PHYSICAL REVIEW VOLUME 95, NUMBER 5 SEPTEMBER 1, 1954

Diffusion of Co^{60} in Some Ni-Al Alloys Containing Excess Vacancies*

A. E. BERKOWITZ,† F. E. JAUMOT, JR., AND F. C. NIX
Randal Morgan Laboratory of Physics, University of Pennsylvania, Philadelphia, Pennsylvania

(Received May 20, 1954)

The aluminum-rich compositions in the δ phase of Ni−Al exhibit vacancy densities considerably greater than the normal equilibrium concentrations. Measurements were made of the diffusion of Co^{60} in six compositions in the δ phase of Ni−Al at 1050°C, 1150°C, 1250°C, and 1350°C. The diffusion coefficient had a minimum value at the stoichiometric composition. The activation energies had a maximum value at this composition and remained essentially constant at a lower value for the aluminum-rich alloys. An interpretation of this behavior in terms of a vacancy mechanism is discussed.

INTRODUCTION

IN most cases, experimental studies of diffusion in metals are difficult to interpret uniquely in terms of one or another of the commonly proposed diffusion mechanisms; namely, the interstitial, vacancy, and Ring mechanisms. This is due, in part, to the limited accuracy of many diffusion experiments, but other factors also contribute to this problem. For example, when a vacancy mechanism is considered, there is usually little information available concerning the distribution of vacancies in the lattice. Therefore, diffusion measurements in those systems in which the concentration of excess vacancies is known may be described more precisely in terms of a particular mechanism. The present investigation was concerned with such a system.

THE δ PHASE OF Ni−Al

The δ phase of the Ni−Al system is body-centered cubic and extends from 45 to 60 atomic percent nickel. Bradley and Taylor[1] found that at the composition NiAl, the nickel atoms occupy the cube centers and the aluminum atoms are at the corners. Bradley and Taylor's density and lattice spacing measurements are shown in Fig. 1. The behavior of the density and lattice spacing for the excess nickel concentrations are in accord with a simple replacement process since the nickel atoms are heavier and smaller than the aluminum atoms. On the excess aluminum side, the dashed branch of the density curve indicates the values calculated using the measured lattice spacings and assuming two atoms per unit cell. The considerable discrepancy between the calculated and measured values of the density led Bradley and Taylor to conclude that for the excess aluminum compositions there were less than two atoms per unit cell. Thus, from 60 to 49.5 atomic percent nickel, the composition changes by substituting aluminum atoms for nickel atoms. From this point to the phase boundary at 45.3 atomic percent nickel, the change in composition takes place by dropping nickel atoms out of their lattice positions and leaving these sites vacant. Bradley and Taylor confirmed these conclusions by careful measurements on the degree of order of the alloys. A similar defect structure is found in the ϵ phase of Co−Al.[2]

PREVIOUS DIFFUSION STUDIES ON Ni−Al AND Co−Al

The considerable ranges of vacancy concentrations in these defect alloys have resulted in two previous investigations of the influence of these vacancies on diffusion. Smoluchowski and Burgess[3] studied the diffusion of Co^{60} in a series of compositions in the δ phase of Ni−Al at 1150°C. They found that the diffusion coefficients increased with increasing concentrations of excess nickel but remained essentially constant for the excess aluminum alloys. Smoluchowski and Burgess suggested that their results for the excess aluminum alloys indicated that the nickel vacancies V(Ni) were unable to exchange with the Co^{60} atoms since such an

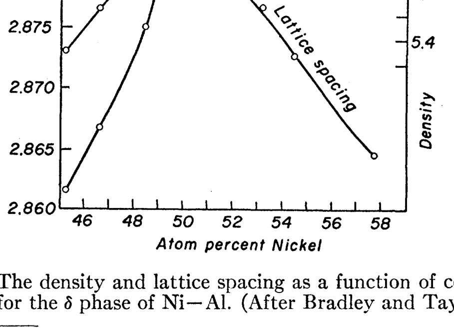

FIG. 1. The density and lattice spacing as a function of composition for the δ phase of Ni−Al. (After Bradley and Taylor.)

