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THE PRESSURE EFFECT ON DEFECT MIGRATION
IN ALUMINUM

by
Brent J. Buescher

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THE UNIVERSITY OF ARIZONA

GRADUATE COLLEGE

I hereby recommend that this dissertation prepared under my
direction by Brent J. Buescher
entitled The Pressure Effect on Defect Migration
in Aluminum
be accepted as fulfilling the dissertation requirement of the
degree of Doctor of Philosophy

Roy M. Emrick
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July 30, 1969
Date

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TABLE OF CONTENTS

	Page
LIST OF ILLUSTRATIONS	v
LIST OF TABLES	vi
ABSTRACT	vii
INTRODUCTION	1
EXPERIMENTAL PROCEDURE	5
Sample Preparation	5
General Experimental Techniques and Equipment	6
Quenching and Annealing Procedure	9
RESULTS	12
DISCUSSION	19
580°C Quenches	19
331°C Quenches	24
SUMMARY	27
LIST OF REFERENCES	28

LIST OF ILLUSTRATIONS

Figure	Page
1. Sample mounted on pressure plug	7
2. Influence of pressure on annealing rate	13
3. Experimental values of (Σ_p/Σ_o) <u>versus</u> ΔP	15
4. Annealing curves for 3 isobars	16
5. Experimental values of the annealing rate <u>versus</u> pressure	18

LIST OF TABLES

Table	Page
I. Influence of Pressure on the Annealing Rate of Aluminum after 580°C Quenches	14
II. Annealing Rate of Aluminum Quenched from 331°C	17

ABSTRACT

The effect of hydrostatic pressure up to 9.5 kbar on the annealing rate of the excess resistivity in quenched aluminum was measured in two annealing regions to determine the vacancy and divacancy motional volumes ΔV_m^V and ΔV_m^{VV} . The two investigated were anneals at -65°C which followed quenches from 580°C and anneals at 0°C which followed quenches from 331°C . The results were interpreted as the annealing of vacancies and divacancies to a random sink distribution. It was found that $\Delta V_m^V = 3.02 \times 10^{-24} \text{cm}^3$ and $\Delta V_m^{VV} = 2.76 \times 10^{-24} \text{cm}^3$.

INTRODUCTION

Large non-equilibrium concentrations of vacancies and vacancy multiples are produced by rapidly quenching an fcc metal from high temperatures. The vacancies and divacancies are mobile in appropriate temperature ranges and can migrate through the lattice until they reach a sink and are absorbed.¹ The application of hydrostatic pressure changes the amount of energy necessary for an atom neighboring a vacant site to jump into it. The change in energy is equal to the external pressure times the motional volume or lattice dilatation as the jumping atom goes from a filled site to the saddle point between vacant sites.² By observing the effect of pressure on the decay rate of excess resistivity caused by the defect concentrations, one can infer a motional volume for a defect.

Pressure studies have been done on aluminum to determine the activation volume of self-diffusion and the formation volumes of vacancies and divacancies. When self-diffusion occurs by the vacancy mechanism, diffusion theory shows that the activation volume of self-diffusion is equal to the sum of the formation volume and the motional volume of vacancies. Butcher, Hutto, and Ruoff³ found the

activation volume of self-diffusion in aluminum to be $\Delta V_{sd} = 1.35\Omega$ in a high temperature creep experiment.

The atomic volume of aluminum Ω at 20°C and atmospheric pressure is $16.6 \times 10^{-24} \text{cm}^3$. The radioactive tracer diffusion technique was used by Beyeler and Adda⁴ who found the activation volume to be $\Delta V_{sd} = 1.29\Omega$. Norris⁵ measured the effect of pressure on the annealing of prismatic dislocation loops in quenched aluminum and concluded that the activation volume of self-diffusion fell between 0.44Ω and 0.87Ω .

