

Diffusion in the Fe-Ni System at 1 Atm and 40 Kbar Pressure

J. I. Goldstein, R. E. Hanneman, and R. E. Ogilvie

The interdiffusion coefficients for the Fe-Ni system were determined as a function of composition in both the α and γ phases at 1 atm pressure. The interdiffusion coefficients were also determined in the γ phase at 40 kbar pressure. The concentration gradients were measured with an electron probe, and the diffusion coefficients were calculated by the Matano analysis. At 1 atm, \tilde{D}_γ increases with nickel content up to 65 at. pct Ni. The relationship of D_γ with temperature and nickel concentration, up to 50 at. pct Ni, is given by the equation

$$\tilde{D}_{\gamma-1 \text{ atm}} = \exp(.0519 C_{Ni} + 1.15) \times \exp - \left(\frac{76,400 - 11.6 C_{Ni}}{RT} \right)$$

The activation energy Q at 1 atm decreases from pure iron to 60 to 70 at. pct Ni and decreases from pure nickel to 60 to 70 at. pct Ni. The Kirkendall marker movement indicates that D_{Fe} is greater than D_{Ni} up to about 60 at. pct Ni. Above 60 at. pct Ni, however, D_{Ni} becomes greater than D_{Fe} . The interdiffusion coefficients were also compared with those calculated from self-diffusion data. A comparison between calculated and measured coefficients shows only rough agreement. The effect of 40 kbar pressure is to decrease $\tilde{D}_{\gamma-1 \text{ atm}}$ by an order of magnitude. The activation volumes for high-pressure diffusion are in favorable agreement with theoretical models developed for self-diffusion.

MANY of the transformations that occur in the solid state are diffusion-controlled, especially those involving precipitate growth in most metallurgical systems. Multicomponent diffusion is usually expressed in terms of a chemical or an interdiffusion

coefficient which determines the rate at which material is transferred from the matrix phase to the precipitate and hence determines the growth rate of the precipitate. Since the numerical values of the diffusion coefficients differ widely as a function of the metallic system, temperature, and pressure, the diffusion coefficients must be determined for each particular environmental condition.

J. I. GOLDSTEIN, Student Member AIME, is Physical Metallurgist, Goddard Space Flight Center, Greenbelt, Md. R. E. HANNEMAN, Junior Member AIME, is Physical Metallurgist, General Electric Research Laboratories, Schenectady, N.Y. R. E. OGILVIE is Associate Professor, Massachusetts Institute of Technology, Cambridge, Mass. This paper is based on a thesis submitted by J. I. GOLDSTEIN to the Department of Metallurgy, Massachusetts Institute of Technology, in partial fulfillment of the requirements for the degree of Doctor of Science, 1964.

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Of long-standing interest is the growth of the classic Widmanstätten pattern in metallic (Fe-Ni) meteorites. The growth rate of the pattern is controlled by the diffusion coefficients in the Fe-Ni system. Since these coefficients are essential to calculating the growth rate of the pattern, we found it necessary to determine the diffusion coefficients

as a function of temperature and pressure for this purpose. The interdiffusion coefficients have been measured over a wide range of temperature and composition in both the α and γ phases at 1 atm. The interdiffusion coefficients were also determined over a range of temperature in the γ phase at a pressure of 40 kbar.

THEORY

Darken¹ derived an approximate relationship between the interdiffusion coefficients in a binary system and the intrinsic diffusion coefficients. From a knowledge of the interdiffusion coefficients and the velocity of Kirkendall markers placed in the diffusion zone, the intrinsic diffusion coefficients D_A and D_B can be evaluated.

The Darken equation is given by the expression

$$\tilde{D} = D_A(1 - X_A) + D_B X_A \quad [1]$$

where X_A is the number of moles of component A per unit volume divided by the total number of moles of A and B per unit volume. The velocity v of the bulk flow of atoms is given by

$$v = (D_A - D_B) \frac{dX_A}{dy} \quad [2]$$

From Eqs. [1] and [2] we evaluated D_{Ni} and D_{Fe} for the diffusion couples for which v could be measured accurately. In terms of the self-diffusion coefficients D_A^* and D_B^* in the alloy, Eq. [1] becomes

$$\tilde{D} = (D_A^*(1 - X_A) + D_B^* X_A) \left(\frac{\partial \ln a}{\partial \ln X_A} \right) \quad [3]$$

Both pure iron and pure nickel are fcc between 910° and 1390°C.² They are completely soluble in each other at this temperature range and form a nearly ideal solid solution^{3,4} and therefore the thermodynamic factor is approximately 1. Thus it follows that

$$\tilde{D} \approx (D_A^*(1 - X_A) + D_B^* X_A) \quad [4]$$

The derivation of Eq. [3] is based on two fundamental assumptions: 1) that the vacancy concentration is everywhere at an equilibrium value ($\mu_v = 0$), and 2) that the mobilities of an element are the same in a homogeneous alloy and in a chemical concentration gradient at that composition ($B_i = B_i^*$).⁵ The effect of $\mu_v \neq 0$ has not been measured, although various attempts have been made. In addition, volume changes in the diffusion zone are neglected. Manning⁶ has shown that the difference between B_i and B_i^* is proportional to the net flux of vacancies in a Kirkendall experiment. This leads to an additional positive term in the equation for the velocity of the Kirkendall marker, which is proportional to the vacancy flow and takes the correlation effect into account. The interdiffusion coefficients calculated from Eq. [4] will also be increased by this factor.

