

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 nonsteady 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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