Effects of Alloying Elements on the Activity of Nitrogen in Austenite. II Effect of Nickel and Solubility of Nitrogen in Pure Iron

By

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Solubility of nitrogen in austenite was measured in iron-nickel alloys in order to study the effect of nickel on the activity of nitrogen in austenite and to obtain the value of their interaction parameter. The composition of samples covered the whole range of iron-nickel alloys biginning from pure iron to pure metallic nickel, and the experimental temperatures were 1050° and 1250°C. The presence of nickel increased the activity of nitrogen in austenite and the interaction parameters were obtained as:

$$\varepsilon_N^{(Ni)}=4.1 \text{ at } 1250°C \text{ and } \varepsilon_N^{(Ni)}=4.5 \text{ at } 1050°C.$$

The solubility of nitrogen in pure gamma-iron under the various partial pressures of less than 1 atm of nitrogen was measured at 1150°C and it was shown that Sieverts' law was obeyed on the dissolution of nitrogen in austenite. The free energy of solution of nitrogen in austenite is given as:

$$\Delta G^\circ = -2{,}430 + 9.23T.$$

A close relationship between the interaction parameters and the atomic number of alloying elements was observed and it was also found that the absolute value of the interaction parameters was decreased with the increase in temperature.

The differences of the interchange energies between the pair of iron-nitrogen and that of alloying element-nitrogen were calculated from two theoretical equations, but the results of calculation did not show a good agreement.

1. Introduction

The present investigation was carried out to measure the solubility of nitrogen in iron-nickel alloys and to know the effect of nickel on the activity of nitrogen in austenite. The solubility of nitrogen at various temperatures and under various partial pressures of nitrogen in austenite was measured and was calculated directly from the data on pure iron and indirectly from the extrapolated values obtained from the data on iron-chromium, iron-manganese

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and iron-nickel alloys. It was also one of the objects of this investigation to know the relationship between the interaction parameters at various temperatures and the atomic number of alloying elements.

2. Experimental Procedures

The experimental apparatus and procedures for the measurements of solubility of nitrogen in iron-nickel alloys and in pure iron are the same as described in the previous paper[1]. In the case of the measurements of solubility of nitrogen in pure gamma-iron, the partial pressure of nitrogen was controlled by mixing the argon gas with the nitrogen to keep the desired gas ratio. It could not exceed atmospheric pressure because the gas outlet of the experimental apparatus was opened to the air.

2-1. Chemical analysis

The chemical analysis of nitrogen was performed by the same micro-Kjeldahl method as described in the previous paper[1]. The gravimetric method as nickel-dimethyl glyoxime[2] was applied for the determination of nickel in samples. A volumetric method was used for the analysis of gas mixtures. When a known volume of the gas mixture was passed through a

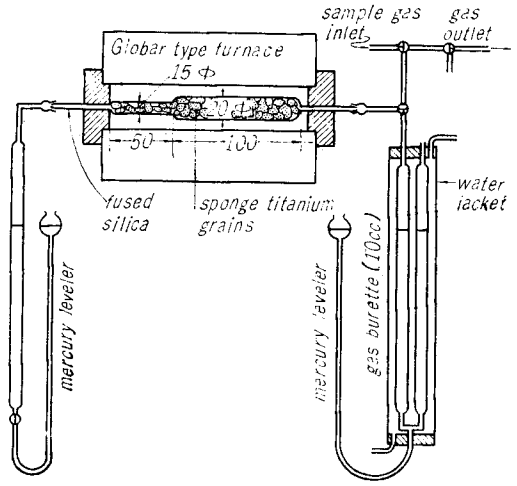

Fig. 1. Titanium furnace for gas analysis.

fused silica tube filled with sponge titanium grains which was kept at about 1000°C, both nitrogen and hydrogen were absorbed quantitatively; thus, the remainder should have been argon. If the content of argon thus determined and that of hydrogen which was analysed by the combustion method[1] are known, the percentage of nitrogen can be calculated as the balance i.e. 100−

($\%H_2+\%A$). The apparatus for gas analysis is shown in Fig. 1.

