Recovery of Electrical Resistivity in Gold Quenched from Below 700°C†

M. MESHII, T. MORI,* AND J. W. KAUFFMAN
Department of Materials Science, Northwestern University, Evanston, Illinois
(Received January 3, 1961; revised manuscript received November 3, 1961)

The residual electrical resistivity as measured at liquid helium temperature was determined as a function of annealing time at 62.4°C, for high-purity gold quenched from temperatures between 700°C and 400°C at the rate of 25 000°C/sec. For quenches begun from below 500°C an initial increase in resistivity occurs, followed by the usual decrease with aging time. The time to reach maximum resistivity is found to be a function of the quenched-in resistivity. The increase in resistivity may be due to vacancy clustering during the aging process. Further study is required to determine the role of impurity atoms in this process. For quenches above 500°C, some clusters apparently form during the quenching process and grow, acting as stable vacancy sinks during subsequent aging; hence no increase occurs for these quenches. A calculation of the formation of divacancies and trivacancies during the annealing process, neglecting interactions with impurities, shows appreciable clustering upon annealing following a low-temperature quench for binding energies of 0.3 ev. A maximum in the calculated resistivity due to formation of clusters is reached at the same order of magnitude of time as the maximum in resistivity is observed, and is followed by an approximately exponential decay which also corresponds to the experimental observations.

INTRODUCTION

As the quenching temperature is lowered, the number of vacancy-vacancy collisions occurring during the quenching process rapidly decreases; therefore, low-temperature quenches are expected to produce simpler configuration of defects than those quenches from high temperature where considerable clustering can occur. In Fig. 1 is shown the calculated number of jumps that a vacancy makes during the quenching process as a function of quenching temperature. (See Appendix.) The curve decreasing with quenching temperature represents the calculation of the number of jumps necessary for a typical vacancy to encounter another vacancy during the quenching process, assuming a random distribution of vacancies. These two curves intersect at a quenching temperature near 500°C, hence, for low-temperature quenches it becomes improbable that a typical vacancy would encounter another vacancy during the quenching process, and therefore clustering cannot occur during the quench even if the binding energy between vacancies is quite large. However, vacancy-impurity interactions could be more important for the lower temperature quenches where the relative vacancy concentrations are lower. The present research investigates the nature of the quenched-in resistivity for temperatures between 700° and 400°C.

EXPERIMENTAL PROCEDURE

Considerable care was taken to obtain specimens of high purity. The ratio of the room temperature resistivity to that at 4.2°K was above 2700 for all specimens used, with some above 4000. This ratio in resistivity indicates that the concentration of impurities in all specimens used is probably less than 10^{-5}. The samples were in the form of polycrystalline gold wire of 0.016-in. diameter. To reduce thermal emf's in the measuring circuit, the entire circuit was constructed of gold possessing close to the same purity as the specimens. Potential leads of 0.003-in. diameter were sintered to the 0.016-in. diameter specimen during the initial annealing process at 1000°C. All measurements of the residual resistivity were made with the specimens in liquid helium. The sensitivity of the electrical measurements was 10^{-12} ohm cm, which corresponds to 0.3% of the quenched-in resistivity for a quench made from 500°C. The quenching rate was 25 000°C/sec, obtained by immersing the samples in water.

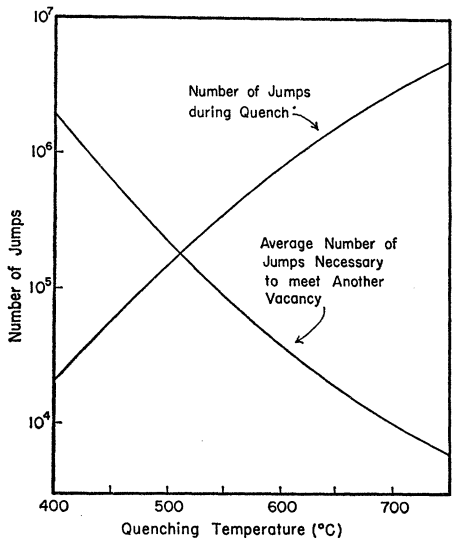

FIG. 1. The calculated number of jumps for a vacancy during the quenching process and the calculated average number of jumps for a vacancy to meet another vacancy as functions of the quenching temperature.