Emrick and McArdle⁶ quenched aluminum wires at high pressure and found a vacancy formation volume of $\Delta V_f^v = 0.64\Omega$. Bourassa, Lazarus, and Blackburn⁷ measured the effect of pressure on the thermoelectric power and the electrical resistance of aluminum. The thermoelectric power experiment yielded a formation volume for a vacancy of $\Delta V_f^v = 0.54\Omega$ and a divacancy formation volume of $\Delta V_f^{vv} = 0.96\Omega$. The pressure effect on the electrical resistance yielded vacancy and divacancy formation volumes of $\Delta V_f^v = 0.60\Omega$ and $\Delta V_f^{vv} < 1.45\Omega$.

The only previous direct motional volume determination was done by Emrick⁸ on quenched gold. His value of $\Delta V_m^v = 0.15\Omega$ added to the vacancy formation volume found for gold⁶ gives a value for ΔV_{sd} that is larger than the value measured in self-diffusion experiments^{4,9} but the agreement is within the experimental errors.

The migration rate of a mobile defect is proportional to its jump frequency. The expression found for this from statistical rate calculations^{10,11} is

$$\Gamma = \nu \exp(-\Delta G/kT) , \quad (1)$$

where ν is an effective frequency and ΔG is the change in the Gibbs free energy of the crystal as the defect goes from an equilibrium position to a saddle point. The motional volume is defined by the relation

$$\Delta V_m = (\partial \Delta G / \partial P)_T \quad (2)$$

or

$$\Delta V_m = (\partial G_s / \partial P - \partial G_e / \partial P)_T , \quad (3)$$

where the saddle point and the equilibrium position Gibbs free energies are given by G_s and G_e .

When the decay of excess resistivity $\Delta\rho$ is controlled by the migration of one type of defect, the decay rate of $\ln(\Delta\rho)$ is given by

$$(1/\Delta\rho)(d\Delta\rho/dt) = -f(\Delta\rho)\Gamma . \quad (4)$$

For convenience, let $-\Sigma(\Delta\rho)$ be defined as the slope of the resistance decay curve $(1/\Delta\rho)(d\Delta\rho/dt)$. The motional volume of the defect is given by

$$\Delta V_m = -kT \left[\left(\frac{\partial}{\partial P} \ln \Sigma \right)_T - \left(\frac{\partial}{\partial P} \ln \nu \right)_T - \left(\frac{\partial}{\partial P} \ln f(\Delta\rho) \right)_T \right] . \quad (5)$$

The first term is determined experimentally. The last term depends on the nature of the defect sinks in the metal and on the kinetics of the anneal. The pressure dependence of the frequency term can be written as

$$(\partial \ln \nu / \partial P)_T = \gamma_G \kappa_T, \quad (6)$$

where γ_G is Grüneisen's constant and κ_T is the isothermal compressibility. The last two terms in Eq. (5) are usually small.

Previous experiments on aluminum^{12,13} have shown that after low temperature quenches (T_Q between 270°C and 331°C), the anneal is controlled by vacancy migration when the vacancy concentration is about 10^{-6} . After high temperature quenches ($T_Q \approx 570^\circ\text{C}$), divacancy migration has been found to be responsible for the initial resistivity decay.¹³

The purpose of this experiment is to determine the motional volumes of vacancies and divacancies in aluminum.

EXPERIMENTAL PROCEDURE

Sample Preparation

The samples consisted of a specimen and a dummy specimen made from 0.014 in. diameter aluminum wire of 99.999% purity supplied by Cominco American, Inc., Spokane, Washington. After the expansion loops were bent into the specimen and dummy wires, the wires were etched in a solution of 73% phosphoric acid, 23% sulphuric acid, and 4% nitric acid. The samples were then mounted in a frame which was fastened to the pressure plug and potential leads of 0.002 in. diameter 99.99% purity aluminum wire were spot welded about 3 in. apart on both the specimen and dummy. During the spot welding, care was taken to position the potential leads to reduce the difference in resistance of the gauge lengths of the specimen and dummy to less than $100\mu\Omega$. This procedure reduced the effect of temperature fluctuations during the experimental runs to below the resolution of the measuring circuit. The samples were then annealed for $\frac{1}{2}$ hour at 550°C , 1 hour at 300°C , and $\frac{1}{2}$ hour at 100°C to remove any strains due to cold work. This procedure was repeated after each run to remove any strains produced in quenching and to anneal out any remaining quenched-in defects.