2-2. Preparation of samples

The processes of vacuum melting and shaping of samples were quite the same as described in the first report[1].

Iron-nickel alloys Iron-nickel alloys containing 5, 10, 15, 25, 50 and 75% Ni were vacuum melted and cast into ingots of about 4.5 kg and were forged and cold-rolled into the form of foils of 0.1 mm thickness. The alloy containing 25% Ni was so hard and brittle that cracks occured during the forging process, therefore this alloy could not be used for the experiments. The samples of pure nickel were prepared by cold-rolling electrolytic nickel plates into thin foils. The chemical composition of the electrolytic nickel used in this experiments is shown in Table 1.

Table 1. Chemical composition of electrolytic nickel. (%)

C	Si	Mn	S	Co	Fe	Al	O
0.02	0.005	0.0005	0.001	1.3	0.007	0.004	0.0014

Pure iron Basic electric furnace pure iron was melted and refined in a vacuum induction furnace and cast into ingots of about 4.5 kg and then the ingots were forged and cold-rolled into thin foils. The chemical composition the pure iron foils is shown in Table 2.

Table 2. Chemical composition of pure iron sample. (%)

C	Si	Mn	P	S	Cu	Ni	Cr	Sol. Al	Insol. Al	Total Al	N	O	H
0.006	0.063	tr.	0.011	0.005	0.002	0.027	0.003	0.003	0.002	0.005	0.0007	0.0058	0.0002

3. Experimental Results

3-1. Iron-nickel-nitrogen alloys

Iron and nickel are perfectly soluble with each other over the whole range of composition in austenite under the present experimental conditions, therefore the solubility measurements were carried out so as to cover the whole range of iron-nickel alloys under the nitrogen pressure of about 1 atm (with 2.5% hydrogen) at 1050° and 1250°C. The results are shown in Fig. 2 and Fig. 3. The results of H. A. Wriedt and O. D. Gonzalez[3] are also shown in Fig. 2 for the sake of comparison. According to these figures the solubility of nitrogen was decreased as the content of nickel was increased, i.e. the activity of nitrogen in austenite was increased by the presence of nickel. The appropriate equations of the second order representing the curves in

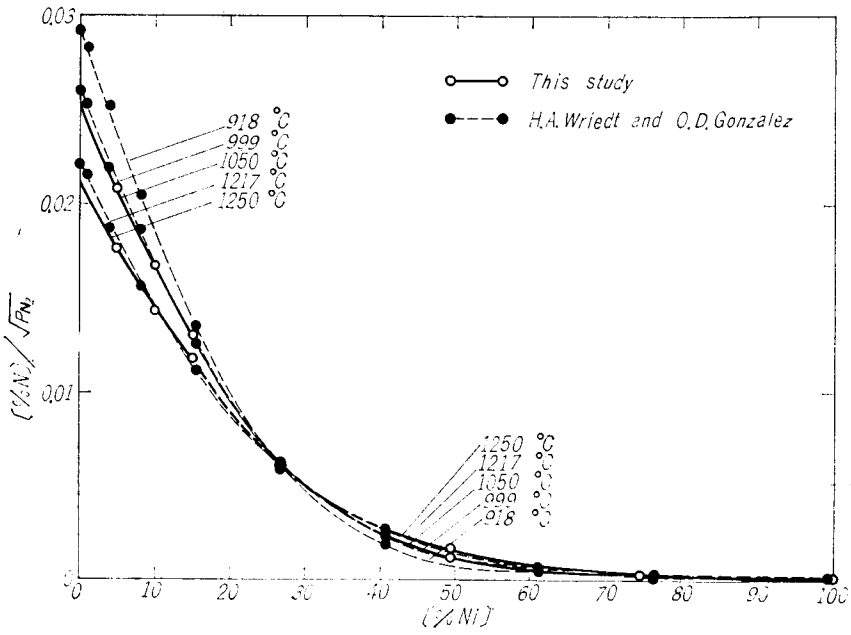

Fig. 2. Relation between nitrogen solubility and nickel content.