† Supported by the U. S. Office of Naval Research and the Advanced Research Projects Agency of the Department of Defense.
* Now at Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo, Japan.

EXPERIMENTAL RESULTS

A. Isothermal Recovery of Quenched-in Resistivity for Temperatures between 700° and 500°C

The isothermal recovery of electrical resistivity at 62.4°C is shown in Fig. 2 for the quenching temperature of 592° and 687°C. It is seen that the recovery follows the relation $\Delta\rho/\Delta\rho_0=\exp[-(t/t_0)^m]$, where m was found to equal 0.8. t_0's were found to be 6.3 hours for the quench from 687°C and 30 hours for the one from 592°C, respectively.

B. Isothermal Recovery of Resistivity for Quenches Made from Below 500°C

The kinetics of the isothermal recovery of the quenched-in resistivity was found to change as the quenching temperature was lowered below 500°C. Isothermal recoveries for quenches from below 500°C are shown in Fig. 3. An initial increase in resistivity to a maximum is followed by the usual decrease in electrical resistivity. The time to reach the maximum in resistivity is plotted against the reciprocal of the quenching temperature in Fig. 4. Following the peak of resistivity the recovery is approximately an exponential decay, with approximately constant reaction times ($t_0=30\pm3$ hr) for the various quenching temperatures.

DISCUSSION

A. The Initial Increase in Resistivity upon Aging for Quenches from Below 500°C

The physical process that gives rise to the increase in resistivity may be the formation of vacancy clusters of higher resistivity per vacancy than the individual vacancies. This assumption, however, is still open to question. A similar suggestion was made by Mott[1] to explain the increase in resistivity observed during formation of clusters of solute atoms in several aluminum alloys. Theoretical calculations by Asdenti[2] and by Harrison[3] assuming a spherical Fermi surface show no corresponding maximum for clusters of solutes in aluminum. Matyas'[4] calculations using a two-band model give a maximum in resistivity corresponding to a zone of about 7A in diameter. Recent experimental investigations of aluminum alloys by Herman and Cohen[5] give evidence that the resistance maxima are due to formation of clusters with an average diameter of 10A; the resistivity per solute atom being a maximum for this size cluster. Asdenti and Friedel[6] have calculated the resistivity introduced in copper by spherical cavities of different sizes and find the resistivity per vacancy exhibits a maximum for voids of two vacancies, and slowly decreases for larger cavities.

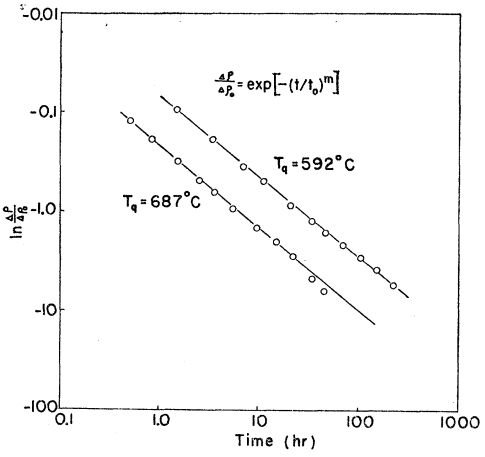

FIG. 2. The isothermal recovery of electrical resistivity at 62.4°C for the quenching temperatures of 592 and 687°C.

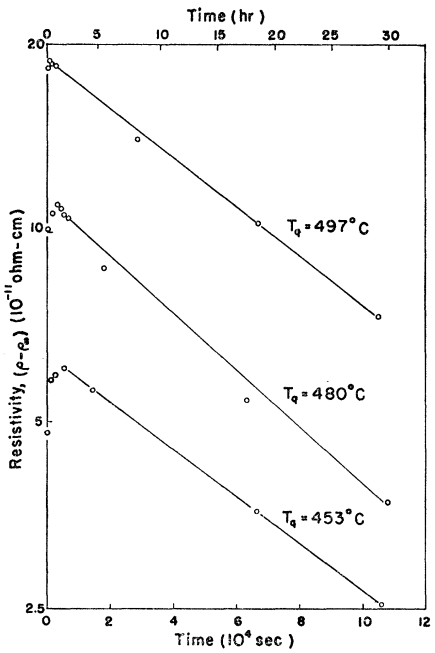

FIG. 3. The isothermal recovery of electrical resistivity at 62.4°C for the quenching temperatures below 500°C.

