PHYSICAL REVIEW B VOLUME 1, NUMBER 8 15 APRIL 1970

Diffusion of Solutes in Aluminum and Dilute Aluminum Alloys*

W. B. ALEXANDER† AND L. M. SLIFKIN‡
University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27514

(Received 6 November 1969)

Diffusion of impurities in single crystals of aluminum and dilute aluminum alloys has been studied by tracer-sectioning techniques. In pure aluminum, the activation energies for Au, Ag, Cd, and Fe are (in kcal/mole) 27.0±0.11, 28.0±0.014, 29.7±0.26, and 46.0±1.4. The pre-exponential factors are (in cm^2/sec) 0.077, 0.13, 1.04, and 135. The values for Ag and Au agree with other available data, while those for Cd and Fe disagree with previously reported anomalous results, which apparently were perturbed by surface oxide. When 1% of various solutes are added to aluminum, sizable enhancements are observed in the diffusion coefficients of Cu and Ag. This is understood in terms of increased jump rates caused by the Friedel oscillations in the screening potential about impurities.

I. INTRODUCTION

THE present investigation began when we observed that atomic diffusion in an aluminum alloy appeared to be extraordinarily slow in the region near the surface of the specimen. However, when the oxide layer that almost always covers the surface of aluminum was removed, diffusion was found to be normal. These observations suggested that oxide on the surface may be one of the factors that has led to the anomalous diffusion results often observed by others in aluminum. For example, in the early studies of the diffusion of Fe, Co, and Ni tracers,[1] diffusion coefficients in the range of 10^{-12}–10^{-14} cm^2/sec near the melting point, activation energies about half that for aluminum self-diffusion, and pre-exponential factors very much smaller than unity were found. The non-Gaussian nature of the penetration profiles led the investigators to propose that diffusion along dislocations was being observed. Later work[2,3] using Cr, Mo, Cd, In, Sn, and Pd gave Gaussian profiles, but similarly anomalous diffusion parameters. On the other hand, impurities such as Cu, Ag, Zn, Ge, and Ga are reported to diffuse at about the same general rate as self-diffusion, around 10^{-8} cm^2/sec at the melting point.[4–7] The initial motivation of this investigation was to examine this inconsistency; however, in doing so we have hoped to contribute to the understanding of the interactions affecting the diffusion process by (1) checking the reproducibility of existing diffusion parameters, (2) providing data on additional impurities, and (3) investigate the long-range vacancy-impurity interactions by studying diffusion in dilute alloys.

II. THEORY

A. Impurity Diffusion

The electrostatic theory proposed by Lazarus[8] and later modified by LeClaire[9] has proven successful in accounting for impurity diffusion in the fcc noble metals[9] and the hcp zinc.[10] On this model, the screened Coulombic interaction between a vacancy and an impurity atom is considered to be predominant. Since aluminum is structurally similar to the noble metals, and since the vacancy mechanism is thought to be also operative here, the electrostatic theory may be of some help in understanding the diffusion results in this metal.

Impurities are considered as point charges of magnitude eZ, where Z is in first approximation, the valence difference between impurity and solvent. The Thomas-Fermi screening potential of the form

$$V(r)=(\alpha Ze/r)e^{-qr} \tag{1}$$

is used, where q is the screening constant characterizing the solvent and α is a constant depending only on Z. In aluminum, the Thomas-Fermi approximation may be in serious error at r as large as the nearest-neighbor distance. More realistic potentials of the Friedel type, which incorporate the long-range oscillations in the charge density, are presumably more accurate. Asymptotically, these potentials usually have the form

$$V(r)\simeq Z\pi e\cos(2k_Fr+\delta)/k_F{}^2r^3\,, \tag{2}$$

where k_F is the Fermi wave vector of the solvent. If the vacancy is considered as a point defect with a zero valence, the change in vacancy formation energy at a nearest-neighbor site is given by

$$\Delta E=-eZ_VV(a)\,, \tag{3}$$

where $V(a)$ is the appropriate potential evaluated at

---

* Supported by the U. S. Atomic Energy Commission under Contract No. AT-(40-1)-2036.

† Present address: Rensselaer Polytechnic Institute, Troy, N. Y. 12181.

‡ Address for 1969-70: Office of Naval Research, London, England.

[1] K. L. Hirano, R. P. Averbach, and M. Cohen, Acta Met. **10**, 857 (1962).

[2] M. S. Anand and R. P. Agarwala, Trans. AIME **239**, 1848 (1967).

[3] M. S. Anand, S. P. Murarka, and R. P. Agarwala, J. Appl. Phys. **36**, 3860 (1965).

[4] J. E. Hilliard, B. L. Averbach, and M. Cohen, Acta Met. **7**, 86 (1959).

[5] N. L. Peterson and S. J. Rothman, Bull. Am. Phys. Soc. **12**, 324 (1967); preceding paper, Phys. Rev. B **1**, 3264 (1970); and (private communication).

[6] M. Beyeler, thesis, University of Paris, 1968 (unpublished).

[7] T. Heumann and H. Böhmer, J. Phys. Chem. Solids **29**, 237 (1968).

[8] D. Lazarus, Phys. Rev. **93**, 973 (1954).

[9] A. D. LeClaire, Phil. Mag. **7**, 141 (1962).