---

* Supported by the U. S. Office of Naval Research. This work is part of a dissertation by A. E. Berkowitz presented in candidacy for the degree of Doctor of Philosophy at the University of Pennsylvania.

† Now at The Franklin Institute Laboratories for Research and Development, Philadelphia 3, Pennsylvania.

[1] A. J. Bradley and A. Taylor, Proc. Roy. Soc. (London) **A159**, 56 (1937).

[2] A. J. Bradley and G. C. Seager, J. Inst. Metals **64**, 81 (1939).

[3] R. Smoluchowski and H. Burgess, Phys. Rev. **76**, 309 (1949).

TABLE I. Values of the diffusion coefficients as a function of temperature for various compositions in the δ phase of Ni—Al.

Atom percent nickel	D (cm^2 sec^{-1}) 1050°C	1150°C	1250°C	1350°C
47.3	2.5×10^{-11}	8.85×10^{-11}	3.68×10^{-10}	1.05×10^{-9}
48.5	1.66×10^{-11}	6.00×10^{-11}	2.30×10^{-10}	8.32×10^{-10}
49.4		3.96×10^{-11}	1.14×10^{-10}	3.96×10^{-10}
50.7		2.46×10^{-11}	1.52×10^{-10}	8.36×10^{-10}
53.1	2.44×10^{-11}	1.03×10^{-10}	5.66×10^{-10}	1.97×10^{-9}
55.5	7.84×10^{-11}	4.00×10^{-10}	1.38×10^{-9}	3.11×10^{-9}

exchange would necessitate the intermediate step of the V(Ni) exchanging with a nearest-neighbor aluminum atom. It was assumed that this latter exchange was precluded by the fact that a V(Ni) is considerably smaller than an Al atom.

Significantly different results were reported by Nix and Jaumot[4] who investigated the diffusion of Co^{60} in five compositions in the ϵ phase of Co—Al. Their measurements were made for diffusion temperatures of 1050°C, 1150°C, and 1250°C. For each of these temperatures, they found that the diffusion coefficient had a minimum value in the vicinity of the 50 atomic percent cobalt composition. Furthermore, the activation energies calculated from these data had a maximum value at the same composition. Nix and Jaumot concluded that their data showed that the excess vacancies V(Co) in the aluminum-rich alloys did increase the diffusion rate. They argued that at the relatively high temperatures of the diffusion anneals there must exist an appreciable degree of disorder which would permit some of the excess V(Co) to be distributed over the lattice sites in a random fashion. They further suggested that the large numbers of excess V(Co) would greatly increase the probability of a V(Co) being adjacent to a lattice defect (e.g., a cobalt atom in a cube corner or another vacancy). Both these situations would increase the mobility of the vacancies.

The increase in the rate of diffusion with increasing amounts of excess nickel or cobalt is compatible with either an interstitial or a vacancy mechanism. The substitution of nickel or cobalt atoms for the larger aluminum atoms certainly enlarges the interstices. This enlargement could either aid interstitial diffusion or increase the mobility of vacancies. Also, the opportunity for exchange of a Co^{60} atom with a V(Al) would be increased by the replacement of aluminum atoms by nickel or cobalt atoms since this would lead to the creation of additional V(Al) by a process such as $V(\text{Ni})+\text{Ni atom}\rightarrow V(\text{Al})$ where the nickel atom was one occupying an aluminum site. It is also possible that the operation of a Ring mechanism would be facilitated by the enlargement of the interstices.

For the aluminum-rich alloys, both the replacement of nickel or cobalt by the larger aluminum atoms and the decrease in lattice spacing with increasing aluminum would decrease the interstices. This would be unfavorable to the operation of either an interstitial or a Ring mechanism. However, it might be argued that the presence of the excess vacancies would relax the lattice to a degree sufficient to offset the influence of the decreased interstices on Ring or interstitial diffusion. Such an interpretation would probably suffice to explain the results obtained by Smoluchowski and Burgess for the Ni—Al alloys, where the diffusion coefficients remained essentially constant for the excess nickel compositions. It is considerably more difficult to interpret the data of Nix and Jaumot on this basis, since these authors found that the diffusion coefficients increased with increasing amounts of excess aluminum in the ϵ phase of Co—Al. It seems more reasonable to consider a vacancy mechanism to be responsible for this type of behavior. This involves assuming a sufficient mobility of the defect V(Co) in the manner discussed in the foregoing. In addition, the sharp drop in activation energy for the aluminum-rich alloys is more readily explained by a vacancy mechanism.