In order to investigate the possibility of considerable clustering occurring during aging for low vacancy concentrations the numerical solution, using the 650 IBM computer, was obtained for three simultaneous differential equations similar to those used by Koehler, Seitz, and Bauerle[7] which describes the formation of divacancies and trivacancies and the migration of single

[1] N. F. Mott, J. Inst. Metals **60**, 267 (1937).

[2] M. Asdenti, Acta Met. **9**, 587 (1961).

[3] W. Harrison, Acta Met. **8**, 168 (1960).

[4] Z. Matyas, Phil. Mag. **40**, 324 (1949).

[5] H. Herman and J. B. Cohen, Nature **191**, 63 (1961).

[6] M. Asdenti and J. Friedel, J. Phys. Chem. Solids **11**, 115 (1959).

[7] J. S. Koehler, F. Seitz, and J. E. Bauerle, Phys. Rev. **107**, 1499 (1957).

vacancies and divacancies to fixed random sinks. The distribution of single vacancies, divacancies, and trivacancies was assumed to be random throughout the process. The calculated results for the following equations[8]:

$$dC/dt = -NC\nu e^{-E_1/kT} - 12C^2\nu e^{-E_1/kT} 2C_2\nu e^{-(E_1+B)/kT} - 18CC_2\nu e^{-E_2/kT} + C_3\nu e^{-(E_2+B')/kT},$$

$$dC_2/dt = -NC_2\nu e^{-E_2/kT} + 6C^2\nu e^{-E_1/kT} - C_2\nu e^{-(E_1+B)/kT} - 18CC_2\nu e^{-E_2/kT} + C_3\nu e^{-(E_2+B')/kT},$$

$$dC_3/dt = +18CC_2\nu e^{-E_2/kT} - C_3\nu e^{-(E_2+B')/kT}$$

are shown in Fig. 5. C, C_2, C_3 are the fractional concentrations of single vacancies, divacancies, and trivacancies. For this calculation the binding energy of a divacancy B was taken to be 0.3 ev, and that for a trivacancy relative to a divacancy B' was taken to be 0.3 ev. The migration energy for single vacancies E_1 was taken to be 0.8 ev and for divacancies E_2, 0.7 ev. The sink density N equals 10^{-7}, and the vibrational frequencies were all taken to be 10^{13} per sec. It should be remarked here that the preceding simultaneous equations neglect the motion of trivacancies, the formation of clusters larger than trivacancies, and interactions with impurities. Instead of justifying simplification, the results indicate that for a binding energy of 0.3 ev considerable clustering of vacancies will occur upon aging, even for the low vacancy concentration of 6×10^{-7}. The time required to reach the peak concentration of clustered vacancies is about four hours. After this peak, the decay in the number of defects is of exponential form (Fig. 5) and from the graph t_0 is found to be 50 hr for $2C_2+3C_3$ compared with 30 hr found for the experimental decay of resistivity. These considerations do not exclude the possibility of impurities acting as nucleating sites for the formation of vacancy clusters. Indeed this appears likely.

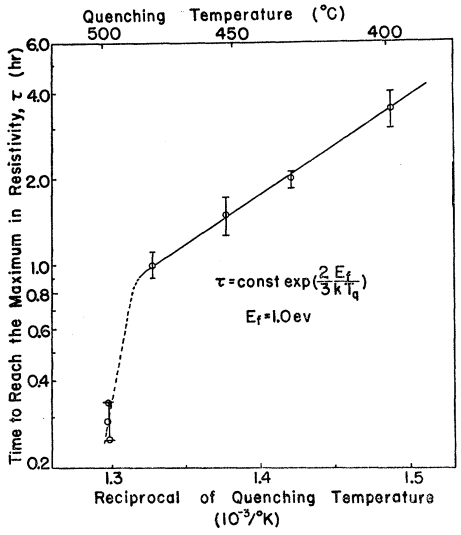

FIG. 4. Time to reach maximum in electrical resistivity plotted against reciprocal of quenching temperatures for quenches made from below 500°C.