General Experimental Techniques and Equipment

The pressure system is a standard liquid system with a separate intensifier and pressure vessel. The pressure fluid used was a mixture of equal volumes of pentane and isopentane, which remains liquid in the pressure range 1 bar to 10 kbar down to -78°C . A manganin gauge calibrated at the freezing point of mercury at 0°C (7574 bar) was used to measure the pressure in the system. The pressure vessel was made from 4340 tool steel hardened and drawn to Rockwell 40C.

The sample and frame were mounted on the pressure plug as shown in Fig. 1. A Chromel-Alumel thermocouple was used to monitor the internal temperature of the pressure vessel. Steel cones were used for electrical leads from the sample through the plug. For the thermocouple, the cones were of Chromel and of Alumel. Lavite insulators with a wall thickness of 0.012 in. were used between the cones and the plug. Since it was found that water which condensed on the plug during the transfer from the quench tank to the pressure vessel reduced the cone to plug resistance to below 1 megohm, the high pressure face of the plug was potted with Eccobond 76 epoxy.

During the anneals, the pressure vessel was immersed in a bath maintained at constant temperature. The 0°C bath was made by packing wet ice around a bath of kerosene

Fig. 1. Sample mounted on pressure plug.

1. Lead to Bridge	6. #18 Copper Wire
2. Pressure Plug	7. 0.002" Aluminum Wire
3. Steel Cone	8. Aluminum Leads
4. Spot Weld	9. 0.014" Aluminum Wire
5. Copper Frame	10. Internal Thermocouple

and allowing the vessel and bath to come to equilibrium. The -65°C bath was made by packing dry ice around an insulated container of ethanol. The bath and pressure vessel temperature was maintained by a heating coil in the bath. The bath temperatures were measured by ASTM thermometers and found to be $0.0 \pm 0.1^{\circ}\text{C}$ and $-65.0 \pm 0.1^{\circ}\text{C}$. The temperature fluctuations inside the pressure vessel were measured by the internal thermocouple and were found to be less than $0.01^{\circ}\text{C}/\text{hour}$, except for the transient produced by a pressure change. This transient decayed to less than $0.01^{\circ}\text{C}/\text{hour}$ in about 1 hour.

The quenched-in resistance was measured using the procedure first described by Bauerle and Koehler.¹⁴ The measuring current passed through the specimen and dummy was 0.100000 ± 0.000001 A. The steady thermal emf's in the circuit were cancelled out by measuring with currents in the forward and reverse directions. A Rubicon microvolt potentiometer with a Rubicon photoelectric galvanometer made it possible to determine δR , the specimen minus the dummy resistance, to $\pm 0.05\mu\Omega$.

The base resistance difference, δR_0 , of the well annealed specimen and dummy shifted during the 300°C and the 550°C anneals. Also it was found to shift when the specimen was just brought up to the quench temperature of 331°C and then annealed at 100°C for $\frac{1}{2}$ hour. This change

in δR_0 was small and in the case of the 580°C quenches the base resistance was taken to be the δR_0 measured before the quench. However, in the analysis of the annealing runs after the 331°C quenches, the shift was significant. Consequently the base resistance difference was taken to be the resistance difference δR_f measured at the end of these runs after an anneal at room temperature for $2\frac{1}{2}$ hours.

The room temperature annealing time was found to be long enough to stabilize the resistance difference δR_f as it did not change with further aging at room temperature. Since Desorbo and Turnbull¹⁵ have found that all of the excess resistance produced by quenching from 270°C to 332°C anneals out during isothermal holds at 0°C and 27°C using a low temperature measuring technique, δR_f was assumed to be the base resistance difference.

Quenching and Annealing Procedure

The specimen was placed horizontally over a quench bath of hexane at -78°C and heated by a dc current to the quench temperature. The quench was performed by allowing the sample and pressure plug to fall into the quench bath just before shutting off the heating current. The quench rate is estimated to have been 10⁴°C/sec by comparing the quenched-in resistivity with the results obtained by Bass,¹⁶ who studied quenched-in resistivity as a function of quench rate.