Thus, the interpretation of the behavior of the diffusion coefficients for the aluminum-rich defect alloys is critically dependent on the details of the data. In view of the decided lack of agreement between the previous investigations as to the trend of the diffusion coefficients for the defect alloys, it was decided to investigate in more detail the diffusion of Co^{60} in the δ phase of Ni—Al.

THE EXPERIMENT

We studied the diffusion of Co^{60} in six compositions in the δ phase of Ni—Al. Three of these compositions were nickel-rich and three had excess aluminum. The alloys were prepared by melting under vacuum in an induction furnace. The resulting ingots, which were extensively annealed, were cut into samples $\frac{1}{2}$ in.$\times\frac{1}{2}$ in. $\times\frac{1}{8}$ in. The samples used were uniformly free from visible porosity and their grain sizes ranged from one to three mm. The composition was determined by chemical analysis and by x-ray lattice spacing measurements, using the data of Bradley and Taylor in Fig. 1.

Since the alloys were extremely hard and often very brittle, sectioning techniques, using available equipment, were precluded. We used the standard method of surface counting. The use of this method requires knowledge of the absorption of the β rays from Co^{60} by the Ni—Al alloys. Since we were unable to fabricate foils of the alloys sufficiently thin to make useful absorption measurements, we obtained the absorption in

TABLE II. Values of the activation energies Q and diffusion constants D_0 in the equation $D_0e^{-Q/RT}$, for various compositions in the δ phase of Ni—Al.

Atom percent nickel	47.3	48.5	49.4	50.7	53.1	55.5
Q (kcal/mol)	56.6	59.9	52.5	80.6	67.6	47.1
D_0 (cm^2/sec)	4.7×10^{-2}	9.3×10^{-2}	4.4×10^{-3}	57.7	2.6	7.2×10^{-3}

---

[4] F. C. Nix and F. E. Jaumot, Jr., Phys. Rev. 83, 1275 (1951).

nickel and aluminum foils and combined these data to give the absorption in the alloys. These data revealed a considerable departure from exponential absorption; this phenomenon is discussed more fully in another paper.[5]

Co^{60} was evaporated onto the polished faces of the samples. Pairs of samples of the same composition and similar surface activities were annealed with active faces together. Six compositions were given diffusion anneals in vacuum at 1150°C, 1250°C, and 1350°C, for 24, 18, and 12 hours, respectively. Four compositions were annealed at 1050°C for 18 hours. A minimum of three pairs of samples of each composition were used at each temperature investigated. The summed activity of a pair was used to calculate the diffusion coefficients.

RESULTS

The results of the diffusion measurements are presented in Tables I and II. Figures 2 and 3 are semilog plots of the diffusion coefficient *versus* reciprocal temperature for the excess aluminum alloys and the excess nickel alloys, respectively. The data spreads in Figs. 2 and 3 indicate the extreme values of the diffusion coefficients measured at the given temperature and composition. The straight lines were drawn according to a least squares fit of the data for the three highest temperatures. The data at 1050°C are much less reliable than those for the higher temperatures. The reasons for this relative unreliability are the following: First, the diffusion anneals at 1050°C were rather short (18 hours) so that the mean diffusion distance was within the anomolous β-absorption region[5] which resulted in the surface activities after diffusion being greater than those before diffusion. Not only did this involve a larger probable error, but it also indicated that an appreciable amount of undiffused Co^{60} remained on the surface of the samples. Second, we used Lavite sample holders for the 1050°C anneals. Although these holders were carefully cleaned and baked in vacuum, there was considerable outgassing during the diffusion anneals which resulted in some contamination of the samples. This difficulty was eliminated in subsequent anneals at higher temperatures by using sample holders made of pure aluminum oxide. For these reasons and because of the scatter in the positions of the 1050°C data with respect to the straight lines in Figs. 2 and 3, we do not feel justified in basing any conclusions on the lower temperature data. The probable error for the three higher temperatures was estimated to be 15 percent for each point. From the data spread and the fit to the straight lines, it seems that this estimate is somewhat too high.