[10] P. B. Ghate, Phys. Rev. **133**, A1167 (1964).

the nearest-neighbor distance a and Z_V is the valence of the solvent. The difference in migration activation energy between solute and solvent ΔH_2, obtained by considering the saddle-point configuration with two half-vacancies flanking the impurity, is given by

$$\Delta H_2 = Z_V eV(11a/16) - \Delta E. \tag{4}$$

Consequently, ΔQ, the difference in impurity and solvent activation energies, becomes

$$\Delta Q = Z_V eV\left(\frac{11a}{16}\right) - R\frac{\partial \ln f_2}{\partial(1/T)}, \tag{5}$$

where f_2 is the correlation factor for the impurity, and accounts for nonrandomness of the impurity motion. The temperature dependence of f_2 arises from differences in the activation energies of the various vacancy jumps near an impurity. The first term is usually dominant and the one that determines the sign of ΔQ.

B. Diffusion in Dilute Alloys

When a small percentage of a second metal is mixed into a solvent, there is often an observable effect on the diffusion coefficients of both solute and solvent. In the limit of small impurity concentrations (about 1% or less), the change in either diffusion coefficient can generally be approximated by

$$D(c) = D(0)(1+bc), \tag{6}$$

where c is the concentration of the impurity, $D(0)$ is the diffusion coefficient at zero impurity concentration, and b is a constant characterizing the sensitivity of D to changes in c. There are two factors that lead to a dependence on solute concentration: an altered equilibrium vacancy concentration, and a change in lattice parameter caused by atomic misfits.

Lidiard[11] gives a theory for the change brought about by the first factor. If the impurities introduced into the lattice have a binding energy for vacancies, the vacancy concentration at the nearest-neighbor sites is increased. Because these vacancy-impurity complexes are mobile, the over-all diffusion coefficients of the solvent atoms is increased.

For dilute alloys, Santoro[12] has given a semiquantitative technique for assessing the effect on self-diffusion of the oscillating nature of the screening potential about the impurities. Each jump taking place in the vicinity of an impurity has its frequency altered by the factor $e^{U/kT}$, where U is the vacancy-impurity interaction energy, evaluated at the saddle-point position.

The second factor, alteration of the lattice parameter, may result in a change in migration energy and in the normal-mode frequencies of the crystal.[13] Since the migration energy is related to the size of the gate through which the jumping atom must pass, a contraction of the lattice should cause a corresponding increase in the migration energy, and vice versa. As for the normal-mode effect, the interatomic "spring constant" increases upon lattice contraction and decreases upon expansion, bringing about a corresponding change in the frequency factor. This change in frequency factor would affect the diffusion rate in the opposite sense to that caused by the altered migration energy.

III. EXPERIMENTAL PROCEDURE

Single crystals of 99.999% purity were grown in graphite crucibles under a vacuum in a modified Bridgman-type furnace. They were cut into $\frac{1}{2}$-in. lengths with a spark cutter, and polished flat on emery paper. Prior to use, the specimens were vacuum annealed. The compositions of the alloy specimens were determined from density measurements.

Tracers in the form of Ag^*Cl, Au^*Cl_3, Cu^*Cl_3, Cd^*Cl_2, and Fe^*Cl_2 were used. For diffusion, the specimens were sealed in vycor tubes under a pressure of about 400 mm Hg of He and 10 mm Hg of Cl_2. At high temperatures, the chlorine acts as an etchant, removing a thin layer of material from the surface and thereby allowing the tracer to diffuse into the bulk, unimpeded by oxide. We are indebted to Dr. Y. Adda of Saclay for the suggestion of this technique. The metallic tracer is produced by the reaction of the respective chlorides with Al. This proceeds sufficiently rapidly at diffusion temperatures so that no error in the effective diffusion time is introduced. The by-product $AlCl_3$ is a gas at these temperatures. The He acts as a buffer, slowing down the rate of evaporation and giving the respective chlorides time to react with Al. Once the tracer is in metallic form, the amount of evaporation becomes very small. The diffusion temperatures were measured with external chromel-alumel thermocouples, calibrated against a platinum-rhodium couple obtained from the National Bureau of Standards. Corrections were made for sample warmup time.

In diffusing the iron tracer, a slight change in procedure was followed, in an attempt to minimize any effect of the rapidly decreasing solubility of iron at lower temperatures. Before diffusing the tracer at a low temperature, a short anneal at a higher temperature, 620°C, was carried out. In this way, the initial phase of diffusion, when the surface concentration of the tracer is in excess of the solubility, is similar for all the specimens. The diffusion taking place during this period (about 5% of the total diffusion) necessitated only a small correction.

The specimens were sectioned on a lathe, using standard techniques. Because of the chlorine attack at the onset of diffusion, the surface was slightly pitted. However, this presented no problem and was so small that the first section removed it all. The thickness of

---

[11] A. B. Lidiard, Phil. Mag. **5**, 1171 (1960).

[12] C. J. Santoro, Phys. Rev. **179**, 593 (1969).

[13] J. S. Koehler and T. Kino, J. Phys. Chem. Solids **28**, 317 (1967).

TABLE I. Diffusion of Ag*, Au*, Cd*, and Cu* in aluminum.

Tracer	Temperature (°C)	Diffusion coefficient (cm^2/sec)
Ag*	342	1.44×10^{-11}
	420.5	1.92×10^{-10}
	470	7.47×10^{-10}
	581	8.76×10^{-9}
	610	1.51×10^{-8}
Au*	423	2.5×10^{-10}
	423	2.7×10^{-10}
	496.5	1.61×10^{-9}
	566	7.25×10^{-9}
	578	9.0×10^{-9}
	609	1.59×10^{-8}
Cd*	441	8.4×10^{-10}
	482	2.44×10^{-9}
	550	1.36×10^{-8}
	615	4.77×10^{-8}
	634	7.36×10^{-8}
Cu*	608	5.4×10^{-9}
	489	3.44×10^{-10}

each section was determined from its weight, and the specific activity was obtained by counting in a well crystal. Half-life and coincidence loss corrections were made when necessary.