After the quenches from 331°C, the samples were annealed isobarically at pressures ranging from 1 atmosphere to 10 kbar at a temperature of 0°C for about 26 hours. Resistance measurements were made during the first 8 to 12 hours of the anneal to determine the rate of decay. A final resistance measurement was made at the end of the 0°C anneal. It was observed that the introduction of impurities into the specimen raised the value of the final excess resistance by a factor of 2 or 3. The base resistance difference between the specimen and the dummy was measured at the annealing temperature and pressure after an anneal at 25°C for 2½ hours.

The quenches from 580°C produced a large excess resistivity, about $4 \times 10^{-3} \mu\Omega\text{cm}$, which allowed the use of the slope intercept method. The initial anneal was done at various hydrostatic pressures ranging from 1 atmosphere to 9.5 kbar at an annealing temperature of -65°C. After about $5 \times 10^{-4} \mu\Omega\text{cm}$ had annealed out, the pressure was changed to the reference pressure of 1 atmosphere and resistance measurements were continued until an additional $5 \times 10^{-4} \mu\Omega\text{cm}$ annealed out. After an additional anneal of 14 hours, the resistance difference between the specimen and dummy was measured at both the initial and reference pressure. By this time about 60% of the quenched-in resistance had annealed out and the resistance difference δR_f was almost

constant, $d\delta R/dt < 0.05\mu\Omega/\text{hr}$. The remaining excess resistance was assumed to be due to the stage II defect concentration¹⁷ and the remaining vacancy concentration.

RESULTS

Two resistance decay curves following quenches from 580°C are shown in Fig. 2. Table I lists the results obtained in the anneals after the high temperature quenches. Σ_p is the slope of the decay curve measured at high pressure and Σ_o is the slope measured at 1 atmosphere. The values of (Σ_p/Σ_o) versus pressure are plotted in Fig. 3. Within the experimental error, the pressure dependence of $\ln(\Sigma_p/\Sigma_o)$ is linear and the value found for the slope using a least squares fit is

$$[\partial \ln(\Sigma_p/\Sigma_o)/\partial P]_T = -0.096 \pm 0.009 \text{ kbar}^{-1} . \quad (7)$$

Fig. 4 shows resistance decay curves for 3 isobars after the quenches from 331°C. Table II lists the values of the slopes of the resistance decay curves found in this region between the excess resistivity values $\Delta\rho_1$ and $\Delta\rho_2$. Fig. 5 is a semilog plot of Σ as a function of pressure. The pressure dependence of $\ln(\Sigma)$ is also linear within the experimental scatter and a least squares analysis gives

$$[\partial \ln(\Sigma)/\partial P]_T = -0.080 \pm 0.008 \text{ kbar}^{-1} . \quad (8)$$

Fig. 2. Influence of pressure on annealing rate.

Table I. Influence of Pressure on the Annealing
Rate of Aluminum after 580°C Quenches

Specimen	Σ_p (hours ⁻¹)	Σ_o (hours ⁻¹)	(Σ_p/Σ_o)	ΔP (kbar)
A	0.117	0.100	1.17	0.00
A	0.090	0.092	0.98	1.00
B	0.146	0.160	0.91	3.00
B	0.102	0.146	0.70	4.97
B	0.098	0.167	0.54	6.96
B	0.068	0.147	0.46	9.12
B	0.064	0.125	0.51	9.10

Fig. 3. Experimental values of (Σ_p/Σ_0) versus ΔP .

Fig. 4. Annealing curves for 3 isobars.

Table II. Annealing Rate of Aluminum Quenched
from 331°C

Specimen	$\Delta\rho_1$ $10^{-4}\mu\Omega\text{cm}$	$\Delta\rho_2$ $10^{-4}\mu\Omega\text{cm}$	Σ (hours ⁻¹)	P (kbar)
C	3.7	2.5	0.043	9.20
C	3.7	2.5	0.055	9.06
D	3.6	1.7	0.089	1.00
E	3.6	2.1	0.064	3.00
E	3.2	1.7	0.064	3.00
F	4.8	2.0	0.082	4.97
F	3.6	1.7	0.070	4.97
G	3.6	1.9	0.070	6.97
G	3.2	1.9	0.058	6.97
H	3.1	1.2	0.121	0.00
H	3.0	1.2	0.094	0.00
I	3.6	2.1	0.049	9.40
I	2.6	1.2	0.122	0.00
J	3.1	1.7	0.075	2.00
J	4.5	2.6	0.050	9.20
J	3.3	1.8	0.112	0.00
K	3.5	2.5	0.043	9.25

Fig. 5. Experimental values of the annealing rate versus pressure.

