

Kinetics of Vacancy Motion in High-Purity Aluminum

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It is shown that in very high-purity aluminum, Al_{II}, the rate of vacancy annealing depends on vacancy concentration and annealing temperature but is independent of the temperature T_i of vacancy injection *per se*. The rate can be described as the sum of first and second order components. The first order component becomes most prominent at a monovacancy concentration estimated to be 10^{-6} atom fraction. It is shown that the results are consistent with the Koehler-Seitz-Bauerle dissociative mechanism. The activation energy for diffusion of monovacancies in Al_{II} is found to be 0.65 ± 0.06 ev. This, combined with earlier results on the formation energy of vacancies, gives 1.44 ± 0.11 ev for the activation energy for self-diffusion in aluminum by a monovacancy mechanism.

In zone-refined aluminum, Al_I, of lesser purity the rate of vacancy annealing depends upon T_i *per se* and falls off more rapidly with decreasing vacancy concentration than in Al_{II}. Two hypotheses for the impurity effects are considered, namely: (1) trapping of vacancies by impurity atoms and (2) inhibition of dislocation climb by adsorbed impurities.

WHEN metals are quenched to some low temperature, T_a ("annealing temperature"), after having been heated at a relatively high temperature, T_i ("injection temperature"), it is found that their resistivity,¹ specific volume¹ and energy² all change ("recover") with time and finally approach limiting values presumed to be characteristic of the equilibrium state at T_a . It is generally supposed that this "recovery" corresponds to the falling of the concentration of point lattice defects, retained in cooling from the injection temperature, to its equilibrium value at the annealing temperature.

The temperature dependence of the total resistivity recovery $\Delta\rho_0$ in aluminum has been determined by Bradshaw and Pearson,³ Panseri and Federighi,⁴ and the authors.⁵ The results are described by the equation:

$$\Delta\rho_0 = A \exp[-E_f/kT_i], \quad (1a)$$

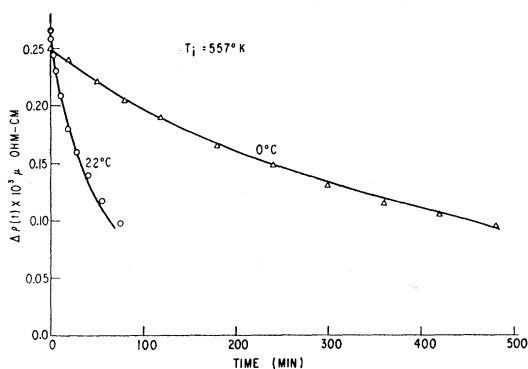


FIG. 1. Resistivity recovery isotherms for Al_{II} (injection temperature 557°K). The experimental points are fitted by Eq. (4) (corresponding to solid curves) with constants given in Table II.

¹ J. E. Bauerle and J. S. Koehler, Phys. Rev. **107**, 1493 (1957).

² W. DeSorbo, Phys. Rev. Letters **1**, 238 (1958).

³ F. J. Bradshaw and S. Pearson, Phil. Mag. **2**, 570 (1957).

⁴ C. Panseri and T. Federighi, Phil. Mag. **3**, 1223 (1958).

⁵ W. DeSorbo and D. Turnbull, Acta Met. **7**, 83 (1959).

with the values of the constants given in Table I. Also given is $\Delta\rho_0$ at the melting point T_m of aluminum. All three investigations are in fair agreement on the magnitude of E_f , the energy of formation of point defects (presumed to be lattice vacancies).

Takamura⁶ and the authors⁵ have found that the length of aluminum specimens decreases during recovery.

The simplest view⁷ of the recovery mechanism is that single-vacancies migrate to dislocations and are there annihilated with resultant climb of the dislocations. Then, if the density and efficiency of dislocation annihilation sites remains constant,⁸ the isothermal recovery kinetics should be of first order, i.e.

$$-\Delta\rho(t)/\Delta\rho(t) = k_1, \quad (1)$$

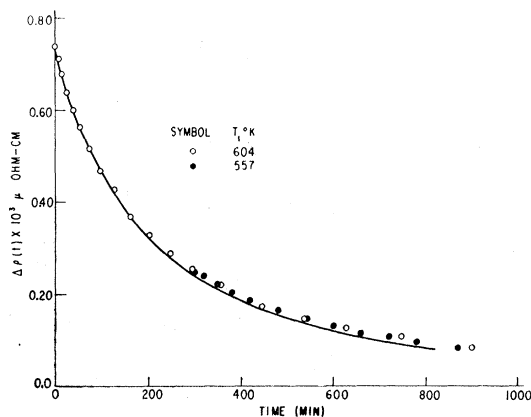


FIG. 2. Resistivity recovery in Al_{II} at 0°C for injection temperatures 557 and 604°K. The experimental points are fitted by Eq. (4) (corresponding to solid curve) with constants given in Table II for $T_i = 604^\circ\text{K}$.