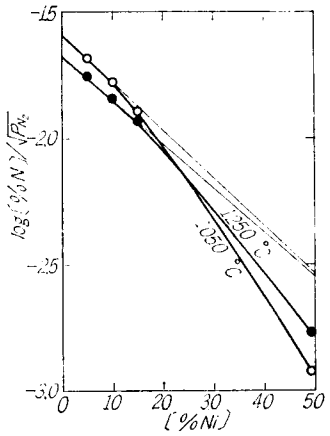

Fig. 3. Relation between the logarithm of nitrogen solubility and nickel content.

Fig. 2 can not be obtained by the method of least squares because these curves must be calculated as equations higher than the third order. The tangent lines drawn through the points at %Ni=0 in Fig. 3 are given as:

$$\log [\%N]/\sqrt{P_{N_2}} = -1.674-0.0169\ [\%Ni] \quad (1250°C) \qquad (1)$$

$$\log [\%N]/\sqrt{P_{N_2}} = -1.590-0.0187\ [\%Ni] \quad (1050°C) \qquad (2)$$

The solubility of nitrogen in austenite is decreased with the increase in temperature, while it is slightly increased in pure nickel with the increase in temperature, and, therefore, the solubility curves at different temperatures should intersect each other in the range between the nickel content of from 15% to 50%. It is clear that the solubility of nitrogen in the alloy represented by the intersection point is not influenced by the change of temperature.

To obtain the change of standard free energy ΔG^0 for reaction:

$$1/2\ N_2\ (\text{gas}) = \underline{N}\ (\text{in Fe-Ni alloy}) \qquad (3)$$

the logarithm of solubility of nitrogen under the pressure of 1 atm of nitrogen in alloys containing up to 50% Ni were plotted against the reciprocal of absolute temperature in Fig. 4. Changes of enthalpy ΔH^0 and of entropy ΔS^0 on the solution of nitrogen in alloys containing various percentages of nickel

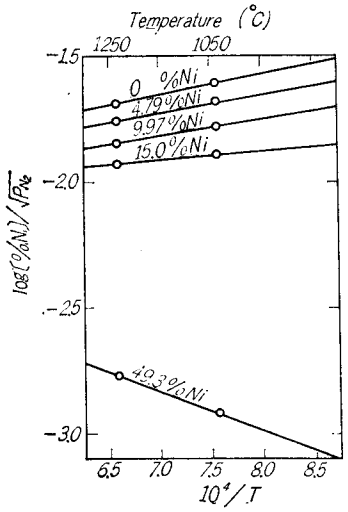

Fig. 4. Relation between logarithm of nitrogen solubility in iron-nickel alloys and reciprocal of temperature.

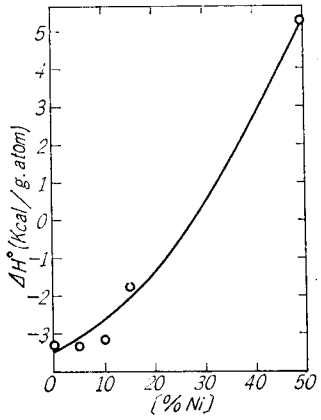

Fig. 5. Effect of nickel on the heat of solution of nitrogen in iron-nickel alloys.

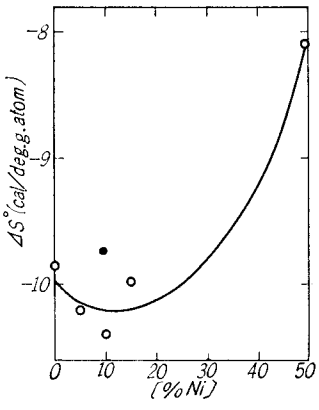

Fig. 6. Effect of nickel on the entropy of solution of nitrogen in iron-nickel alloys.

calculated from Fig. 4 are shown in Figs. 5 and 6 as functions of the concentration of nickel. The best curves representing the plots in Figs. 5 and 6 obtained by the method of least squares are given by:

$$\Delta H^0 = 0.00251\ [\%\text{Ni}]^2 + 0.0528\ [\%\text{Ni}] - 3.48 \qquad (4)$$

$$\Delta S^0 = 0.00154\ [\%\text{Ni}]^2 - 0.0376\ [\%\text{Ni}] - 9.99 \qquad (5)$$