Since the vacancy mechanism of diffusion appears to be dominant at high temperatures in most metal-

lic systems, we shall consider it here. The application of pressure in a vacancy-controlled diffusion process lowers the diffusion coefficients, because the equilibrium number of vacancies present is decreased and the energy required for an atom to move from one lattice site to another is increased. The theoretical calculations of the effect of P on diffusion in solids have been presented by Girifalco.⁷

We may consider the pressure effect on diffusion in terms of the "activation volume"

$$v = (\partial \Delta G / \partial P)_T$$

Since a vacancy mechanism involves both the creation of a vacancy and the motion of an atom, the activation volume will be a sum of two terms— ΔV_f , the change in volume of the crystal in the formation of the defect, and ΔV_m , the increase in volume of a crystal attending the elementary diffusion jump under pressure. The expression for D_P in terms of the activation volume is⁷

$$D_P = D_1 \exp(-P \Delta V / RT) \quad [5]$$

or

$$D_P = D_0 \exp(-Q_P / RT) \quad [6]$$

where $Q_P = Q_1 + P \Delta V$. The terms \tilde{D}_P and \tilde{D}_1 are the diffusion coefficients under pressure and under atmospheric conditions, and $\Delta V = \Delta V_f + \Delta V_m$.

Several measurements of ΔV have been made at low pressures in self-diffusion experiments. The results are summarized in Table I. A recent measurement by Hanneman¹¹ of ΔV for interdiffusion in Fe-V at high pressures (20, 40 kbar) yields a value of $\Delta V / V^M = 0.75$.

The dependence of ΔV on pressure and temperature has been calculated by Girifalco.¹² Since the effect is less than 10 pct, it cannot be measured in this study.

EXPERIMENTAL PROCEDURE

Alloys with varying amounts of nickel were obtained through the courtesy of the International Nickel Co. These alloys, in addition to two supplied by the MIT Diffusion Laboratory, were used for the determination of the Fe-Ni calibration curve used in the electron microanalysis of the diffusion couples. The chemical analyses of the iron, nickel, and Fe-Ni alloys are given in Table II. Alloys 5 and 7 were used to make the majority of the incremental diffusion couples.

In order to anneal out any local inhomogeneities and to produce an average grain size of 1 mm, the

Table I. Measurements of ΔV

Experiment	$\Delta V / V^M$	References
Self-diffusion in silver	0.9	Tomizuka <i>et al.</i> ⁸
Self-diffusion in lead	0.71	Nachtrieb <i>et al.</i> ⁹
Ag diffusion in Ag-/ 27.7 at. pct Zn	0.89	Tichelaar and Lazarus ¹⁰

Table II. Chemical Analysis of Fe-Ni Alloys, wt pct

Alloy	Pct Ni	Fe, ppm	Pct C	Pct Mn	Pct P	Pct S	Pct O	N, ppm	H, ppm
Fe	<0.004	—	0.007	<0.002	—	—	0.020	10	<0.5
Ni	—	5	0.001	—	—	—	0.006	3	5
1	5.17 ± 0.02	—	—	—	—	—	—	—	—
2	10.34 ± 0.02	—	—	—	—	—	—	—	—
3	15.17 ± 0.03	—	—	—	—	—	—	—	—
4	19.40 ± 0.07	—	—	—	—	—	—	—	—
5	25.18 ± 0.05	—	0.006	<0.003	0.002	0.003	0.020	4.0	0.8
6	35.32 ± 0.10	—	—	—	—	—	—	—	—
7	50.19 ± 0.30	—	0.006	<0.003	0.002	0.002	0.045	6.0	<0.5
DL-1	75.75	—	0.002	—	—	—	—	—	—
DL-2	90.47	—	0.002	—	—	—	—	—	—

alloys were vacuum-annealed at 1300°C for 1 day. This treatment helped to eliminate any grain boundary effects that might occur during diffusion.

To make the diffusion couples, wafers were cut from the selected alloys, polished through 0.25- μ diamond using standard metallographic techniques, and sandwiched together by a compression picture-frame technique. Before bonding, 0.001-in.-diam tungsten wires were inserted at the interface for subsequent use as Kirkendall markers. The bonding was carried out under a dynamic vacuum of 10^{-5} mm of Hg at 800°C for 1 hr.

The schedule of diffusion treatments at 1 atm is given in Table III. Temperature-controlled tube furnaces were used for the low-temperature, long-time diffusion runs, and a high-temperature vacuum furnace¹³ was used for all the high-temperature diffusion couples. The fluctuations in temperature in each furnace were within 2°C.

One type of apparatus used for the high-pressure runs was a tetrahedral press located at the MIT Lincoln Laboratories. The Fe-Ni diffusion couple was held in a BN liner within the lava specimen cylinder. The diffusion couple was heated by an internal graphite heater, which used a high-current, low-voltage supply. An inconel-sheathed, Pt-Pt 13 pct Rh thermocouple was used for temperature measurement. Pressure control was of the order of ± 1 kbar at 40 kbar. Temperatures were held to better than $\pm 2^\circ\text{C}$ by means of a Minneapolis-Honeywell controller.