⁶ J. Takamura, Met. Phys. **2**, 112 (1956).

⁷ Koehler, Seitz, and Bauerle, Phys. Rev. **107**, 1499 (1957).

⁸ Hirsch, Silcox, Smallman, and Westmacott [Phil. Mag. **3**, 897 (1958)] found that dislocation loops are formed in some metals, presumably by vacancy condensation, after being quenched to room temperature from some high temperature. However, such loop nucleation should be appreciable only at high injection temperatures, corresponding to very large vacancy supersaturations.

where $\Delta\rho(t)$ is the unrecovered resistivity after time t and k_1 is a constant which should depend on the annealing but not on the injection temperature.

Actually $\Delta\dot{\rho}(t)/\Delta\rho(t)$ usually turns out to be dependent upon $\Delta\rho(t)$ and in some cases apparently upon the injection temperature as well. Koehler *et al.*⁷ pointed out that the $\Delta\rho(t)$ dependence might result from vacancy association. In particular they showed that, if only association to divacancies is considered, the effective diffusion coefficient, D_e , of vacancies in a face centered cubic metal would be

$$D_e = \frac{D_1 + 8D_2C_1 \exp(B/kT)}{1 + 8C_1 \exp(B/kT)}, \quad (2)$$

where D_1 and D_2 are the diffusion constants of the monovacancies and divacancies, respectively, C_1 is the atom fraction of the monovacancies, and B is the binding energy of a divacancy.

Earlier investigations^{8,9,10} on the recovery rate in aluminum had shown $\Delta\dot{\rho}(t)/\Delta\rho(t)$ to be nearly proportional to $\Delta\rho(t)$. In this paper we shall describe some results on the very high-purity aluminum which indicate that some of the kinetic complexity in the earlier results may have been due to impurity effects.

RESULTS

Our experimental procedures have already been described.⁵ The aluminum used in the earlier investigation will henceforth be referred to as Al_I. It was zone refined and the residual resistivity ratio α , defined as

$$\alpha = R_{273^\circ\text{K}}/R_{4.2^\circ\text{K}},$$

was 800. The aluminum used in this investigation, Al_{II}, was from a zone refined specimen which had a residual resistivity ratio $\alpha = 4200$.

The isothermal time dependence of the vacancy resistivity in Al_{II} at 0° and 22°C for an injection temperature 284°C, is shown in Fig. 1. At a given vacancy resistivity the recovery rates $\Delta\dot{\rho}(t)$ at 0°C

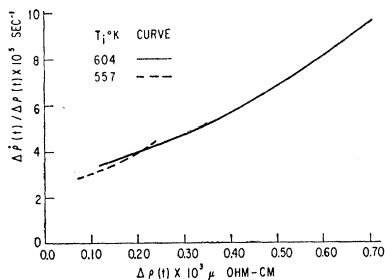


FIG. 3. Relation between $\Delta\dot{\rho}(t)/\Delta\rho(t)$ and $\Delta\rho(t)$ in Al_{II} for two injection temperatures. The slopes $\Delta\dot{\rho}(t)$ are evaluated from the best curves through the experimental points shown in Fig. 2.

⁹ T. Federighi and F. Gatto, Meeting of the Societa Italiano di Fisica, Padua, September 22, 1957 (unpublished).

¹⁰ W. Wintenberger, Rev. mét. 54, 942 (1957).

TABLE I. Constants of Eq. (1a).