The value $\log [\%\text{N}]/\sqrt{P_{N_2}}$ can be related to ΔH^0 and ΔS^0 as:

$$\log [\%N]/\sqrt{P_{N_2}} = -\Delta H^0/4.575T + \Delta S^0/4.575 \quad (6)$$

thus, the solubility of nitrogen in the alloy is not influenced by the change of temperature, if ΔH^0 is equal to zero. The nickel content of this alloy was calculated to be 28.01% by solving equation (4) at the condition of $\Delta H^0=0$. Substitution of this value for %Ni in equations (5) and (6) made it possible to calculate the solubility of nitrogen to be 0.007% in the case of 1 atm nitrogen pressure. But equation (6) is only applicable in the range of less than about 15% Ni because the calculated value of nitrogen becomes gradually higher than the observed solubulity value if this equation is used for higher nickel ranges.

H. A. Wriedt and O. D. Gonzalez[3] have recently investigated the effect of nickel on the solubility of nitrogen in austenite. The agreement is excellent between these two sets of data as shown in Fig. 2. The intersection point of curves determined by them are 27% Ni and 0.0061% N. This is better than the calculated value by equation (6) because this equation is not applicable in such a high nickel range.

3-2. Iron-nitrogen binary alloys

The solubility of nitrogen in austenite has been measured by many investigators[3)~7)], but their results do not show a good agreement as shown in Fig. 7 because of experimental difficulties. There can be seen a wide

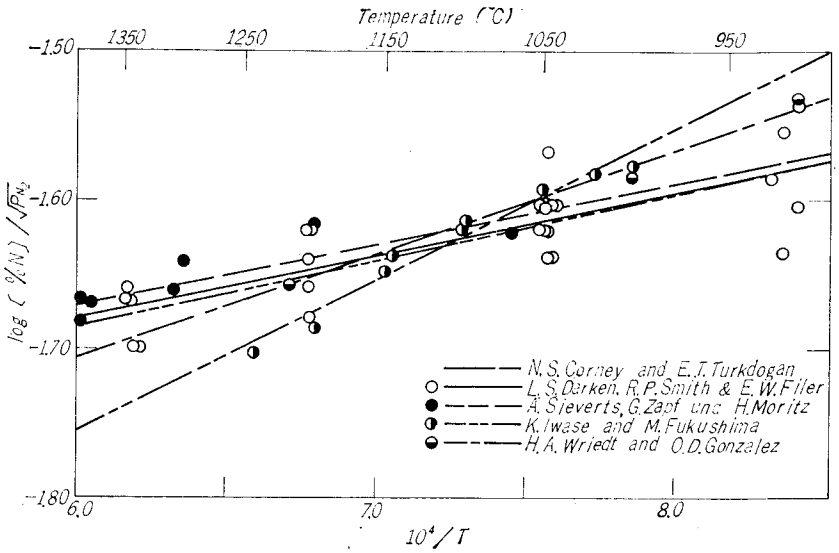

Fig. 7. Relation between logarithm of nitrogen solubility in austenite and reciprocal of temperature.

scatter of data for nitrogen solubility even at one temperature. The authors determined the solubility of nitrogen at 1 atm pressure and at 1050°, 1150° and 1250°C. The experimental results are tabulated in Table 3, and the logarithms of the mean solubility values of nitrogen at 1 atm pressure are plotted as full points against the reciprocal of absolute temperature in Fig. 8. The solubility

Table 3. Solubility of nitrogen in austenite at various temperatures.