Table III. Time and Temperature of Diffusion Anneals for Various Alloy Compositions

Sample No.	Composition Range, at. pct Ni				Time, sec	Temperature, °C
1	0 to 100,	0 to 25,	25 to 50,	50 to 100	4.27×10^4	1288
2	0 to 100,	0 to 25,	25 to 50,	50 to 100	8.49×10^4	1205
3	0 to 100,	0 to 25,	25 to 50,	50 to 100	1.72×10^5	1099
4	0 to 100,	0 to 25,	25 to 50,	50 to 100	7.68×10^5	1000
5	0 to 25	25 to 50			2.68×10^6	800
6	0 to 15				4.85×10^6	700

The second type of high-pressure equipment used was the "belt" apparatus. Runs were made on two different units, one at Lincoln Laboratories and one at the General Electric Research Laboratories. In both pieces of equipment the pressure was held to ± 0.5 kbar at 40 kbar.

In the belt apparatus at Lincoln Laboratories the Fe-Ni diffusion couple was held in a BN liner within the lava specimen cylinder and a Pt-Pt 10 pct Rh thermocouple was spot-welded at the diffusion couple interface. In the GE specimen cell the diffusion couple was surrounded by NaCl that became molten at diffusion pressures and temperatures. Two thermocouples were used to monitor the temperature; one of chromel-alumel was spot-welded to one end, and the other of Pt-Pt 10 pct Rh was spot-welded to the other end of the diffusion couple. The temperature gradients determined between the ends of the couples in the General Electric apparatus were less than 5°C, or less than 0.1°C across the diffusion zone.

The effect of pressure on the electromotive-force of thermocouples has been measured by Bundy¹⁴ and by Hanneman and Strong.¹⁵ The former investigation was limited to 0° to 100°C, while the latter study was completed for temperatures up to 1300°C and pressures up to 50 kbar. Over the temperature and pressure ranges of common measurement (0° to 100°C and 0 to 50 kbar) the two studies are in excellent agreement. At 40 kbar the absolute correction in temperature readings is $\sim +8^\circ\text{C}$ at 1000° to 1300°C for chromel-alumel. The correction for Pt-Pt 10 pct Rh at 40 kbar varies almost linearly from $+34^\circ\text{C}$ at 1000°C to $+42^\circ\text{C}$ at 1300°C. Corrections for Pt-Pt 13 pct Rh at 40 kbar were found to be $+37^\circ$ to $+45^\circ\text{C}$ over the range 1000° to 1300°C. These temperature corrections were applied to all of the high-pressure diffusion runs reported in this paper.

The Fe-Ni high-pressure couples run in this study are listed in Table IV.

An Applied Research Laboratories electron microanalyzer was used to measure the iron and nickel concentrations across the diffusion couples. All data were taken at 30 kv with a specimen cur-

Table IV. Time and Temperature of Diffusion Anneals at 40 Kbar (Fe-Ni Couples)

Number	Apparatus	Thermocouple	T corrected, °C	t , sec
LL #1	Belt	Pt-Pt, 10 pct Rh	1284	0.567×10^5
LL #2	Belt	Pt-Pt, 10 pct Rh	1182	0.618×10^5
LL #3	Tetrahedral	Pt-Pt, 13 pct Rh	1346	0.238×10^5
GE #1	Belt	Cr-Al, Pt-Pt, 10 pct Rh	1304	0.72×10^4
GE #2	Belt	Cr-Al, Pt-Pt, 10 pct Rh	1154	0.288×10^5
GE #3	Belt	Cr-Al, Pt-Pt, 10 pct Rh	1233	0.144×10^5

rent between 0.035 and 0.05 μ a. To convert the iron and nickel intensity data to composition, a calibration curve was determined with the nine Fe-Ni alloys. The calibration curve is shown in Fig. 1, along with the calculated correction curves of Castaing¹⁶ and Wittry.¹⁷

The calculation of composition from measured X-ray data has been greatly simplified by use of the algebraic function A_{AB} developed by Ziebold.¹⁸ This function fits the entire experimental calibration curve by means of a single conversion parameter. The X-ray intensity from iron and nickel was converted to composition by means of this function. The whole conversion process was programmed and run on the IBM-7094 computer. For the Fe-Ni system at 30 kv, for iron and nickel concentrations calculated in atomic percent, and for a take-off angle $\theta = 52.5$ deg, $A_{AB} = 0.847$ for the iron, and $A_{BA} = 1.158$ for the nickel intensities.

Quantitative scans using fixed-time counting were taken in three different places across each couple perpendicular to the interface. At least thirty points were taken along the gradient in each scan. The alloys on each end of the couples were used as standards.

EXPERIMENTAL RESULTS

The interdiffusion coefficients were determined from curves of composition vs distance by means of the Matano analysis. Fig. 2 shows an example of the electron-probe data. The values of composition determined in the three individual scans superimpose within the accuracy of measurement (± 2 rel. pct or better).

Fig. 3 shows the values of D vs composition at four different temperatures (1288°, 1205°, 1099°, 1000°C) in the γ phase. A logarithmic dependence of \tilde{D}_γ on composition was found between 0 and 60 pct Ni at each temperature. A plot of $\log \tilde{D}_\gamma$ vs the reciprocal of the temperature is given in Fig. 4. The data fall on straight lines at each composition with very little scatter. The values Q and D_0 at 1 atm were determined by a least-squares fit of the data in Fig. 4. These data are given in Table V along with the rms errors of each determined by standard statistical analysis.

