	1550
							0.0213	1550
							0.0324	1600
	9.8		0.076	0.0175	1565			
				0.0184	1565			
				0.077	0.0155	1525		
					0.0105	1525		
					0.0260	1600		
	15.7		0.071	0.020	1600			
					0.0245	1700		
					0.0253	1700		
				20.0		0.084	0.0105	1600
								0.0245
	0.0253	1700						
Fe-Cr-Ni	18.0	8.0	0.22				0.024	1565
							0.065	1638
				0.025	1578			
				0.090	1685			
				0.25	0.055	1558		
	20.0	5.0		0.144	0.046	1576		
					0.113	1645		
					0.13	0.045	1557	
						0.105	1660	
						0.19	0.040	1600
25.0	20.0		0.13	0.080	1688			
					0.122	1758		

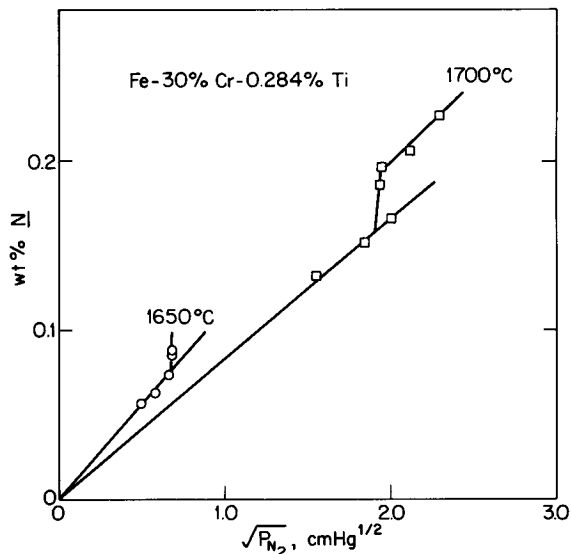


Fig. 6—Nitrogen solubility and TiN precipitation in Fe-30 pct Cr-0.284 pct Ti alloy.

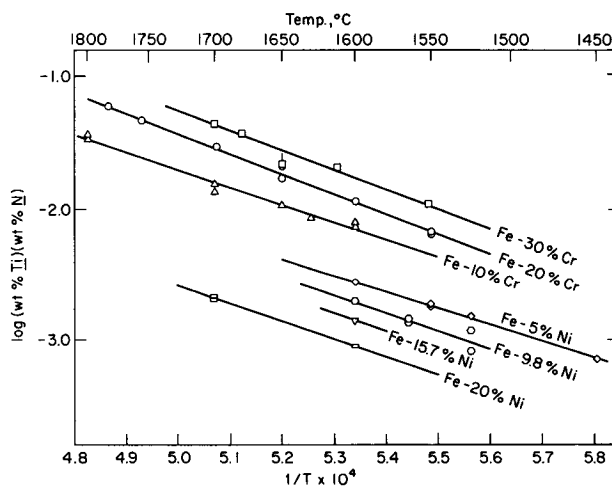


Fig. 7—Solubility product of titanium nitride in Fe-Cr and Fe-Ni alloys.

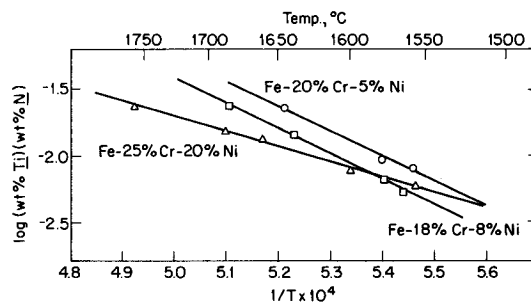


Fig. 8—Solubility product of titanium nitride in Fe-Cr-Ni alloys.

$$\begin{aligned}
& -2.55 - (\log K' + 0.53 (\text{pct Ti}) - 0.053 (\text{pct Ti}) \\
& + 1.81 (\text{pct N})) = (0.046 + e_{\text{Ti}}^{\text{Cr}}) (\text{pct Cr}) + (0.0063 \\
& + e_{\text{Ti}}^{\text{Ni}}) (\text{pct Ni}) + 1/2 (0.00063 + e_{\text{Ti}}^{\text{Cr}}) \\
& \times (\text{pct Cr})^2 + 1/2 (0.00014 + e_{\text{Ti}}^{\text{Ni}}) \\
& \times (\text{pct Ni})^2 + (-0.00008 + e_{\text{Ti}}^{\text{CrNi}}) \\
& \times (\text{pct Cr}) (\text{pct Ni}). \quad [20]
\end{aligned}$$

The third, fourth and fifth terms on the left-hand side of Eq. [20] represent mutual interactions between titanium and nitrogen, titanium and titanium, and nitrogen and titanium, respectively. These three terms were calculated for each alloy from the titanium concentration in the alloy and the nitrogen concentration at the break point.