A ($\mu\text{ohm-cm}$)	$E_f(\text{ev})$	$\Delta\rho_0(\mu\text{ohm-cm})$		Reference
		$T_i = T_m$	at	
1240	0.76 ± 0.04	0.09		3
800	0.76 ± 0.03	0.06		4
3055	0.79 ± 0.04	0.17		5

were nearly the same for two different injection temperatures 284° and 331°C. The resistivity-time curves for the two injections are shown in Fig. 2 and the corresponding rate curves, (from the experimental points) $\Delta\dot{\rho}(t)/\Delta\rho(t)$ vs $\Delta\rho(t)$, are shown in Fig. 3. The rate of isothermal recovery can be described by the equation

$$\Delta\dot{\rho}(t)/\Delta\rho(t) = k_1 + k_2\Delta\rho(t) + k_3[\Delta\rho(t)]^2. \quad (3)$$

Actually the isotherms, $\Delta\rho(t)$ vs t , almost can be described by carrying only the first two terms of Eq. (3). Thus we obtain

$$\ln \left[\frac{\Delta\rho(0)\{k_1 + k_2\Delta\rho(t)\}}{\Delta\rho(t)\{k_1 + k_2\Delta\rho(0)\}} \right] = k_1 t. \quad (4)$$

The curves shown in Fig. 1 were calculated from this equation with the constants given in Table II. The fit to the data would be improved by carrying an additional term from Eq. (3), but considering the possibilities for systematic errors at low $\Delta\rho(t)$, this would hardly be justified.

Our results are consistent with the Koehler-Seitz-Bauerle dissociative mechanism. According to this interpretation the first order constant k_1 should be proportional to the diffusion constant D_1 of monovacancies, and the second order constant k_2 to the diffusion constant D_2 of divacancies. More specifically,

$$D_1 = bL^2k_1, \quad (5)$$

where L is the spacing of vacancy annihilation centers (presumably dislocations) and b is a factor, determined by the distribution of centers, which is probably within an order of magnitude of unity in most cases. Similarly [see Eq. (2)]

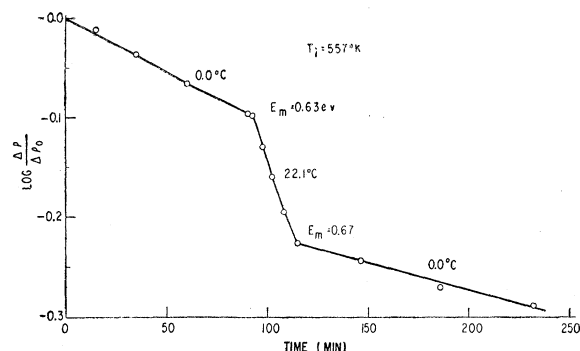
$$k_2 = \frac{8D_2 \exp(B/kT)}{bL^2\beta}, \quad (6)$$

where β is defined by

$$\Delta\rho(t) = \beta C_1(t) \quad (7)$$

TABLE II. Constants of Eq. (4) for Al_{II}.

T_i (°K)	T_a (°K)	$k_1(\text{sec}^{-1})$	$k_2(\text{sec}^{-1} \mu\text{ohm-cm}^{-1})$
557	273	2.33×10^{-5}	0.067
604	273	2.33×10^{-5}	0.092
557	295	1.2×10^{-4}	0.83

FIG. 4. Evaluation of E_m in Al_{II} by method B.

and it is assumed that C_2 is negligible in comparison to C_1 .

The first order component of recovery becomes dominant at $\Delta\rho(t) \lesssim 0.15 \times 10^{-3}$ $\mu\text{ohm-cm}$. If we take β to be 1.5 $\mu\text{ohm-cm}$ per atom $\%$, this would correspond to a monovacancy concentration $\sim 10^{-6}$ atom fraction. This result implies that $D_2 \exp(B/kT)$ is about 10^5 times the monovacancy diffusion coefficient and that $E_2 - B$, where E_2 is the activation energy for motion of divacancies, is about 0.3 eV less than the activation energy for motion of monovacancies. Thus the divacancy contribution to the recovery rate appears to be much more prominent in aluminum than in gold.

The temperature dependence of the recovery can be described by

$$\Delta\dot{\rho}(t)/\Delta\rho(t) = K \exp[-E_m/kT_a], \quad (8)$$

where K and E_m depend in general upon $\Delta\rho(t)$. One method (A) of evaluating K and E_m is to use the data from different isotherms following different injections. A possible disadvantage of this method is that the concentration and distribution of dislocations may vary from one injection to another even at constant T_i . This disadvantage is avoided in the procedure (B) of Kauffman and Koehler¹¹ in which the constants are evaluated from the $\Delta\dot{\rho}(t)/\Delta\rho(t)$ values immediately before and after an abrupt change in T_a during a single recovery (see Fig. 4 for some results obtained by this method). Actually the constants for Al_{II} , which are summarized in Table III, obtained by the two methods agree within the experimental error.