A relationship between $\log \tilde{D}_\gamma$, C_{Ni} , and T can be determined for the composition range between 0 and 50 at. pct Ni. The equation relating these three factors is

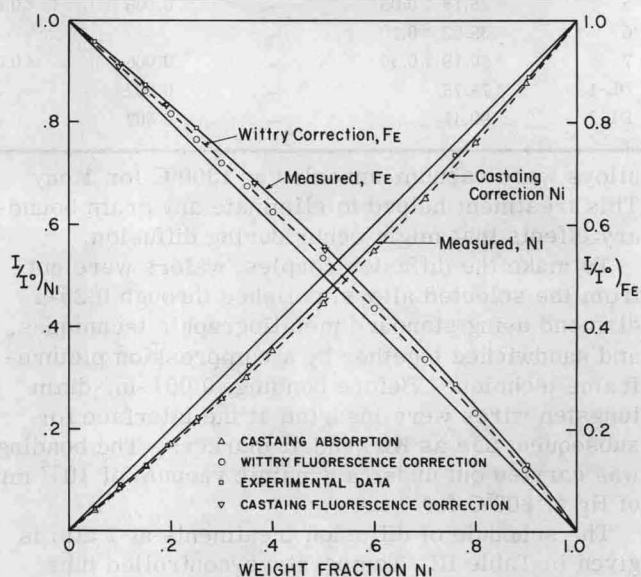


Fig. 1—Measured and calculated I/I° vs composition curves for the Fe-Ni system.

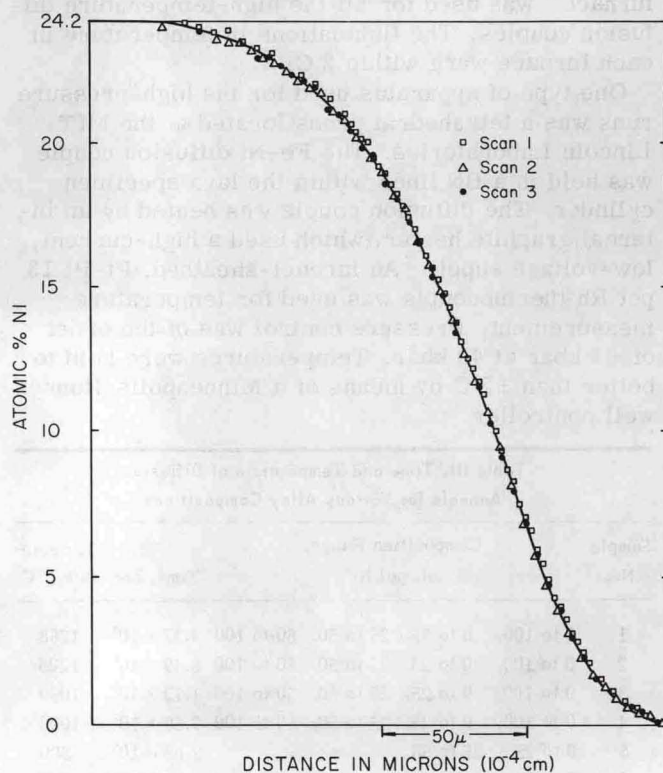


Fig. 2—Electron-probe scans across Fe-Fe, 24.2 pct Ni diffusion couple, 1288°C.

Table V. Experimental Values of Activation Energy, Q, Frequency Factor, D_0 , and Activation Energy at 40 Kbar, Q_p , for the Fe-Ni System

At. Pct Ni	Q, kcal per mole ± 1 pct	D_0 , cm ² per sec ± 20 pct	Q_p , kcal per mole
10	76.2	5.3	82.0
20	76.0	8.9	82.2
30	75.9	15.0	82.4
40	75.8	24.5	82.5
50	75.7	41.5	82.7
60	75.7	58.5	82.4
70	73.4	38.5	80.2
80	73.8	44.5	79.8
90	74.8	49.5	80.5

$$\tilde{D}_\gamma = \exp[(0.0519)(C_{Ni}) + 1.15] \times \exp\left(-\frac{76,400 - 11.6(C_{Ni})}{RT}\right) \quad [7]$$

with C_{Ni} given in atomic percent. The values of \tilde{D}_γ determined by this equation are in agreement with the measured values of \tilde{D}_γ to ± 10 pct.

The interdiffusion coefficients in the α phase were measured at 800°C with an Fe-Fe, 24.2 pct Ni couple and at 700°C with an Fe-Fe, 14.5 pct Ni couple. The gradients obtained from both couples exhibit a concentration discontinuity. This occurs between the solubility limits of the α and γ phases at 800° and 700°C. The diffusion coefficients in the