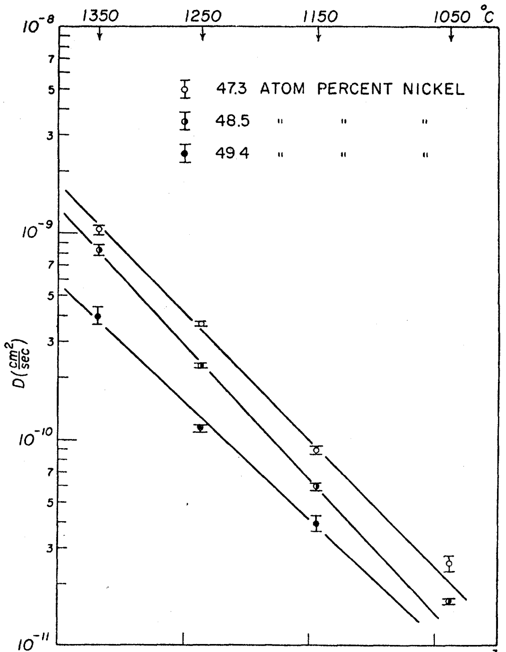

FIG. 2. Values of the diffusion coefficients for excess aluminum alloys in the δ phase of Ni—Al.

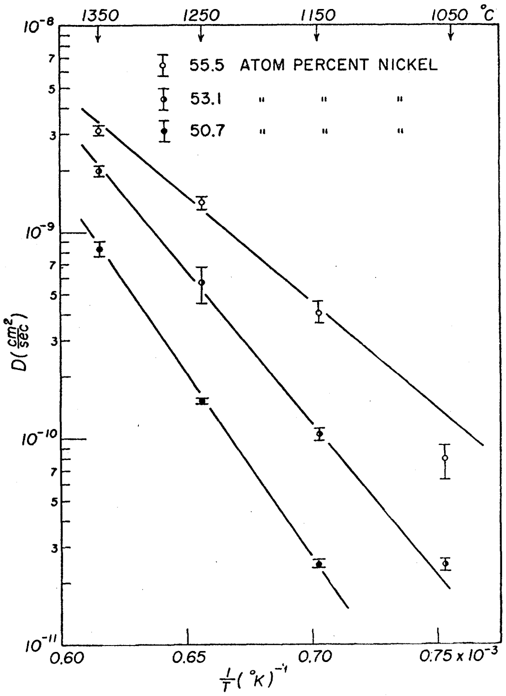

FIG. 3. Values of the diffusion coefficients for the excess nickel alloys in the δ phase of Ni—Al.

In Fig. 4, the diffusion coefficients are plotted against composition for the four annealing temperatures. The composition spreads indicate the difference between the chemical analyses and the x-ray measurements. Figure 4 shows very clearly that for each of the annealing

---

[5] Submitted to the *Journal of Applied Physics*. A brief report of this behavior was presented at the 1954 Michigan Meeting of the American Physical Society, see A. E. Berkowitz, Phys. Rev. **94**, 1407 (1954).

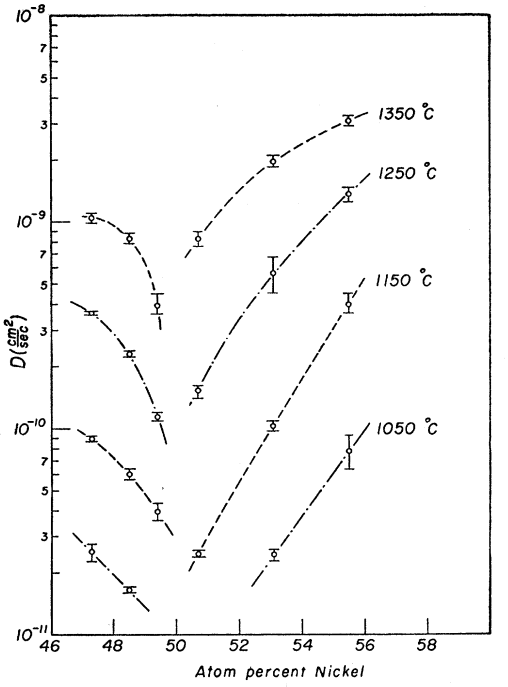

FIG. 4. The composition dependence of D in the δ phase of Ni—Al.

temperatures, the diffusion coefficients have a minimum value in the vicinity of 50 atomic percent nickel. The absence of any overlap in the data spreads for adjacent compositions indicates that the general trend of the diffusion coefficients is as shown in Fig. 4.