IV. RESULTS AND DISCUSSION

A. Diffusion of Silver, Gold, Cadmium, and Copper in Pure Aluminum

The results for the diffusion of Ag^{110}, Au^{198}, Cd^{115m}, and Cu^{64} are given in Table I. The penetration profiles shown in Fig. 1 for cadmium are typical. The Arrhenius plots are shown in Fig. 2 and the activation energies and frequency factors, with their probable errors, are given in Table II. The calculated probable errors in activation energies, including those of random nature, vary from less than 0.1% for silver to almost 1% for cadmium. The shorter diffusion times and the smaller quantities of tracer used in the latter case could account for the increase in scatter. Including probable errors in temperature, a reasonable estimate of the total uncertainty in Q and D_0 is about 2 and 40%, respectively.

Our data on the diffusion of silver and gold and our two measurements with copper are in excellent agreement with the corresponding measurements in aluminum by Peterson and Rothman.[5] Most of the diffusion coefficients are within 5%. For the diffusion of silver in aluminum, a similar agreement exists with the results of Heumann and Böhmer.[7] There is good, but less striking, agreement with the results of Beyeler[6] for the diffusion of copper, silver, and gold, and there is only fair agreement with the results of Anand and Agarwala[2] on the diffusion of silver in aluminum. For cadmium, however, both our diffusion coefficients and our activation energies are in gross disagreement with those of Anand and Agarwala.[2] It would appear that Anand and Agarwala's 21.7-kcal/mole activation energy and 8×10^{-8}-cm^2/sec pre-exponential factor must characterize a surface effect, discussed later, rather than bulk diffusion.

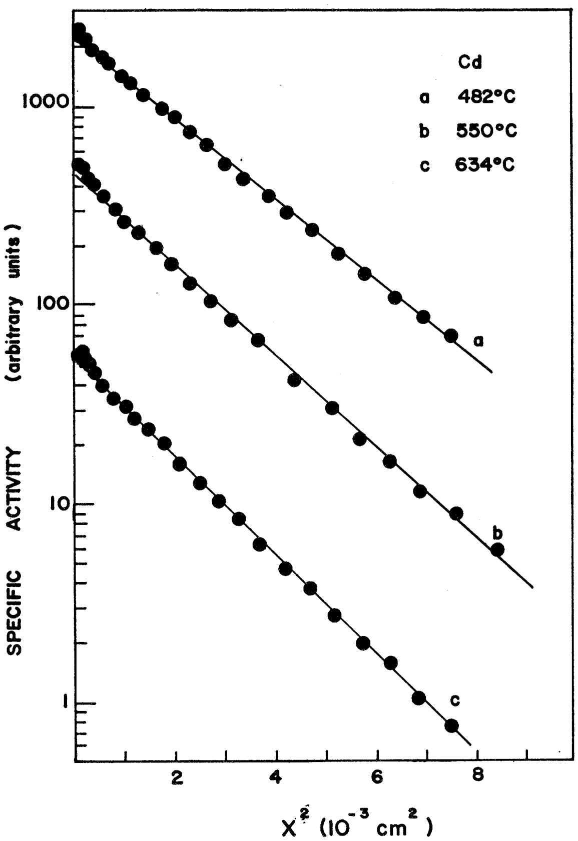

FIG. 1. Penetration profiles for the diffusion of Cd^{115m} in aluminum.

Other non-transition-metal impurities have been diffused in aluminum by Peterson and Rothman[5]; these include germanium, gallium, and zinc, all of which are found to have an activation energy of 29 kcal/mole. Since, other than transitional impurities, only impurities with closed d-electron shells have been studied in aluminum, the generality of any conclusions to be drawn may be limited.

Interpretations of impurity diffusion begins with a comparison of activation energies with that for self-diffusion. Unfortunately, because of the difficulties involved in using the aluminum radioactive tracer, the tracer self-diffusion activation energy has not been determined as precisely as for other metals. For this reason, Peterson and Rothman[5] have considered the NMR work of Fradin and Rowland[14] to yield the most accurate value for the activation energy. Then, from the high-temperature tracer measurement of Lundy and Murdock,[15] which should give the best absolute value for a self-diffusion coefficient, they have obtained D_0. They, thus, arrive at the expression

$$D=0.11\exp(-29\,000/RT)\ \mathrm{cm^2/sec}$$

---

[14] F. Y. Fradin and T. J. Rowland, Appl. Phys. Letters **11**, 207 (1967).

[15] T. S. Lundy and J. F. Murdock, J. Appl. Phys. **33**, 1671 (1962).