The average value of E_m obtained in method B, which is preferred, is 0.65 ± 0.06 eV. We may take this to be, approximately, the activation energy E_1 for the motion of monovacancies since it also holds for the region in which the first order contribution to (3) is dominant. Thus the activation energy for self-diffusion in aluminum by a monovacancy mechanism would be: $E_f + E_m = 1.44 \pm 0.11$ eV which is in good agreement with Spokas¹² value of 1.4 ± 0.1 eV from nuclear

TABLE III. Constants of Eq. (8) obtained (A) from time scale factors for superposition of two isotherms at given T_i ; (B) From $\Delta\dot{\rho}(t)/\Delta\rho(t)$ before and after abrupt change in annealing temperature during a single recovery.

Method	T_i (°K)	T_a (°K)	$\Delta\rho(t)$ ($\mu\text{ohm-cm}$)	K (sec^{-1})	E_m (eV)
(A)	557				0.60 ± 0.05
(B)	573	273 \rightarrow 295	0.22		0.68 ± 0.06
(B)	557	295 \rightarrow 273	0.17		0.66 ± 0.06
(B)	573	273 \rightarrow 295	0.17		0.62 ± 0.06
(B)	557	273 \rightarrow 295	0.11		0.63 ± 0.06
(B)	557	295 \rightarrow 273	0.078		0.67 ± 0.06
(B)			0	2.3×10^7	0.65 ± 0.06
					Ave. for (B)

magnetic resonance experiments. The value of K corresponding to $E_1 = 0.65$ eV and k_1 (see Table II) at 273°K is $2.3 \times 10^7 \text{ sec}^{-1}$. If the frequency factor ν_0 and entropy of activation ΔS_a for vacancy diffusion were known the dislocation spacing L could be estimated from the value of K . If, for example, we set $\nu_0 \approx 10^{13} \text{ sec}^{-1}$ and $\Delta S_a \approx 10$ eu, we obtain $L \sim 2$ microns.

In contrast with these results for very high-purity aluminum (Al_{II}) we had found⁵ that for less pure zone-refined aluminum (Al_{I}) the major part of the recovery follows second order kinetics with an apparent activation energy 0.52 ± 0.04 eV evaluated at somewhat higher vacancy concentrations corresponding to $\Delta\rho = 0.5 \times 10^{-3}$ $\mu\text{ohm-cm}$. Further in Al_{I} , $\Delta\dot{\rho}(t)$ at constant T_a appears to depend upon the injection temperature *per se* as well as upon $\Delta\rho(t)$. Actually the recovery rates in the two kinds of aluminum under the same conditions are not so different. Typical recovery rates for Al_{I} are compared with those for Al_{II} in Fig. 5. Immediately after injection, the recovery rate in Al_{I} is nearly but not quite as large as that in Al_{II} . However, as recovery proceeds, the rate falls off more rapidly in Al_{I} than in Al_{II} and after long recovery is less than $\frac{1}{2}$ as large in Al_{I} as in Al_{II} . It is noteworthy that the rate, $[\Delta\dot{\rho}]_{\Delta\rho, T_a}$, at a given vacancy concentration and annealing temperature, which is independent of injection temperature in Al_{II} , is always *higher* in Al_{I} after a fresh injection than at a later stage in a single recovery (alternatively it may be said that $[\Delta\dot{\rho}]_{\Delta\rho, T_a}$ in Al_{I} is higher the lower the injection temperature). The near correspondence of $[\Delta\dot{\rho}]_{\Delta\rho, T_a}$ in the two kinds of aluminum immediately after injection can be significant only if the density and distribution of dislocations in the two aluminums are the same.

Impurities can affect recovery by trapping vacancies or by being adsorbed on dislocations and thereby inhibiting their climb. The possibly important role of impurities in trapping vacancies was pointed out by Lomer and Cottrell.¹³ Evidence that such trapping may occur in aluminum has been adduced by Panseri *et al.*¹⁴ and by Hart.¹⁵

¹¹ J. W. Kauffman and J. S. Koehler, Phys. Rev. **97**, 555 (1955).

¹² J. J. Spokas and C. P. Slichter, Phys. Rev. **113**, 1462 (1959).

¹³ W. M. Lomer and A. H. Cottrell, Phil. Mag. **46**, 71 (1955).

¹⁴ Panseri, Gatto, and Federighi, Acta Met. **6**, 198 (1958).