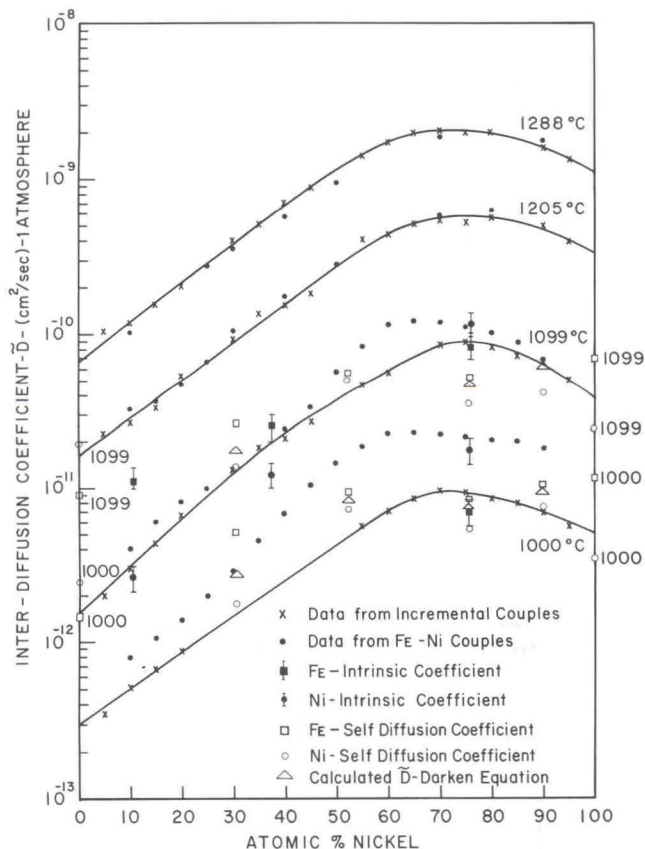


Fig. 3—Fe-Ni interdiffusion coefficient vs composition at 1 atm.

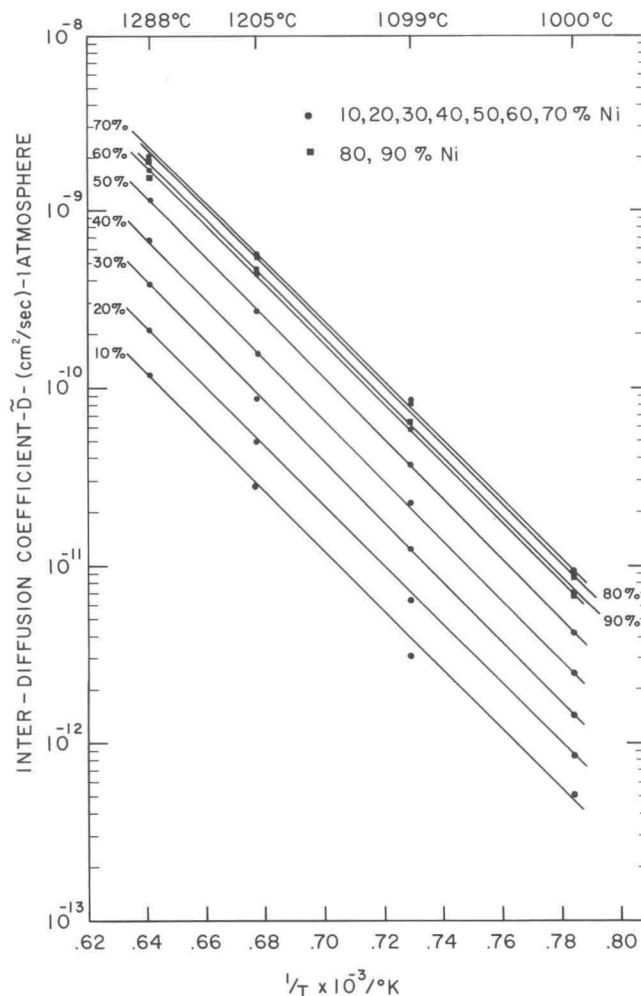


Fig. 4—Fe-Ni interdiffusion coefficient vs 1/temperature (per °K) at 1 atm.

α phase were also determined by means of the Matano analysis. The values of \tilde{D}_α at 1 pct are 2.75×10^{-12} sq cm per sec ± 10 pct at 800°C and 2.9×10^{-14} sq cm per sec ± 20 pct at 700°C.

Intrinsic diffusion coefficients were measured in four couples, since at temperatures over 1100°C the tungsten wires diffused into the Fe-Ni, and below 1000°C the width of the diffusion zone was so small ($< 50 \mu$) that the marker movements could not be measured accurately. The displacement of the Kirkendall markers was measured by correlating the regular line of contamination spots from the electron probe with the nearby Kirkendall markers when viewed with the filar eyepiece of a microhardness tester. The values of D_{Fe} and D_{Ni} are listed in Table VI and plotted in Fig. 3. The accuracy in the measurement of D_{Fe} and D_{Ni} was calculated as ± 20 pct.

The intrinsic data show that D_{Fe} is $> D_{Ni}$ from 0 to about 60 pct Ni. At 75 pct Ni, however, D_{Ni} becomes greater than D_{Fe} , which indicates a change in the relative motion of nickel with respect to iron.