No.	Temperature °C	P_{N_2} atm	Holding time hr	[%N]	Selected value of [%N]	$\frac{[\%N]}{\sqrt{P_{N_2}}}$	P_{H_2} atm
2-0-32	1050	0.9900	189	0.0244, 0.0237, 0.0240	0.0240	0.0241	0.0100
1-0-33	1150	0.9897	72 200	0.0221 0.0219, 0.0222, 0.0222	0.0221	0.0222	0.0103
1-0-34	1250	0.9899	94	0.0213, 0.0214, 0.0216 0.0217	0.0215	0.0216	0.0101

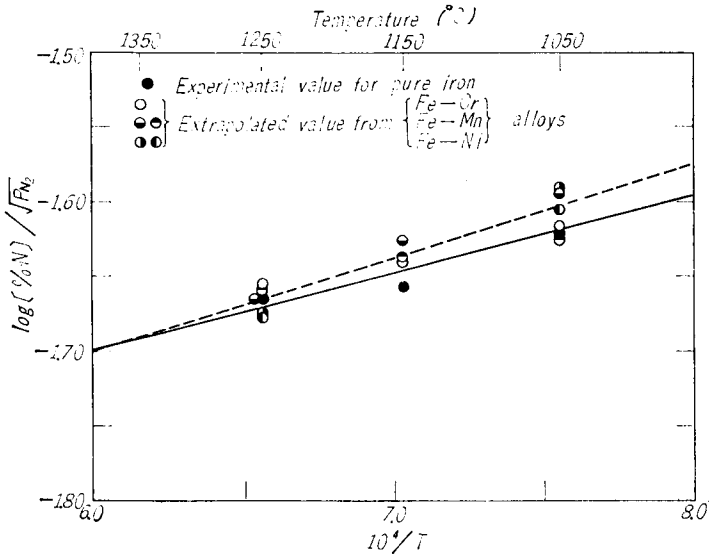

Fig. 8. Present results of nitrogen solubility in austenite.

values obtained by extrapolating the data of iron-chromium, iron-manganese and iron-nickel alloys to zero concentration of alloying elements are also shown in the figure. There are two sets of extrapolated values; the one is the values extrapolated from curves representing the relationship between the solubility of nitrogen versus concentration of alloying elements (shown by the symbols ◓ and ◐), and the other is the values calculated from the relationship between

the logarithms of solubility of nitrogen versus concentration of alloying elements (shown by the symbols ○, ◒ and ◑).

The full line in Fig. 8 was drawn by the method of least squares to represent the binary experimental values and the extrapolated values by the former method, while the broken line was drawn to represent the binary data and that of the latter; and these two lines are written:

$$\log [\%N]/\sqrt{P_{N_2}} = -2.018+532/T \quad (7)$$

$$\log [\%N]/\sqrt{P_{N_2}} = -2.085+638/T \quad (8)$$

where T is the absolute temperature.

The increase in standard free energy of solution of nitrogen in austenite can, therefore, be calculated by equations (7) and (8) as follows:

$$\Delta G^0 = -2{,}430+9.23T \quad (9)$$

$$\Delta G^0 = -2{,}920+9.54T \quad (10)$$

Experimental results of earlier investigators are shown in Fig. 7 in which the lines were drawn by the authors' calculation except for the line of N. S. Corney and E. T. Turkdogan[6]. The present data are shown in Fig. 8 for the sake of comparison and to avoid confusion. These lines can be expressed in the form of free energy equations:

A. Sieverts, G. Zapf and H. Moriz[4]: $\Delta G^0 = -1{,}850+8.76T$ (11)

L. S. Darken, R. P. Smith and C. W. Filer[5]: $\Delta G^0 = -1{,}960+8.87T$ (12)

Table 4. Solubility of nitrogen under various partial pressure of nitrogen gas at 1150°C.

No.	P_{N_2} atm	Holding time hr	[%N]	Selected value of [%N]	$\frac{[\%N]}{\sqrt{P_{N_2}}}$	P_{H_2} atm
1-0-29	0.1830	120 144 168	0.0088 0.0092 0.0086, 0.0084, 0.0090, 0.0091	0.0088	0.0206	0.0117
1-0-28	0.3597	72 144 216	0.0142, 0.0142 0.0125, 0.0113, 0.0133 0.0130, 0.0133	0.0132	0.0220	0.0121
1-0-32	0.6377	72 168	0.0173, 0.0174 0.0172, 0.0175, 0.0178, 0.0176	0.0175	0.0219	0.0118
1-0-33	0.9897	72 120 200	0.0221 0.0208, 0.0204 0.0219, 0.0222, 0.0222	0.0221	0.0222	0.0103

N. S. Corney and E. T. Turkdogan[6]: $\Delta G^0 = -2{,}060+8.944T$ (13)

K. Iwase and M. Fukushima[7]: $\Delta G^0 = -4{,}640+10.81T$ (14)

H. A. Wriedt and O. D. Conzalez[3]: $\Delta G^0 = -3{,}160+9.70T$ (15)

where equation (13) was given by the original authors.