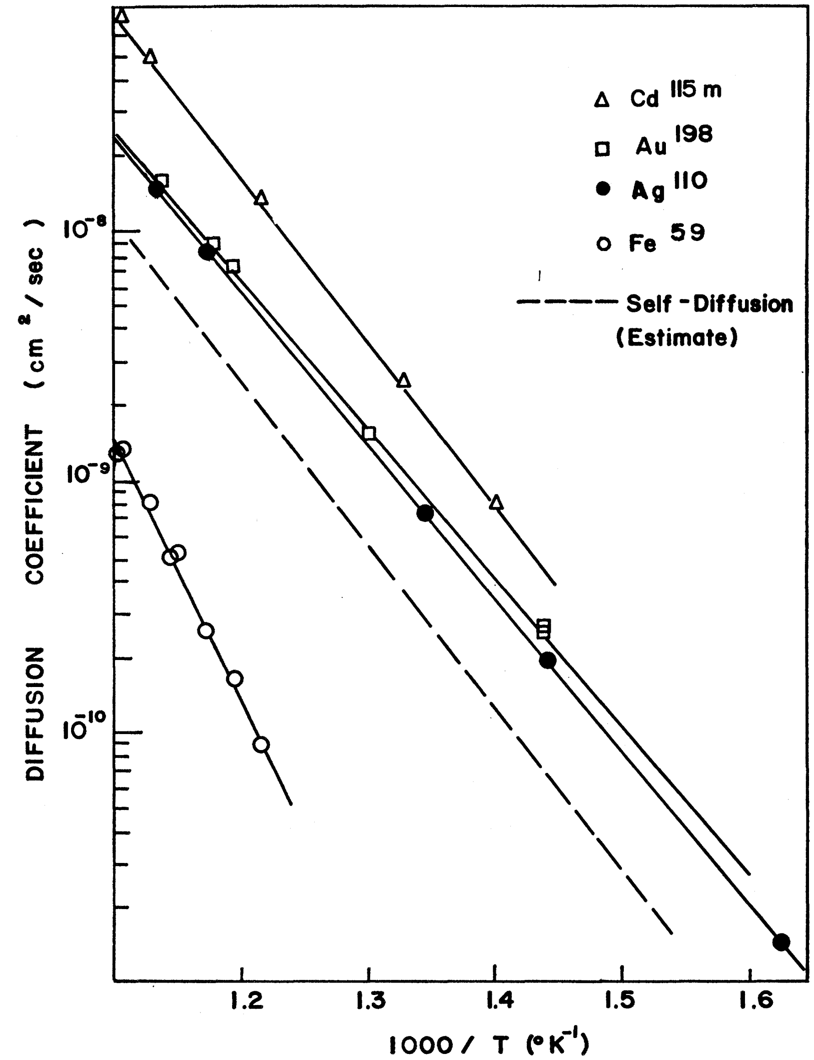

FIG. 2. Arrhenius plots for the diffusion of Cd^{115m}, Au^{198}, Ag^{110}, and Fe^{59} in aluminum. For self-diffusion, the estimate mentioned in the text is shown.

for self-diffusion. If one accepts this expression (included in Fig. 2), then it is seen that all of the impurities yet studied which contain closed *d* shells have activation energies near that for self-diffusion. The diffusion coefficients themselves, however, are about the same as or larger than that for self-diffusion. Thus, although the small variations in activation energy do not appear to correlate with impurity ion valence, there does seem to be a relation between diffusion coefficient and valence, when only impurities from the same row of the periodic table are considered. The fact that the higher the valence, the faster the ion diffuses, is an observation in apparent agreement with the expectations of the electrostatic model.

The fact that diffusivities vary more regularly with valence than the activation energies has been noted previously for diffusion of impurities in the divalent zinc.[16] The reason for this behavior is in part attributed to the nonlinear way in which the compensating effect of the temperature dependence of the correlation factor enters into the determination of the activation energy. This, together with the fact that relative diffusion rates can be determined more precisely than the corresponding temperature dependences, probably makes relative diffusion coefficients a better indicator of systematics.

The row of the periodic table in which the impurity is found is, however, apparently as important a factor as is valence in determining diffusion rates. For homo-

TABLE II. Impurity-diffusion parameters in aluminum.

Tracer	Activation energy (kcal/mole)	Pre-exponential factor (cm²/sec)
Ag^{110}	28.0±0.014	0.13 ±0.0013
Au^{198}	27.0±0.11	0.077±0.005
Cd^{115m}	29.7±0.26	1.04 ±0.17
Fe^{59}	46.0±1.4	135 ±68

---

[16] J. S. Warford and H. B. Huntington, Phys. Rev. (to be published); and (private communication).

TABLE III. Diffusion of silver and copper in dilute aluminum alloys.

Tracer	Temperature (°C)	Pure aluminum	1% silver alloy	1% copper alloy	1% zinc alloy
Ag^{110}	342.0	1.44×10^{-11}	1.49×10^{-11}	1.55×10^{-11}	
	411.3	1.6×10^{-10}[a]	1.64×10^{-10}	1.76×10^{-10}	1.72×10^{-10}
	469.8	7.6×10^{-10}[a]		7.87×10^{-10}	
	558.0	5.4×10^{-9}[a]	5.3×10^{-9}		5.74×10^{-9}
	581.2	8.76×10^{-9}	8.89×10^{-9}	9.52×10^{-9}	
	613.2	1.5×10^{-8}[a]		1.88×10^{-8}	
	634.0	2.2×10^{-8}[a]		3.64×10^{-8}	
Cu^{64}	489.0	3.44×10^{-10}	3.88×10^{-10}	4.02×10^{-10}	
	608.0	5.4×10^{-9}	6.17×10^{-9}	7.92×10^{-9}	

[a] Values taken from the graph (Fig. 2).

valent impurities, the diffusion coefficient in aluminum increases from Cu to Ag to Au, with a corresponding decrease in activation energy. Likewise, comparing with the data of Peterson and Rothman[5] shows that Cd diffuses faster than Zn, even though its activation energy is larger by 1 kcal/mole.

The inappropriateness of the Thomas-Fermi screening potential in aluminum is apparently important, but not sufficient to explain the data. Numerical potentials similar to that calculated by Worster and March[17] may be better. Even the Friedel[18] asymptotic form may be satisfactory at the nearest-neighbor site and beyond. In either case, a potential minimum occurs in the region of the nearest-neighbor position. This screening overshoot is expected to give rise to an attractive binding energy between a vacancy and a screened impurity of like charge. The effect of this screening valley on the diffusion coefficient stems from a reduction in the vacancy formation energy next to the impurity and possibly through an altered correlation factor. However, it appears that the effect of incorporating the Friedel-type potential into the LeClaire[9] form of the electrostatic theory is insufficient to alter the qualitative prediction of ΔQ. From Eq. (5), one can see that the screening potential at the saddle-point distance $11a/16$, rather than at the nearest-neighbor distance, is dominant in determining the sign of ΔQ. At this distance reasonable point-charge Friedel-type potentials are similar to the Thomas-Fermi potential.