The diffusion coefficients at 40 kbar were evaluated for six diffusion couples in the temperature range from 1150° to 1350°C. The effect of pressure

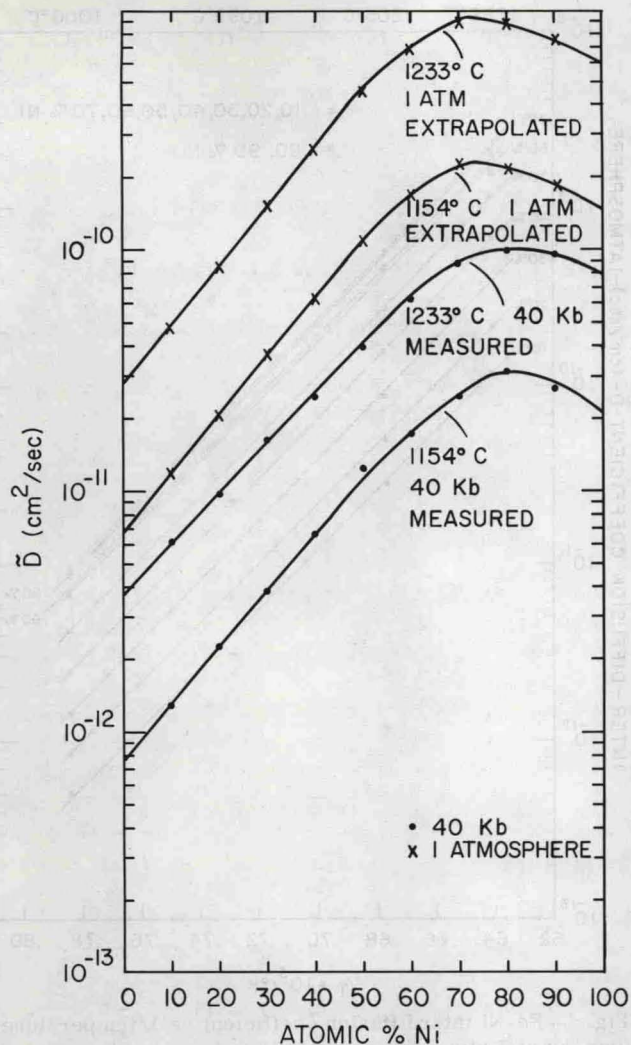


Fig. 5—Fe-Ni interdiffusion coefficient vs at. pct Ni at 1 atm and 40 kbar pressure.

on the diffusion coefficient is shown in Fig. 5, where \tilde{D}_γ at 1 atm and 40 kbar for the temperatures 1233° and 1154°C are plotted vs atomic percent nickel. The effect of the high pressure was equivalent to an average decrease in diffusion temperature of 120°C at 1 atm. The activation volume was calculated by use of Eq. [5], and the values of ΔV are shown in Fig. 6 as a function of nickel content. The self-consistency in the value of ΔV evaluated at various temperatures is ± 5 pct, which is well within the expected experimental error in ΔV of ± 10 to 15 pct.

The activation energy for diffusion at 40 kbar ($Q_P = Q_1 + P\Delta V$) and Q_1 are given as a function of nickel

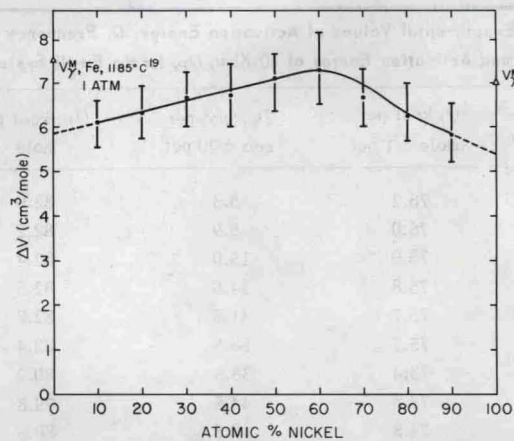


Fig. 6—Activation volume for diffusion vs concentration (evaluated at 40 kbar).

content in Table V. The effect of this pressure is to raise Q_1 by 6 to 7 kcal, about 8 to 10 pct.

Kirkendall markers were placed in all the high-pressure couples. Owing to the limited length of the diffusion zones, however, no measurement of intrinsic diffusion coefficients could be made.

There are a number of sources of error because of the method used for measuring interdiffusion coefficients. Although each source contributes only a small error to the measurements, the sum of the error limits the accuracy in the analysis of \tilde{D} to ± 10 pct.

One source of error occurs in the use of the Matano analysis. The Matano interface and the area under the curve of concentration vs distance were obtained by counting squares; the error in measurement is estimated to be about 1 pct. The largest error, however, occurs in determining the slope dx/dc of the concentration curve. Because of the 1 pct error in the determination of composition, a subjective judgment must be made concerning the best curve through the data points. The variance in measured slope in this study was not more than 5 pct, since the slope was not taken near the ends of the concentration curves.

The Matano analysis can be used independently only if the partial molar volumes of the two components do not vary with composition. Since in the Fe-Ni system the molar volumes of iron and nickel do vary with composition, we employed a correction to the Matano analysis given by Balluffi.¹⁹ The lattice parameters of various γ -phase Fe-Ni alloys for temperatures up to 600°C have been meas-

Table VI. Intrinsic Diffusion Coefficients, 1 Atm

Temperature, °C	At. Pct Ni	D_{Fe} , cm ² per sec	D_{Ni} , cm ² per sec	Marker Movement, γ_m , μ	Length of Diffusion Zone, μ
1100	12	1.1×10^{-11}	0.25×10^{-11}	2.5	65
1100	37	2.5×10^{-11}	1.2×10^{-11}	2.0	100
1100	76	8.4×10^{-11}	11.7×10^{-11}	4.0	225
1000	76	0.7×10^{-11}	1.75×10^{-11}	6.0	160

ured by Owen and Yates,²¹ and the lattice parameter of γ iron has been measured by Basinski *et al.*²² By extrapolating the measured alloy lattice parameters to 1000°C the molar volumes of iron and nickel can be calculated at this temperature. The correction in \tilde{D} resulting from a change in molar volume with concentration is positive and ranges linearly from no change at low nickel contents to an 8 pct correction at pure nickel.

