

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

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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, $\tilde{D}_\gamma$ 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

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

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

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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.

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.

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