DISCUSSION

580°C Quenches

After high temperature quenches, the defect concentration in aluminum consists of vacancies, divacancies, higher vacancy multiples, and dislocation loops. At the cooling rate attained by quenching into cold hexane, 10^4 C°/sec, the concentrations of vacancies and divacancies present after the quench are quite different from the equilibrium concentrations at the high temperature. During the quench, a large concentration of divacancies is formed from the initial vacancy concentration. The ratio of divacancies to vacancies in quenched aluminum has been calculated by Doyama¹⁸ for various cooling rates and divacancy binding energies. From his results the divacancy concentration is calculated to be about 30% of the vacancy concentration, assuming a final vacancy concentration of 10^{-4} , a quench rate of 10^4 C°/sec, and a divacancy binding energy of 0.20 eV.

The excess resistance of the quenched specimen is given by

$$\Delta R = \beta(\rho_v c_v + \rho_{vv} c_{vv} + \Delta \rho_m + \Delta \rho_d) , \quad (9)$$

where β depends on the dimensions of the specimen, ρ_v and ρ_{vv} are the vacancy and divacancy resistivities, and c_v and c_{vv} are the vacancy and divacancy concentrations. The terms $\Delta\rho_m$ and $\Delta\rho_d$ are the resistivities of the vacancy multiples or clusters and the dislocation loops. At the annealing temperature, -65°C , the clusters and dislocation loops are stable and their concentration remains constant. The jump frequency of the divacancies is about 10^3 times the vacancy jump frequency,¹³ and the initial anneal is controlled by the migration of divacancies. In this temperature range the vacancy concentration is assumed constant during the anneal and the decay of the divacancy concentration is described by

$$(1/c_{vv})(dc_{vv}/dt) = -\alpha\lambda^2\Gamma_{vv}, \quad (10)$$

where α is the sink density and λ is the lattice parameter. Since the excess resistance $\Delta R'$ due to the divacancies is proportional to their concentration, the decay of $\Delta R'$ is given by

$$(1/\Delta R')(d\Delta R'/dt) = -\alpha\lambda^2\Gamma_{vv}. \quad (11)$$

The final resistance difference δR_f is taken to be the sum of the base resistance difference and the excess resistance due to the vacancies, the clusters, and the dislocation loops. Thus,

$$\delta R_f = \Delta R_v + \Delta R_m + \Delta R_d + \delta R_o. \quad (12)$$

The excess resistance at high pressure and at atmospheric pressure caused by the divacancy concentration is given by

$$\Delta R'(t)_p = \delta R(t)_p - \delta R_{fp} \quad (13)$$

and

$$\Delta R'(t)_o = \delta R(t)_o - \delta R_{fo} , \quad (14)$$

where $\delta R(t)_p$ and $\delta R(t)_o$ are the resistance differences measured during the initial anneal at high pressure and at the reference pressure. The final resistance differences δR_{fp} and δR_{fo} are determined at the high pressure and at the reference pressure.

The pressure dependence of the anneals is determined by comparing the decay rate before and after a pressure change. The motional volume is given by the expression

$$\Delta V_m^{vv} = -kT \left[\left(\frac{\partial}{\partial P} \ln \frac{\Sigma_p}{\Sigma_o} \right)_T - \kappa_T \gamma_G - \left(\frac{\partial}{\partial P} \ln \alpha \lambda^2 \right)_T \right] . \quad (15)$$

The contribution of the frequency term $\kappa_T \gamma_G$ is less than 2% of the first term and is neglected because of the error involved in determining the pressure dependence of the resistance decay.