The error resulting from the heating and cooling cycle and the temperature variances during diffusion was less than 5 pct. The thermal contraction decreases the true \tilde{D} by less than 2 pct, even though part of the sample changes its crystal structure from fcc to bcc.

DISCUSSION

The interdiffusion coefficients for the Fe-Ni system at 1 atm were measured as functions of composition and temperature. The diffusion coefficients vary exponentially with nickel concentration from low nickel contents to 50 pct. The maximum value of the diffusion coefficient falls at about 70 pct Ni. The fact that a Kirkendall marker movement occurs strongly indicates that diffusion in the Fe-Ni system is vacancy-controlled. The invariance of D with the chemical gradient has already been demonstrated by Chollet *et al.*²³ for the Fe-Ni system.

The diffusion coefficients obtained from pure Fe-Ni couples diffused at 1100° and 1000°C lie increasingly above the diffusion coefficients obtained from incremental couples, see Fig. 3. This same effect was observed by Reynolds²⁴ for diffusion in the Au-Ni system. These high values of \tilde{D} are not caused by any of the sources of error discussed previously, but they may be explained by another cause. The large initial differences in molar volume found in the pure Fe-Ni couples may result in progressive recrystallization and other non-steady structural defects even at 1000°C. These conditions may lead to an excess of vacancies or to the formation of short-circuiting paths such as subboundaries and so forth. At temperatures above 1200°C, the nonsteady effects probably annealed out very rapidly.

The variation of Q and \tilde{D} can be considered in

Table VII. Interdiffusion Coefficients in the Fe-Ni System

Temperature, °C	C_{Ni} , at. pct	\tilde{D} Wells and Mehl,	\tilde{D} This Study,
		± 20 pct, cm ² per sec	± 10 pct, cm ² per sec
1300	4	16×10^{-11}	12×10^{-11}
	16	24×10^{-11}	22×10^{-11}
	30	47×10^{-11}	48×10^{-11}
1205	4	3.6×10^{-11}	2.2×10^{-11}
	16	4.55×10^{-11}	3.7×10^{-11}
1100	4	0.88×10^{-11}	0.22×10^{-11}
	16	1.1×10^{-11}	0.45×10^{-11}

terms of the melting point. The relationship of melting point T_m to activation energy Q has been pointed out by Sherby and Simnad²⁵ for the self-diffusion case. At a given temperature, the higher the ratio T/T_m , the higher will be the vacancy concentration for diffusion, and the smaller will be the amount of work necessary for an atom to move through the saddle point. On this basis, Q would be expected to decrease from pure iron to 60 to 70 pct Ni and to decrease from pure nickel to 60 to 70 pct Ni, Table V. The fact that Q varies over only a few kilocalories is the result of the small variation of T_m (<5 pct) across the diagram.

The only interdiffusion data for Fe-Ni published to date are those of Wells and Mehl.²⁶ The values of \tilde{D} are compared in Table VII.

The values at 1300°C agree very closely. At 1200°C they agree within the limits of experimental error. At 1100°C, however, their values fall above those of this study. Probably at the lower temperatures grain boundary diffusion began to play a significant role, and its effect was not recognized by Wells and Mehl.

According to the Darken equation, $\tilde{D} = D_{Ni}^*$ in pure iron and $\tilde{D} = D_{Fe}^*$ in pure nickel for the Fe-Ni system. The values of Hirano *et al.*²⁷ and Fraden²⁸ are plotted in Fig. 3, which shows that D_{Ni}^* is about one order of magnitude greater than \tilde{D} in pure iron and D_{Fe}^* is about 100 pct greater than \tilde{D} in pure nickel. The data themselves are much more difficult to challenge than the theory relating self-diffusion measurements to interdiffusion measurements.

The self-diffusion coefficients in the Fe-Ni system have been determined by Fraden,²⁸ whose values were measured in the temperature range 725° to 1075°C. The values of D_{Ni}^* and D_{Fe}^* as well as the calculated values of \tilde{D} at 1100° and 1000°C are plotted in Fig. 3. Except at 0 pct Ni, D_{Fe}^* is greater than D_{Ni}^* . This agrees with the intrinsic measurements made between 0 and 50 pct Ni at 1100°C. The ratios of D_{Fe}^*/D_{Ni}^* to D_{Fe}/D_{Ni} are also in rough agreement. Unfortunately, at 76 pct Ni, where both the intrinsic and the self-diffusion coefficients are known, there is no correlation between the measurements.