The suggestion of Edelglass and Ohring[19] that $14a/16$ be used as the distance between impurity and half-vacancy rather than $11a/16$ of the LeClaire theory[9] makes the effect of the screening overshoot more important. However, this model is both arbitrary and cannot account, simultaneously, for the fast diffusion of the monovalent and divalent impurities in aluminum as well as the fast diffusion of the quadrivalent germanium.[5]

Three features suggest that considerations beyond valence effects are needed: (1) the fast diffusion of monovalent and divalent impurities, (2) the smallness of the variations in activation energies, and (3) the apparent sensitivity of diffusion coefficients to the row of the periodic table. Certainly the effects arising from dissimilarity of the core states of solvent and solutes are not without significance. The aluminum ion cores are quite small (about 0.5 Å) and do not overlap, probably not even during the atomic jumps. On the other hand, the closed *d* shells of the solute cores (especially the monovalent ones) are very large and may extend as far as the nearest-neighbor site. Because of this disparity in size and electronic structure, cancellation of core effects may not occur as completely as when solute and solvent are more similar. One of the more obvious consequences of the core-size effect is the exclusion of conduction electrons from the core regions of the impurity ions, through the action of the Pauli principle. This alters the distribution of screening charge, making the ion appear more positive. A second effect, somewhat more difficult to assess, is the extension of core wave functions beyond the half-vacancy positions. For example, for the copper ion, where accurate wave functions have been calculated,[20] the charge of the *d* electrons outside a sphere of radius $11a/16$ is $0.015e$. If one considers point half-vacancies located at this distance as interacting with the unshielded portion of the nuclear charge, then there is an interaction energy of 7 kcal/mole directed opposite to, and, thus, tending to cancel, the electrostatic interaction of Eq. (5). For silver and gold, the extension of the closed *d* shells is even larger. Of course, the extension of the core wave functions and the screening by the conduction electrons probably cannot be treated independently, but in aluminum the consideration of both may be required, especially when solvent and solute core structures are very much different.

B. Diffusion of Silver and Copper in Aluminum Alloys

Several measurements of diffusion coefficients in dilute aluminum alloys were made. Because of the difficulties involved in using the aluminum radioactive tracer, the effect of small concentrations of impurities on self-diffusion can be determined only with great difficulty. For this reason, we have chosen to observe the effect that a small concentration of a solute has on

---

[17] J. Worster and N. H. March, J. Phys. Chem. Solids **24**, 1305 (1963).

[18] J. Friedel, Phil. Mag. **43**, 153 (1952).

[19] S. M. Edelglass and M. Ohring, Trans. AIME **245**, 186 (1969).

[20] D. R. Hartree and W. Hartree, Proc. Roy. Soc. (London) **157**, 490 (1936).

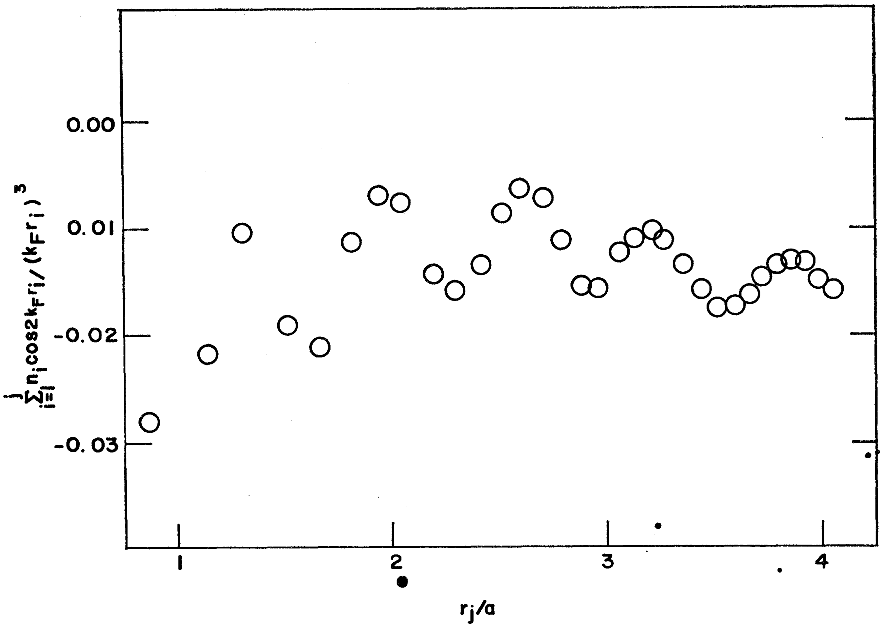

FIG. 3. Summation of terms contributing to the altered jump rates.

the diffusion of the solute itself or another impurity. A number of measurements were made of silver tracer diffusion in aluminum alloyed with 1 at.% copper or 1 at.% silver, and less extensive measurements were made in the same alloys using copper as a tracer. Additionally, silver tracer was diffused in two samples containing 1 at.% zinc. The diffusion coefficients, along with the corresponding values in pure aluminum, are given in Table III. Measurements above 600°C appear to give very large values for diffusion in the copper alloy. Since the enhancement is so much larger than that observed at the lower temperatures, and since the melting point is around 615°C and highly concentration-dependent, it may be that some local melting took place. Therefore, these values will not be considered.