In Fig. 5, the activation energy is plotted as a function of composition. The activation energy was obtained from the slopes of the straight lines in Figs. 2 and 3. On the basis of the extreme values of the slopes of the straight lines that can be drawn through the data spreads in Figs. 2 and 3, we can assign a probable error of less than 10 percent to the values of the activation energies. The dashed curve in Fig. 5 serves only to indicate the general trend of the activation energies. Considerably more data would be necessary to define the structure of the curve accurately. However, we have no reason to doubt that the dashed curve represents the general behavior of the activation energies.

DISCUSSION

A fairly simple interpretation of the behavior of the activation energies can be made in terms of a vacancy model. In general, the vacancy mechanism predicts that[6]

$$D \propto A e^{-Q_f/RT} e^{-Q_e/RT};$$

where $Ae^{-Q_f/RT}$ = fractional concentration of vacancies at thermal equilibrium (Q_f being the energy required for formation of a vacancy), and Q_e = energy required for exchange of a vacancy with a neighbor. When the vacancies are present only in the normal equilibrium concentration the activation energy measured is

$$Q = Q_f + Q_e.$$

If $n(v)$ = fractional concentration of excess defect vacancies, we have $n(v) \gg Ae^{-Q_f/RT}$. In addition, if we assume that the excess vacancies in the aluminum-rich alloys are sufficiently mobile,

$$D \propto n(v) e^{-Q_e/RT}. \tag{1}$$

On this model the activation energy measured for the excess aluminum alloys is only Q_e. The fact that Fig. 5 indicates that Q_e is essentially constant for the aluminum-rich alloys is reasonable if one considers that the excess V(Ni) must exchange with a nearest neighbor. Bradley and Taylor have shown that the nearest neighbors to nickel sites are all aluminum atoms, irrespective of the composition of the excess aluminum alloys. Furthermore, if this model is correct, then the difference between the maximum activation energy measured for the nickel-rich alloys, and Q_e should correspond to Q_f. Assuming that Q_e is the approximately constant value of the activation energy for the aluminum-rich alloys, Q_f is calculated to be about 23 kcal/mole, which is a very reasonable value. From (1) and the constant value of Q_e for the aluminum-rich alloys it follows that for these defect alloys,

$$D \propto n(v) \propto D_0 \tag{2}$$

for constant temperature; where D_0 is defined by the equation $D = D_0 \exp(-Q/RT)$. From Table II it is seen that the values of D_0 do not obey (2). The values for $n(v)$ are approximately 0.002, 0.0195, and 0.038 for

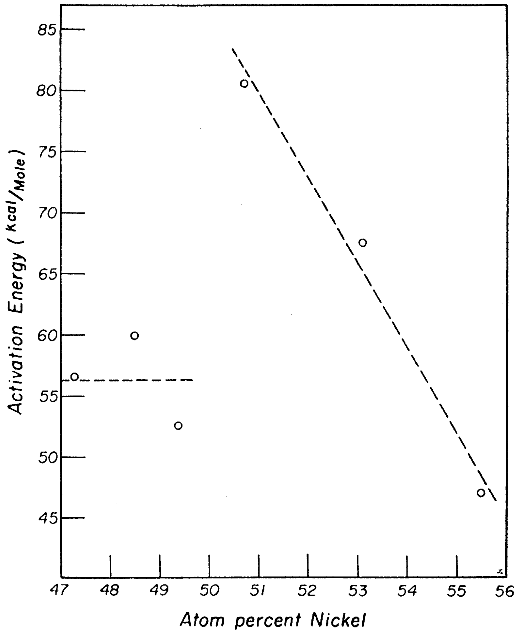

FIG. 5. Values of the activation energies for various compositions in the δ phase of Ni—Al.