Except at about 76 pct Ni, the calculated values of \tilde{D} from the Darken equation lie above the measured values of \tilde{D} . The difference is only 50 pct at 1100°C, but about 100 pct at 1000°C. Since Manning predicts that \tilde{D}_{calc} is less than \tilde{D}_{meas} , his correction for vacancy flow is lost in the differences between the two measurements. We should note that the values of the penetration distance $2\sqrt{Dt}$ measured by Fraden are less than 10 μ . Duhi²⁹ has recently shown that short penetration distances lead to an increase in D^* of about 30 pct. This effect can explain in part why \tilde{D}_{calc} is greater than \tilde{D}_{meas} . Since two different methods of measuring \tilde{D} were used, however, and since these measurements were made in different alloys in only partially overlapping temperature ranges, the differences between

Table VIII. Diffusion in the α Phase of the Fe-Ni System

Reference	D_0 , paramagnetic, cm ² per sec	Q , paramagnetic, kcal per mole	\tilde{D}_α , 800°C, cm ² per sec	\tilde{D}_α , 700°C, cm ² per sec
Borg and Lai ³⁰	9.9	61.9	2.56×10^{-12}	3.75×10^{-14}
Hirano <i>et al.</i> ²⁷	1.3	56.0	5.3×10^{-12}	8.5×10^{-14}
This study	—	—	2.75×10^{-12}	2.9×10^{-14}

calculated and measured \tilde{D} are not really unexpected. In summary, therefore, the Darken equation applies for the Fe-Ni system only as a first approximation.

Diffusion measurements were also made in the α phase at 800° and 700°C. Two papers have been published on the self-diffusion coefficient of nickel in α iron.^{27,30} The values of D_0 and Q in the paramagnetic range above the Curie temperature are given in Table VIII, along with a comparison of the measured values of \tilde{D}_α and D_{Ni}^* . The values of \tilde{D}_α from this study agree very closely with those of Borg and Lai.

The effect of 40 kbar pressure on \tilde{D} in the γ phase of the Fe-Ni system is approximately equivalent to a lowering of the diffusion temperature by 120°C. The thermocouple corrections (chromel-alumel) resulting from the pressure effect are more than an order of magnitude smaller than the actual effect of pressure on D at 40 kbar.

Recent detailed studies on the effect of nonhydrostatic strain on diffusion³¹ have demonstrated that for $T > 1/2 T_m$ the bulk-diffusion coefficient is not altered by strain deformation at relatively low stresses. The present data, along with the recent work of Hanneman,¹¹ show that the above observation holds to very high stresses by comparing diffusion results from a BN liner with those from a molten-salt environment. The theoretical value of the activation volume in the fcc element copper was calculated to be approximately 0.75 of the molar volume.^{7,32,33} Measurements of silver and lead have given values of 0.9 to 0.71 V^M . The recent measurement by Hanneman¹¹ of ΔV fcc in Fe-V at 0.007 at. pct V gives $\sim 0.75 V^M$. Extrapolation of the measured values of ΔV in this study gives $\Delta V_{Fe} \sim 0.8 V_{Fe}^M$ and $\Delta V_{Ni} \sim 0.8 V_{Ni}^M$. These measurements agree very closely with those of previous investigators for both self-diffusion and interdiffusion. The apparent agreement in ΔV between metals of varying size, bonding strengths, and valences shows the relatively insensitive nature of the activation volume in fcc metals.

Fig. 6 shows the change of the activation volume with composition. Within experimental error, it appears that ΔV increases slightly with increasing nickel content, to a maximum at 60 pct Ni, and then decreases. The reason this may occur is not readily apparent. The effect of pressure on the bonding characteristics of Fe-Ni may, however, cause the slight increase in ΔV . Evidence of the change in the bonding strengths may be inferred by noting that

the maximum \tilde{D}_P falls between 80 and 90 pct Ni instead of between 65 and 75 pct Ni at 1 atm.

CONCLUSIONS

1) The diffusion coefficient at 1 atm pressure increased with increasing nickel content up to 65 pct Ni, that at 40 kbar pressure up to 80 pct. The relationship of $\tilde{D}_{\gamma-1 \text{ atm}}$ to temperature and composition, up to 50 pct Ni, is given by the equation

$$\tilde{D}_{\gamma-1 \text{ atm}} = \exp(0.0519 C_{Ni} + 1.15) \times \exp - \left(\frac{76,400 - 11.6 C_{Ni}}{RT} \right) \quad [10]$$

2) The activation energy at 1 atm decreases from pure iron to 60 to 70 pct Ni and decreases from pure nickel to 60 to 70 pct Ni. The variation is only a few kilocalories, which is directly correlated to the variation in melting point across the Fe-Ni diagram.

3) A small Kirkendall movement was measured at 1 atm, indicating that the diffusion process is almost certainly vacancy-controlled. Up to about 60 pct Ni, D_{Fe} is greater than D_{Ni} . Above 60 pct Ni, however, a shift in the relative values of the intrinsic coefficients occurs, and D_{Ni} becomes greater than D_{Fe} .

4) A comparison was made between the interdiffusion coefficients calculated from the Darken equation and the measured coefficients. In the Fe-Ni system the use of the Darken equation gives values of \tilde{D} that can be used only as a first approximation to the interdiffusion coefficients.

5) The values of the interdiffusion coefficients in the α phase were measured at 800° and 700°C. The values of \tilde{D}_α agree very closely with the measured self-diffusion coefficients, D_{Ni}^* in pure iron, of Borg and Lai.

6) The activation volumes for high-pressure diffusion in γ Fe-Ni agree favorably with theoretical and semiempirical models developed for self-diffusion.

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