The relationship between partial pressure and solubility of nitrogen was measured at 1150°C, and the results are shown in Table 4 and Fig. 9. It is clear from the figure that solution of nitrogen in austenite obeys Sieverts' law within the experimental range of pressure.

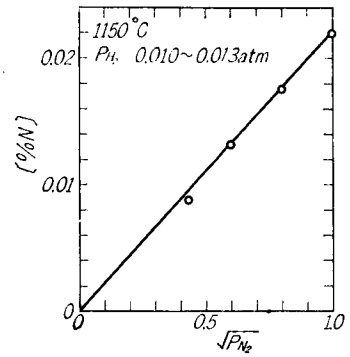

Fig. 9. Relation between nitrogen solubility and partial pressure of nitrogen gas at 1150°C.

4. Discussion

4-1. Effect of hydrogen

About 1% of hydrogen gas was mixed to nitrogen gas in the present study as shown in Table 3 to prevent oxidation of samples, and several percentages of hydrogen were also mixed to nitrogen gases in the preceding experiments of iron-chromium, iron-manganese and iron-nickel alloys.

If the content of hydrogen is increased, the dissolved hydrogen atoms may have some effect on the solubility of nitrogen in austenite because both of these atoms are interstitial solutes. It may be necessary, therefore, to revise the numerical values of equations (9) and (10) after the determination of the interaction parameter $e_N^{(H)}$. Concerning the earlier reports, A. Sieverts, G. Zapf and H. Moriz[4] and K. Iwase and M. Fukushima[7] used the Sieverts' method for the determination of solubility of nitrogen, and, therefore, there was no problem of hydrogen dissolution. But about 1% of hydrogen was mixed to the nitrogen gases in the experiments by L. S. Darken, R. P. Smith and C. W. Filer[5], and also by H. A. Wriedt and O. D. Gonzalez[3]. In the case of experiments by N. S. Corney and E. T. Turkdogan[6] about 5% of hydrogen was mixed to the gases. The plots and lines in Fig. 7 may be more or less influenced by the presence of hydrogen except for the data of Sieverts et al.[4] and Iwase and Fukushima[7], but the effect of hydrogen cannot be detected from these results. Further experiments are, therefore, necessary to confirm the effect of dissolved hydrogen though it may be very little.

The changes in solubility of nitrogen caused by alloying elements may not be seriously affected by the presence of hydrogen because it is thought that

the solubility curves may show some parallel shifts under the constant effect of dissolved hydrogen, and, therefore, the values of interaction parameters may not be influenced by hydrogen.

4-2. Interaction parameters

The interaction parameter which indicates the degree of effect of nickel on the activity of nitrogen can be calculated (i) from equations (1) and (2) i.e. from the tangents shown in Fig. 3, (ii) from the tangents drawn to the curves at %Ni=0 in Fig. 2, (iii) from equations (4), (5) and (6), and (iv) from a statistical thermodynamic relation. Details of the statistical thermodynamic calculation were discussed elsewhere[8]. Only the results of calculations were shown here in Table 5. It is surprizing that some differences caused by the deriving methods are inevitable among the values of the interaction parameters, even where the same experimental data was used for calculation. The recommended values are:

Table 5. Comparison of the interaction parameters of nitrogen by nickel calculated by different methods.