The pressure dependence of the last term is determined by the nature of the sinks present in the quenched metal. Electron microscope studies of quenched aluminum have shown that the vacancy multiple or void concentration

is quite high after quenches from 570°C at cooling rates of 10⁴ C°/sec.^{19,20} Thus the sinks present are the pre-existing dislocation lines and the voids formed during the quench. The last term can be written²¹

$$\left(\frac{\partial}{\partial P} \ln \alpha \lambda^2\right)_T = \frac{\partial}{\partial P} \ln \left[2\pi N_d \lambda^2 \frac{1}{\ln(r_1/r_o)_d} + 4\pi N_v \lambda^2 r_v \right] . \quad (16)$$

In this expression N_d is the number of dislocation lines per sq cm, $(r_1/r_o)_d$ is the ratio of the average distance between dislocations to their capture radius, N_v is the number of voids per cm², and r_v is the capture radius of a void. The pressure dependence of the contribution by dislocations to the sink density is small and is assumed to be negligible. N_d has no pressure dependence and since the ratio $(r_1/r_o)_d$ is of the order of 10⁶ in a well-annealed metal, $\ln(r_1/r_o)_d$ is insensitive to large variations of the capture radius with pressure.

In the contribution from the void concentration, N_v changes by less than 1% over the pressure range 0 to 10 kbar. Kiritani²⁰ has found that the lattice is highly strained in the neighborhood of a void, which makes the pressure dependence of r_v small. This is seen by assuming the voids to be spherical holes in an isotropic solid and the strain field caused by a pressure on the external surface. In order to cause an observable compression of the solid in the

neighborhood of a void, the pressure would have to be > 10 kbar. In this case applying an additional pressure of 10 kbar on the surface would change the capture radius of a void due to its stress field by less than 25%. Since the observed change in the annealing rate over 10 kbar is $260\% \pm 26\%$, the variation of r_v is neglected.

The motional volume of divacancies is found in this region to be $\Delta V_m^{vv} = 2.76 \pm 0.28 \times 10^{-24} \text{ cm}^3$ or $0.17 \pm 0.02\Omega$. This value compares well with the motional volume calculated from the strain energy model described by Keyes.²² From the expression

$$\Delta V = 2(\gamma_G - \frac{1}{3})\kappa_T \Delta G, \quad (17)$$

the motional volume of divacancies in aluminum is calculated to be $\Delta V_m^{vv} = 0.23\Omega$. Schottky, Seeger, and Schmid²³ have calculated ΔV_m^{vv} for the noble metals. The largest divacancy motional volume they found was for copper which was $\Delta V_m^{vv} = 0.02\Omega$. More recently Doyama and Cotterill²⁴ calculated the divacancy motional volume of copper and found it to be $\Delta V_m^{vv} = 0.06\Omega$.

The large divacancy motional volume observed in aluminum may be due to the large relaxation of the lattice about a divacancy. Bourassa et al.⁷ found $2\Omega - \Delta V_f^{vv} > 0.55\Omega$ for aluminum, while the calculated values in the case of copper were $2\Omega - \Delta V_f^{vv} = 0.17\Omega$ ²³ and 0.47Ω .²⁴

331°C Quenches

After a low temperature quench, the decay of excess resistivity is controlled by vacancy migration with almost first order kinetics when $\Delta\rho \leq 2 \times 10^{-3} \mu\Omega\text{cm}$.¹² In this region the vacancy decay is described by

$$(1/c_v)(dc_v/dt) = -\alpha\lambda^2\Gamma_v . \quad (18)$$

Since the excess resistance is proportional to the vacancy concentration c_v , the resistance decay is given by

$$(1/\Delta R)(d\Delta R/dt) = -\alpha\lambda^2\Gamma_v . \quad (19)$$

The vacancy motional volume is given by the expression

$$\Delta V_m^v = -kT\{[\partial(\ln\Sigma)/\partial P]_T - \kappa_T\gamma_G - [\partial(\ln\alpha\lambda^2)/\partial P]_T\} . \quad (20)$$

The frequency term is again quite small compared to the errors involved in determining the pressure dependence of the resistance decay rate and is neglected. The dominant sinks present in aluminum quenched from below 400°C are pre-existing dislocation lines. Thus the last term is given by

$$[\partial(\ln\alpha\lambda^2)/\partial P]_T = -[\partial \ln(\ln r_1/r_o)_d/\partial P]_T . \quad (21)$$

and the pressure dependence of $\ln(r_1/r_o)_d$ is again assumed small and is neglected.