In the 1% silver alloy, it is observed that the diffusion coefficient of Ag* remains almost unchanged relative to that for diffusion in pure aluminum, in agreement with the observations of Heumann and Böhmer,[7] while that of Cu* is enhanced by about 13%. A similar enhancement has been reported for self-diffusion in this alloy.[7] In the 1% copper alloys, the diffusion coefficient of Ag* is about 10% larger than in pure aluminum, while that for Cu* is one of the order of 17% larger. And in a 1% zinc alloy, Ag* was found to diffuse 7% faster than in pure aluminum.

Since for the copper and zinc alloys there was a contraction in the lattice but an increase in diffusion, and for the silver alloy there was no change in the lattice but an increase in diffusion when copper tracer was used, these results should most likely be interpreted in terms of an increased vacancy concentration in the neighborhood of the impurity atoms. This interpretation is consistent with the results of simultaneous length and lattice-parameter measurements by Beaman *et al.*,[21] where an increase of from 9 to 12% in the vacancy concentration is found near the melting point. To understand this increase, however, it appears that one must recognize the oscillating nature of the screening potential, for a Thomas-Fermi-type potential would predict a reduction in vacancy concentration in the neighborhood of an impurity.

To obtain an estimate of the expected change in diffusion when monovalent or divalent impurities are introduced into the aluminum lattice, we employ the semiquantitative method, first used by Santoro[12] to explain the enhanced self-diffusion in zinc when a small percent of silver is added. This technique is designed to account, not only for the altered vacancy concentration around an impurity, but also for the altered jump rates. In applying it to the diffusion around an impurity, one must assume that the interaction between a vacancy and impurity is not really altered by the fact that the vacancy may be adjacent to a second impurity. Additionally, one must assume that the impurity-impurity interaction during a jump is not greatly different from that at the equilibrium sites. However, it is felt that any effects resulting from these interactions will, to a large extent, cancel out when an average over all the jumps is made. For simplicity, the asymptotic form of the oscillating potential given in Eq. (2) is used. Since the phase factor is not known with any certainty, we assume, as Santoro,[12] that it may be taken to be 0. This approximate form of the potential is not so good at short distances but should be adequate in assessing long-range effects. Thus, the interaction energy between an impurity and an activated complex

---

[21] D. R. Beaman, R. W. Balluffi, and R. O. Simmons, Phys. Rev. **134**, A532 (1965).

TABLE IV. Diffusion of Fe* in aluminum.

Temperature (°C)	Diffusion coefficient (cm²/sec)	Maximum uncertainty (%)
550	8.76×10^{-11}	5
566	1.62×10^{-10}	8
580.5	2.55×10^{-10}	8
595	$5.0\ \times10^{-10}$	10
600	5.14×10^{-10}	15
614	$7.3\ \times10^{-10}$	8
633	1.35×10^{-9}	8
635.5	1.27×10^{-9}	5

at a distance r_i from the impurity is given by

$$U_i \simeq z3e\pi k_F \cos 2k_F r_i/(k_F r_i)^3,$$

where z in the effective charge of the impurity, k_F is the Fermi wave vector, and the factor 3 accounts for the vacancy having an effective charge of $-3e$. Consequently, upon expanding $e^{U/kT}$, the fractional increase in the number of jumps in a given time is given by

$$N=(c/kT)\sum_{i=1}^{j} n_i U_i,$$

where c is the fractional impurity content and n_i is the number of saddle-point sites located at a distance r_i from an impurity. In practice, one need only include the first few terms in the sum, for the later terms become small very rapidly and to a large extent are self-canceling. This is shown in Fig. 3, where

$$\sum_{i=1}^{j} n_i \frac{\cos 2k_F r_i}{(k_F r_i)^3}$$

is plotted as a function of r_j/a, a being the nearest-neighbor distance. It appears that the sum converges to a number close to -0.015. Consequently, it is found that for aluminum alloys containing 1 at.% of a monovalent impurity one would expect about a 10% increase in diffusion coefficient, while a 5% increase is expected for alloys containing 1% of a divalent impurity. With the exception of the diffusion of Ag* in the 1% silver alloy, the agreement with experiment is so good that it seems fortuitous. The lack of agreement in this one case is apparently due to the large (1.26-Å) ionic radius of silver. When two silver impurities and a vacancy are each nearest neighbors of the other, the nearest-neighbor distance is 2.8 Å. However, when the activated complex is formed, the separation of the silver atoms is reduced to 2.43 Å, producing an overlap of the ion cores. When this occurs the repulsion is expected to be much greater than that obtained from the point-charge screening potentials used in this calculation.

C. Diffusion of Fe* in Aluminum

The results for the diffusion of Fe^{59} in aluminum are given in Table IV. Out of the 20 specimens used, only eight were found to give usable results, as judged by the extent to which the penetration plots were Gaussian. The lack of success in the remaining runs is attributed to a number of factors. In the early experiments, excessive amounts of tracer were used, and non-Gaussian profiles resulted, presumably in large part because of the vanishing solubility of iron in aluminum. Sometimes there was insufficient gas pressure in the capsule to retard the evaporation of $FeCl_3$, again resulting in unusable penetration plots. Further, no runs above 640°C were successful because the surface on which the iron was deposited became too rough during the high-temperature anneal to give good one-dimensional geometry (2–10 sections were required to remove the roughness from the surface). The steps subsequently taken to eliminate the first two problems have been mentioned above.