---

[6] A. D. Le Claire, *Progress in Metal Physics* (Interscience Publishers, Inc., New York, 1953), Vol. 4.

49.4, 48.5, and 47.3 atomic percent nickel, respectively. However, since D_0 is so very sensitive to small errors in Q, the estimated probable error for Q includes values of D_0 which are in line with (2). Furthermore, we can test the validity of the left-hand side of (2), i.e., $D\propto n(v)$, using the data for the aluminum-rich alloys. We normalize the values for D, for each temperature, to the value of D at 47.3 atomic percent nickel. If we average these normalized D values for the three highest temperatures and plot these averages against $n(v)$ we find an almost linear dependence. That is, if

$$A_j=\tfrac{1}{3}\sum_i \frac{D_j{}^i}{D_{47.3}{}^i}, \quad \begin{array}{l} i=1150°\text{C},\ 1250°\text{C},\ 1350°\text{C}, \\ j=47.3,\ 48.5,\ 49.4 \text{ atomic percent} \\ \qquad \text{nickel,} \end{array}$$

then $A_j\propto n(v)_j$. That this linear dependence is present may, of course, be entirely fortuitous. However, it is interesting to note that the spread in the A_j values is much smaller than would be expected from the estimated probable error of 15 percent for the individual D values. A significant implication of the relation $A_j \alpha n(v)$ is that $D_0 \alpha n(v)$. This follows from the fact that if $Q=Q_e$ for the aluminum-rich alloys, then

$$A_j=\left\langle\frac{(D_0)_j}{(D_0)_{47.3}}\right\rangle_{\text{Av}}.$$

A commonly accepted interpretation[6] of D_0 is[7]

$$D_0=a^2\nu\exp(\Delta S/R), \qquad (3)$$

where, for a vacancy mechanism, ΔS is the sum of the entropy changes associated with the free energy changes involved in the formation and motion of a vacancy in the lattice, ν is the frequency of the vibration of the atoms in the direction of exchange with a vacancy, and a is the lattice spacing. We can estimate ν in the manner suggested by Wert and Zener[8] for interstitial motion of atoms, by assuming that the potential energy of an atom varies sinusoidally as it exchanges with a vacancy with an amplitude equal to Q_e. This assumption gives

$$\nu=(Q_e/2ma^2)^{\frac{1}{2}},$$

where m is the mass of the atom. Using this expression for ν in (3), we get, within the probable error, positive values for ΔS for all the compositions. Since it can be shown that ΔS should be positive, this is sometimes taken as a criterion of the reliability of the D_0 value. However, it is by no means certain that (3) applies to chemical diffusion, although it seems to hold for most self-diffusion data.

The interpretation of the data presented above also implies the operation of a vacancy mechanism for the nickel-rich alloys. This follows from the identification of Q_f with the drop in activation energy at 50 atomic percent nickel. It is possible, of course, that this drop in activation energy is consistent with either a Ring or an interstitial mechanism by virtue of the general relaxation in the lattice due to the presence of the excess V(Ni) in the aluminum-rich alloys. For this reason and because of the lack of evidence for a vacancy mechanism in body-centered structures, we cannot suggest that a vacancy mechanism is uniquely compatible with our data for the nickel-rich alloys.

In summary, we feel that the data shows that the excess vacancies in the defect alloys markedly influence the rate of diffusion. Although several interpretations of the data can be offered with respect to the mechanism of diffusion, we feel that a vacancy mechanism is most strongly indicated, especially for the defect alloys. The abruptness and magnitude of the changes in the diffusion coefficients and activation energies at the stoichiometric composition suggest a vacancy mechanism. Also, a simple interpretation of the general trends of the diffusion coefficients and activation energies can be made in terms of a vacancy model. In particular, a reasonable value for the energy for formation of a vacancy can be identified. In addition, the variation of the diffusion coefficients with defect vacancy concentration can be satisfactorily explained.

---

[7] This expression applies only to the nickel-rich alloys. For the aluminum-rich alloys, the appropriate expression is

$$D_0=n(v)a^2\nu\exp(\Delta S/R),$$

where ΔS now refers only to the entropy change associated with moving a vacancy.

[8] C. A. Wert and C. Zener, Phys. Rev. **76**, 1169 (1949).