Temperature °C	1050		1250	
Interaction parameter	$e_N^{(Ni)}$	$\varepsilon_N^{(Ni)}$	$e_N^{(Ni)}$	$\varepsilon_N^{(Ni)}$
(i) From eqs. (1) and (2)	0.0187	4.53	0.0169	4.09
(ii) From Fig. 2	0.0142	3.44	0.0138	3.34
(iii) From eqs. (4), (5) and (6)	0.0169	4.09	0.0158	3.83
(iv) From statistical thermodynamic relation	0.0181	4.37	0.0163	3.93

$$e_N^{(Ni)} = 0.017, \quad \varepsilon_N^{(Ni)} = 4.1 \quad \text{at} \quad 1250°C$$

and $$e_N^{(Ni)} = 0.019, \quad \varepsilon_N^{(Ni)} = 4.5 \quad \text{at} \quad 1050°C$$

The reason why the above mentioned values are recommended is that the first method is most frequently used to calculate the value of the interaction parameter.

The values of the interaction parameters $\varepsilon_N^{(Cr)}$, $\varepsilon_N^{(Mn)}$, $\varepsilon_N^{(Ni)}$ and $\varepsilon_N^{(V)}$ can be arranged in order of atomic number as shown in Fig. 10, where the data for $\varepsilon_N^{(V)}$ were calculated from the work of R. W. Fountain and J. Chipman[9].

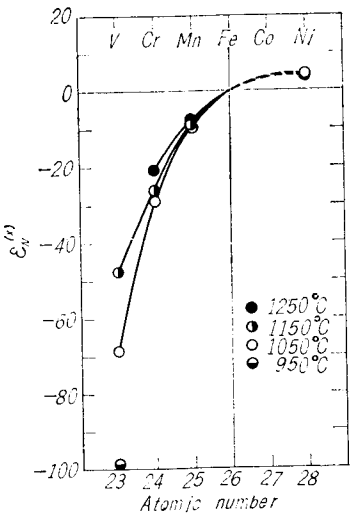

Fig. 10. Relation between interaction parameters and atomic number of alloying elements.

F. Neumann and H. Schenck[10] reported a regular relationship on the interaction parameters of carbon in molten iron alloys and found a periodic relation composed of parallel straight lines, but this straight line relationship could not be observed in the present study. The interaction parameters[11][12] of nitrogen in molten iron alloys are also related to the atomic number of alloying elements in a curved figure similar to the present results.

H. Wada and T. Saito[13] assumed a model of a ternary solution composed of both substitutional and interstitial solute atoms, and by applying Bragg-Williams' approximation, they derived an equation relating the interaction parameter to the interchange energies and temperature. This equation can be written for the iron-nitrogen-X ternary alloy:

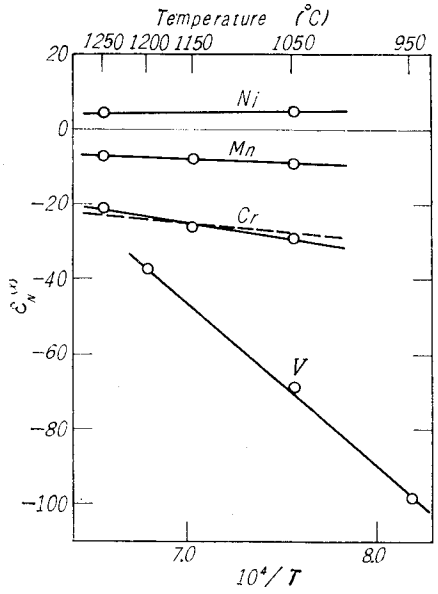

Fig. 11. Relation between interaction parameters and reciprocal of temperature.

$$\varepsilon_N^{(X)} = (\omega_{XN}-\omega_{FeN})/RT \qquad (16)$$

where ω means the interchange energy (cal/mole pair), T is the absolute temperature and R is a gas constant.