¹⁵ E. W. Hart, Acta Met. **6**, 553 (1958).

The total impurity content in our Al_I is about 10^{-4} to 10^{-5} atom fraction. At this concentration level significant vacancy trapping could occur if the binding energy B_{iv} between the impurity and vacancy exceeds about 0.25 eV. Such trapping would affect the divacancy concentration significantly. To account for the results on Al_I, on the basis of impurity trapping, assuming that the dislocation concentration and configuration is the same as in Al_{II}, it seems necessary to suppose that the vacancy-impurity complex is much less mobile than the free vacancy and that the concentration of the impurity responsible for trapping is about the same as the vacancy concentration (10^{-6} atom fraction). In this case significant trapping would occur if $B_{iv} \gtrsim 0.4$ eV. It appears that trapping of vacancies by impurities would not lead to a dependence of $[\Delta\dot{\rho}]_{\Delta\rho, T_a}$ on T_i as observed for Al_I.

An alternative explanation for the impurity effect is that during recovery impurity atoms are swept to the dislocations and inhibit climb after being adsorbed there. For this to occur, the condition

$$L/a_0 \gtrsim (f/C_i C_1)^{1/2} \quad (9)$$

must be fulfilled; where a_0 is the atom diameter, C_i and C_1 are, respectively, the impurity and monovacancy atom fractions, and f is the number of adsorbed solute atoms per dislocation core atom necessary to inhibit climb. Probably f is of the order unity. For example, if $C_1 \sim 10^{-6}$ and $C_i \sim 10^{-4}$, significant adsorption of solute atoms at dislocations could occur during recovery (we suppose that there is significant trapping of impurities at dislocations at the annealing but not at the injection temperatures) if the dislocation spacing equals or exceeds 10^5 atom diameters. The climb inhibition hypothesis requires, as is observed, that $[\Delta\dot{\rho}]_{\Delta\rho, T_a}$ immediately after a high-temperature injection be higher than it was late in a single recovery.

If the dissociative mechanism is correct, the apparent activation energy for recovery should be less the higher is the vacancy concentration at which it is evaluated. There is no trend of this kind, outside the experimental error, in our determinations for Al_{II} (Table III). However, these evaluations were all made at comparatively small vacancy concentrations. If the climb

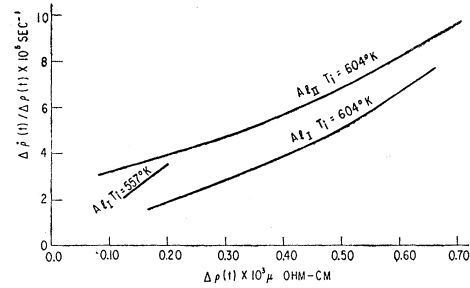


FIG. 5. Comparison of resistivity recovery rates at 0°C for very high-purity aluminum Al_{II} ($\alpha=4200$) and less pure aluminum Al_I ($\alpha=800$).

inhibition hypothesis for the impurity effect is correct or if impurity trapping becomes important only at low vacancy concentrations, the values of activation energy E_m for recovery in the less pure aluminum, as determined by method (B), should be in accord with the dissociative hypothesis. Indeed determinations on less pure specimens at higher vacancy concentrations have yielded considerably lower values for E_m . For example, we had found¹⁶ $E_m=0.37$ eV in Al_I at $\Delta\rho = 3.1 \times 10^{-3}$ $\mu\text{ohm-cm}$, corresponding to a vacancy concentration more than 10 times any at which E_m was evaluated in this investigation. Under similar conditions Bradshaw and Pearson³ found $E_m=0.44$ eV. At these levels of vacancy concentration ($C_1 > 10^{-6}$ atom fraction), the divacancy mechanism should make the major contribution to the recovery rate in pure specimens, and the activation energy does agree fairly well with that estimated for divacancy diffusion from the results on Al_{II}. Also in agreement with the dissociative hypothesis, the value $E_m \sim 0.52$ eV mentioned above for Al_I at an intermediate vacancy concentration, corresponding to $\Delta\rho \sim 0.5 \times 10^{-3}$ $\mu\text{ohm cm}$, lies between the extremal values.

ACKNOWLEDGMENT

The authors thank G. E. Nichols for his assistance in the experimental work. They are indebted to R. E. Hoffman for critically reviewing the manuscript.

¹⁶ W. DeSorbo and D. Turnbull, Bull. Am. Phys. Soc. Ser. II, 2, 262 (1957).