The vacancy motional volume is found in this region to be $\Delta V_m^v = 3.02 \pm 0.30 \times 10^{-24} \text{ cm}^3$ or $0.18 \pm 0.02\Omega$. This is comparable to the value found by Emrick⁸ for the motional volume of vacancies in gold. The strain energy model gives a vacancy motional volume for aluminum of 0.30Ω , which is in reasonable agreement with the experimental value. The sum of the vacancy formation volume found from pressure quenching⁶ plus the present motional volume gives $\Delta V_{sd}^v = 0.73\Omega$ for the activation volume of vacancy diffusion. This falls within the limits determined by Norris⁵ for the annealing of dislocation loops. However, the activation volume of self-diffusion measured at higher temperatures^{3,4} is well above this value.

The measured motional volume may have been lowered by the effect of second-order kinetics. Since the effect of second-order kinetics was not seen in the annealing curves, it can only be estimated. By using the steady state approximation derived by Damask and Dienes,¹ one finds that the "effective" motional volume is given by

$$\Delta V_m^{\text{eff}} = \Delta V_m^v - kT \frac{d}{dP} \ln \left\{ \alpha v_1 \lambda^2 + c_v \right. \\ \left. \times \frac{168 \alpha v_2 v_1 \lambda^2 \exp[-(E_m^{vv} + PV_m^{vv})/kT]}{14 v_1 \exp[-(E_m^v + E_b^v + PV_m^v + PV_b^v)/kT] + 2 \alpha v_2 \lambda^2 \exp[-(E_m^{vv} + PV_m^{vv})/kT]} \right\} \quad (22)$$

The effective frequencies ν_1 and ν_2 are assumed to be constant and to have the value 10^{13}sec^{-1} . The vacancy concentration is assumed to be 10^{-6} , which corresponds to an excess resistance of about $1.5\mu\Omega$.²⁵ The term $\alpha\nu\lambda^2$ is assumed to be $2.3 \times 10^7 \text{ sec}^{-1}$ as found by Desorbo and Turnbull¹² and the change of volume on the formation of a divacancy from two vacancies is taken to be $\Delta V_b = 0.12\Omega$. The migration energies are taken to be $E_m^V = 0.65\text{eV}$ and $E_m^{VV} = 0.50\text{eV}$, and the divacancy binding energy E_b to have the value 0.20eV . The difference of the vacancy motional volume minus the "effective" motional volume found by this calculation is $\Delta V_m^V - \Delta V_m^{\text{eff}} \approx 0.30\Delta V_m^V$. This difference is small compared to the difference needed to give agreement with the high temperature self-diffusion studies^{3,4} and because of the uncertain nature of the assumptions it is neglected.

Another explanation for the large activation volume measured for self-diffusion is that there is a large divacancy contribution. This explanation is supported by the apparent increase of the activation energy of self-diffusion in aluminum with increasing temperature.²⁶

SUMMARY

The pressure effect on the resistivity decays of quenched aluminum was studied. Two annealing regions were investigated and the results were interpreted assuming vacancy and divacancy migration. The motional volumes of vacancies and divacancies were obtained and had the following values:

$$\Delta V_m^v = 3.02 \pm 0.30 \times 10^{-24} \text{ cm}^3$$

$$\Delta V_m^{vv} = 2.76 \pm 0.28 \times 10^{-24} \text{ cm}^3 .$$

The motional volumes had no measurable pressure dependence. The influence of second-order kinetics may have affected the determination of the vacancy motional volume. If the resolution of the quenched-in resistance after the low temperature quenches were improved, the second order effects could be measured and accounted for. This would also allow the use of the slope intercept method in this annealing range and would eliminate the effect of sink density variation, which was a primary source of error.

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