Some of the iron penetration profiles are shown in Fig. 4. Only the data from such Gaussian profiles are included in Table IV. Since as the procedures evolved there were some variations in experimental conditions, such as different ambient pressures of helium and chlorine and different concentrations of tracer, not all the specimens gave equally good penetration plots. When the slope of the penetration plot was slightly ambiguous, the difference between the two extremes in slope was determined, and, thus, a maximum uncertainty is also given in Table IV. Within experimental error, the data appear to be self-consistent.

The best Arrhenius fit to the data gives an activation

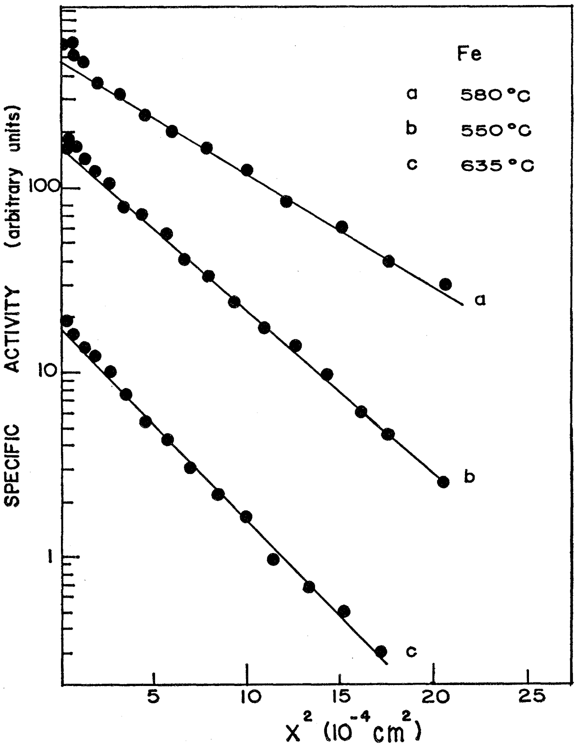

FIG. 4. Penetration profiles for the diffusion of Fe^{59} in aluminum.

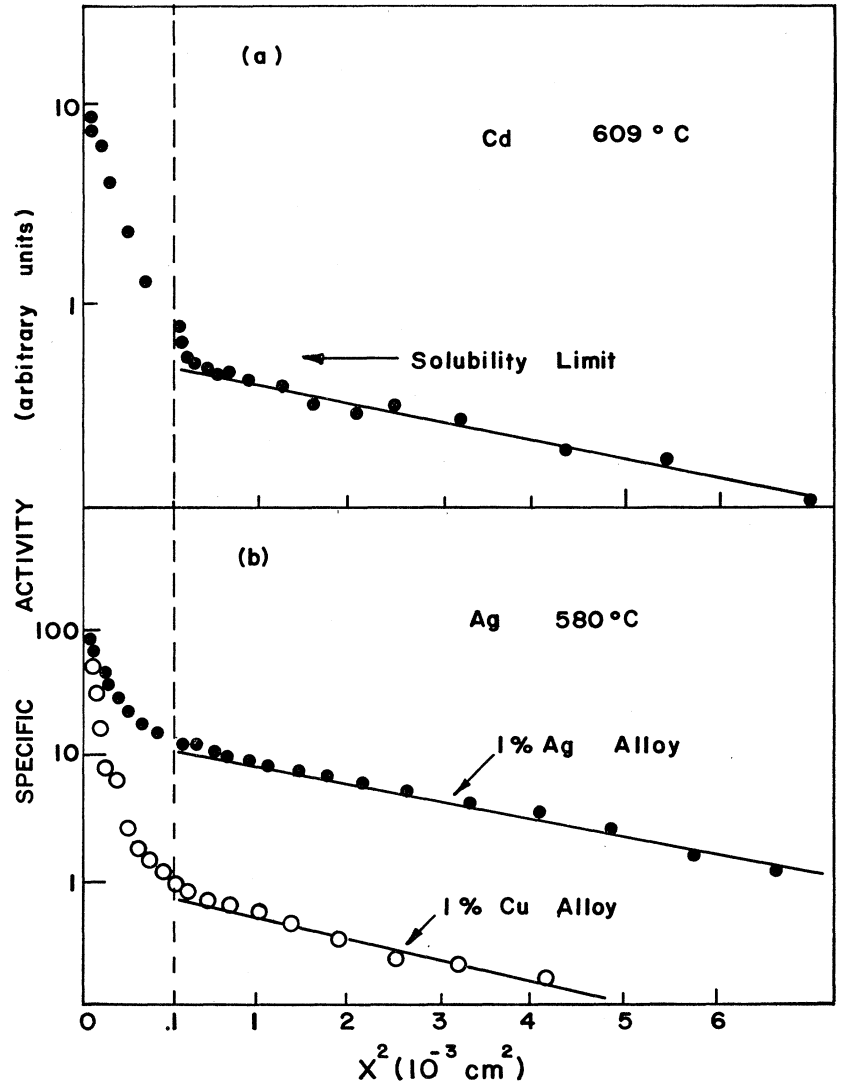

FIG. 5. Surface holdup in activity produced by (a) impurity concentration in excess of the solubility and (b) an oxided surface. For distances less than 100 μ (0.1 on the abscissa), the scale is magnified by a factor of 10.

energy of 46 kcal/mole and a pre-exponential factor of 135 cm^2/sec. The probable error in activation energy is calculated to be 3% and that in the pre-exponential factor 50%. Errors resulting from temperature determinations could amount to 1%. Some error related to the low solubility of iron in aluminum is conceivable. However, the procedure of a brief high-temperature pre-anneal for the lower-temperature runs, as previously described, should minimize the effect of this on the determination of the activation energy.