This relationship is shown in Fig. 11 where interaction parameters are plotted against the reciprocal of absolute temperature. If the value of $\omega_{XN}-\omega_{FeN}$ is assumed to be independent of temperature, each point should lie on straight lines through the origin (shown by a broken line for chromium), and this consideration is thought to be true concerning chromium, manganese and nickel within the range of experimental errors. The mean values of $\omega_{XN}-\omega_{FeN}$ calculated from equation (16) are respectively:

$$\omega_{CrN}-\omega_{FeN} = -71{,}100$$
$$\omega_{MnN}-\omega_{FeN} = -23{,}600$$
$$\omega_{NiN}-\omega_{FeN} = +12{,}100 \quad \text{(cal/mole pair)}$$

There is another equation of the interaction parameter derived by T. Yagi and Y. Ono[14] in which Guggenheim's quasichemical equilibrium method was used. This equation is given as:

$$\varepsilon_N^{(X)} = z_2\left[1-\exp.\left\{(U_{FeN}-U_{XN})/kT\right\}\right] \qquad (17)$$

or $$\ln (1-\varepsilon_N^{(X)}/z_2) = (U_{FeN}-U_{XN})/kT$$

i.e. $$\log (1-\varepsilon_N^{(X)}/z_2) = (\omega_{FeN}-\omega_{XN})/z_2\ 4.575T \qquad (18)$$

where U is the potential energy of bond per pair, z_2 is the number of interstitial sites for nearest neighbors against mother lattice and is equal to six in a face centered cubic lattice, and k is, Boltzmann constant.

This relationship is shown in Fig. 12 where $\log (1-\varepsilon_N^{(X)}/z_2)$ was plotted against the reciprocal of the absolute temperature. The broken line for vanadium was drawn through the origin. It is found also in this case that experimental points for chromium, manganese and nickel lie on straight lines through the origin. It may well be considered that the potential energy differences are constant for these alloys. The mean values of $\omega_{XN}-\omega_{FeN}$ were calculated from equation (18):

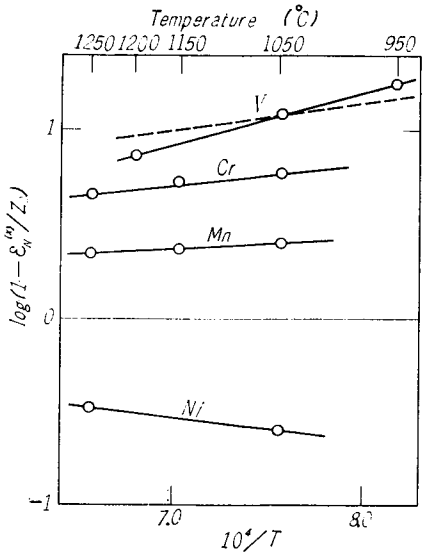

Fig. 12. Relation between functions of interaction parameters and reciprocal of temperature after Guggenheim's quasichemical equilibrium method.

$$\omega_{CrN}-\omega_{FeN} = -27{,}800$$
$$\omega_{MnN}-\omega_{FeN} = -14{,}700$$
$$\omega_{NiN}-\omega_{FeN} = +21{,}100$$

The values of the difference of interchange energies calculated from equation (16) and (18) do not show a good agreement, and this may be due to the methods of approximation used for deriving these equations.

It is evident from Fig. 11 that the absolute value of interaction parameter decreases with the increase in temperature, and it is quite similar to the behavior of activity coefficient in a regular solution.

5. Summary

The solubility of nitrogen in iron-nickel alloys at 1 atm pressure was measured at 1050° and 1250°C. It was found that nickel increases the activity of nitrogen in austenite. The interaction parameters are calculated as:

$$e_N^{(Ni)} = 0.017, \quad \varepsilon_N^{(Ni)'} = 4.1 \quad \text{at} \quad 1250°C$$

and

$$e_N^{(Ni)} = 0.019, \quad \varepsilon_N^{(Ni)} = 4.5 \quad \text{at} \quad 1050°C$$

The relationship between the solubility of nirogen in gamma-iron and temperature was investigated, and the free energy equation for solution of nitrogen was determined as:

$$\Delta G^0 = -2{,}430 + 9.23T$$

It was also confirmed that the solution of nitrogen in austenite obeyed Sieverts' law, if the pressure of nitrogen was lower than one atmosphere.

An intimate relation was observed between the interaction parameters and atomic number, and the tendency was quite similar to that of the interaction parameters of nitrogen in liquid iron alloys.

It is clear that the absolute value of interaction parameters is nearly proportional to the reciprocal of the absolute temperature.

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