The left-hand side of Eq. [20] is plotted against concentration of chromium in Fig. 9. The effect of chromium on the activity coefficient of titanium at 1600°C was determined from the regression coefficients determined for Eq. [20] as:

$$e_{\text{Ti}}^{\text{Cr}} = 0.022 \pm 0.003, e_{\text{Ti}}^{\text{CrCr}} = -0.0002 \pm 0.00007.$$

Chromium increases the solubility product of TiN in liquid iron alloys. Comparing the values of the interaction parameters for chromium and nitrogen, and chromium and titanium, it can be concluded that the effect of chromium on the solubility product of TiN is primarily the result of the effect of chromium on the solubility of nitrogen in the melt. On the other hand, the effect of nickel on the solubility product of TiN is of a different nature. In Fig. 10 the same equation is plotted against the concentration of nickel for Fe-Ni alloys. From the regression coefficients of the solid line, the interaction parameters at 1600°C were determined to be:

$$e_{\text{Ti}}^{\text{Ni}} = 0.009 \pm 0.001, e_{\text{Ti}}^{\text{NiNi}} = 0.001 \pm 0.0001.$$

Addition of nickel to liquid iron decreases the solubility product of TiN in the melt. Nickel increases the activity coefficients of both nitrogen and titanium. The values of the first and second order interactions between nickel and nitrogen are comparable with those between nickel and titanium. Therefore, the effect of nickel on the solubility product of TiN is due both to the effect of nickel on the activity of nitrogen and the activity of titanium.

The evaluation of the left-hand side of Eq. [20] at different temperatures is difficult at present because of the lack of data on the temperature dependence of the interaction parameter, $e_{\text{Ti}}^{\text{Ti}}$, and the limited data on the temperature dependence of e_{N}^{Ti} .

Finally, substituting the values of the interaction parameters into Eq. [20], $e_{\text{Ti}}^{\text{CrNi}}$ was determined at 1600°C from the regression coefficient of the equation as: $e_{\text{Ti}}^{\text{CrNi}} = -0.0006 \pm 0.0001$.

SUMMARY

1) The solubility of nitrogen in liquid Fe-Cr, Fe-Ni and Fe-Cr-Ni alloys has been determined as a function of temperature and composition as

$$\begin{aligned}
\log (\text{wt pct N}) = & (-247/T - 1.22) - (-164/T + 0.0415) \\
& \times (\text{pct Cr}) - (8.33/T + 0.0019) (\text{pct Ni}) \\
& - (1.68/T - 0.0006) (\text{pct Cr})^2 \\
& - (-1.83/T + 0.0011) (\text{pct Ni})^2 \\
& - (1.60/T - 0.0009) (\text{pct Cr}) (\text{pct Ni}).
\end{aligned}$$

2) The solubility of nitrogen in liquid Ni-Cr alloys has been determined at 1600°C as a function of composition as

$$\begin{aligned}
\log (\text{wt pct N}) = & -2.883 + 0.101 (\text{pct Cr}) \\
& - 0.0011 (\text{pct Cr})^2.
\end{aligned}$$

3) The first and second order interactions between nitrogen and chromium and nitrogen and nickel were determined as a function of temperature.

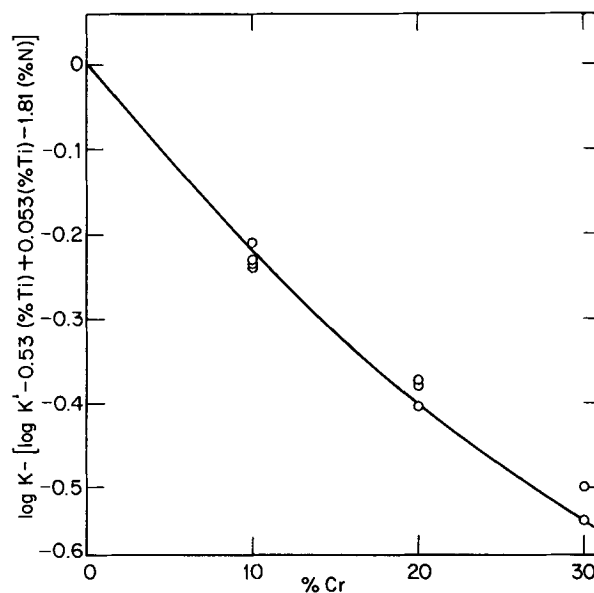


Fig. 9—The effect of Cr on the solubility product of titanium nitride in Fe-Cr alloys at 1600°C.

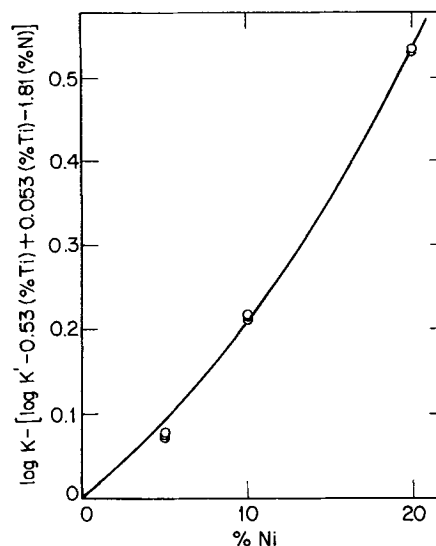


Fig. 10—The effect of Ni on the solubility product of titanium nitride in Fe-Ni alloys at 1600°C.

4) The first and second order interactions between titanium and chromium and titanium and nickel were determined at 1600°C.

5) Nitrogen obeyed Sieverts' Law for all compositions studied.

6) The nitride precipitates were identified as stoichiometric titanium nitride, TiN, by X-ray diffraction analysis.

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