Both of the presently obtained diffusion parameters (activation energy and pre-exponential factor) are considerably larger than those obtained by Hirano *et al.*[1] We give arguments later that their data probably do not pertain to volume diffusion. Our values of the diffusion coefficients do agree reasonably well with those found recently by Hood.[22] However, the present activation energy and frequency factor are much lower than his 69 kcal and 10^5 cm^2/sec, respectively. Our value of the pre-exponential factor leads to a more readily acceptable entropy of activation than the 17*k* deduced from Hood's results. Unfortunately, the rapid decrease in the solubility of iron with decreasing temperature prevents measurements over as large a temperature range as is conventional. A relatively small disparity in values of diffusion coefficient at the extreme temperatures is, thus, responsible for this rather large difference in diffusion parameters. Another transitional impurity, cobalt, has been studied in aluminum by Peterson and Rothman.[5] Their values of activation energy (41.7 kcal/mole) and pre-exponential factor (464 cm^2/sec) are comparable to the present results for iron. Cobalt diffusion coefficients somewhat larger than those for iron were observed.

D. Near-Surface Holdup

A large number of our early diffusion runs gave penetration profiles similar to those shown in Fig. 5(b).

---

[22] G. M. Hood, Bull. Am. Phys. Soc. 13, 487 (1968).

In these runs, conventional electroplating and vacuum anneals were employed. For the most part, silver was the tracer and 1% copper- and 1% silver-aluminum alloy specimens were used. The first portion of such a profile is characterized by a rapid fall in activity, which to a fair approximation could be fit to a Gaussian. The second portion has a much smaller slope that is typical of bulk diffusion. When the experimental procedure was altered, as described above, the first portion was suppressed. Therefore, one can only conclude that this is a surface-related phenomenon, while the deeper regions show bulk diffusion.

The nature of the holdup is not fully understood. The shape of the profile appears to be remarkably similar to that obtained when an excessive amount of tracer with a low solubility is used, as shown in Fig. 5(a) for cadmium diffusing into aluminum. However, the solubility of silver in these alloys is quite high. Additionally, good penetration profiles were obtained later with identical amounts of tracer, but with a different depositing procedure.

The presence of the oxide on the surface must, therefore, be the core of the problem. The phenomenon is not entirely simple, however, for the oxide is, in fact, on the surface (presumably only a few atom-layers deep), while the holdup extends 100 μ or more into the sample. If the oxide were blocking the diffusion, one would expect a sizable fraction of the tracer to remain on the geometric surface. However, the first section, which contains all the oxide layer, usually has no more than twice the activity of the second section. From a simple holdup model, one might expect the data to fit an error curve; however, this is often not the case. The break appears to be much too sharp, and the sum of two Gaussians give a much better fit. In this connection, it is interesting that NMR studies of fine aluminum particles[23] show effects of the surface oxide which seem to influence properties rather deeply into the specimen.

The diffusion coefficient obtained in the second portion of such curves is larger than the value obtained when no holdup occurs. This apparent increase in diffusion coefficient could possibly be attributed to the short circuiting by dislocations. The scatter present in our data points is also indicative of this.

Mortlock[24] has discussed a number of experiments where similar experimental phenomena are observed. He concludes, as we do, that the second portion of the curves characterizes the bulk diffusion and that the first portion is a surface-related effect. Furthermore, he suggests that a number of the anomalously low diffusion coefficients may, in fact, be characteristic of this surface phenomenon rather than bulk diffusion. Recently, however, a number of diffusion coefficients of impurities in aluminum have been reported by Anand and Agarwala.[2] They find that impurities with low solubilities diffuse with anomalously small diffusion coefficients and argue that this is not a surface effect. In the present experiment, however, cadmium, which is one of the impurities reported by Anand and Agarwala to be anomalous, has also been studied. The present paper demonstrates that Cd* diffuses normally, as can be seen from Fig. 2. In addition, it was found that with the chlorine treatment, iron, one of the first impurities that was found by Hirano *et al.*[1] to be anomalous, gives results quite similar to those previously obtained for iron in the noble metals. Thus, the present experiment supports the view that the anomalously low diffusion coefficients which were previously reported in aluminum do not characterize the bulk diffusion, but rather are artifacts due to unfavorable surface conditions. Similar conclusions have been reached in other experimental investigations.[5,22]

V. CONCLUSIONS

The present paper has shown that the surface oxide on aluminum can perturb the diffusion penetration plots to quite large depths, producing the anomalously low diffusion coefficients, such as those previously found for the diffusion of iron and cadmium. The fact that they do not characterize bulk diffusion but a surface phenomenon is shown by the present measurements.

For the nontransitional impurities, the observations are not totally explained by the screened interaction theory. The variations in activation energy were small and no consistent correlation with valence was observed. The diffusion coefficients themselves show a slight but systematic dependence on both valence and row of the periodic table. This latter dependence suggests that dissimilarity of solvent and impurity core states could be important. For the transitional impurity iron, the diffusion coefficient was smaller and the activation energy was larger than that obtained for nontransitional impurities.

In dilute aluminum alloys, an enhanced solute diffusion was observed. A semiquantitative interpretation is made in terms of the oscillating nature of the electrostatic screening potential.

ACKNOWLEDGMENTS

We wish to thank Dr. N. L. Peterson and Dr. S. J. Rothman, and also Dr. M. Beyeler, for making their results available to us prior to publication, and one of us (W. A.) would like to thank Dr. H. B. Huntington for a number of helpful discussions.

---

[23] H. Kessemeier (private communication).

[24] A. J. Mortlock, Acta Met. 12, 675 (1964).