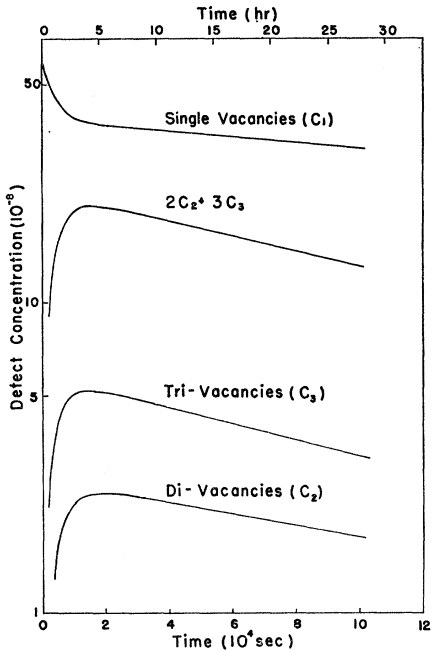

FIG. 5. The calculated concentrations of single vacancies, divacancies, and trivacancies plotted as functions of the aging time at 62.4°C.

Assuming that the resistivity maximum is due to vacancy clusters, the location will depend on the competition between the associative and dissociative terms, and hence on the relative values of the resistivities per vacancy. To consider this point let $\rho_1=\alpha_1 C$, $\rho_2=2\alpha_2 C_2$, and $\rho_3=3\alpha_3 C_3$, where ρ_1, ρ_2, and ρ_3 are the resistivities due to single vacancies, divacancies, and trivacancies, respectively. Then the total resistivity due to vacancies is

$$\rho=\alpha_1 C+2\alpha_2 C_2+3\alpha_3 C_3.$$

To simplify the discussion we let $\alpha_2=\alpha_3$, that is, the resistivity per vacancy is taken to be the same for divacancies as for trivacancies. We consider three cases:

(a) $1.1\alpha_1=\alpha_2=\alpha_3$;

(b) $1.5\alpha_1=\alpha_2=\alpha_3$;

and

(c) $2\ \alpha_1=\alpha_2=\alpha_3$.

For case (a) the maximum resistivity is reached in 1.3 hr, and amounts to only 2%; for case (b) the time to reach the maximum is 2.8 hr and amounts to 15%; and

[8] A numerical error was made in the coefficients since there are 84 ways two vacancies can come to gether to form a divacancy and 14 ways to separate. A similar error is present in the coeficients for the formation and separation of the trivacancies. However, these changes should not affect the machine results by much nor affect the general conclusions.

for case (c) 3.3 hr and 28%. While the agreement is reasonable for the latter two cases the calculations are too simplified to place any importance on the relative values of α. In particular the relatively large concentrations of trivacancies indicate that larger clusters may play an important role. Further, the effective sink density N was somewhat arbitrarily set at $N=10^{-7}$; a smaller value of N will shift the maxima toward longer times, approaching a value about 4 hr for $N=0$, and will also increase the magnitude of the maxima. The calculations, however, do indicate that clustering is a possible plausible mechanism to account for the resistivity maxima.

Alternative mechanisms which could produce the increase in resistivity are clustering of impurity atoms or possibly the association of vacancies and impurity atoms. The clustering of impurity atoms appears unlikely, because the specimens were of high purity and no difference was observed between specimens which had different ratios of room temperature resistivity to that at liquid helium in the range 2700 to above 4000. Also the times (τ) are dependent on the concentration of quenched-in defects as seen in Fig. 3. Finally, the time required for the diffusion of substitutional impurity atoms to form clusters should be greater than that observed. The possibility of the initial increase in resistivity due to the association of vacancies with impurity atoms cannot be eliminated, and further studies are required. The impurity concentration estimated from the ratio in resistivity between 298° and 4.2°K is $2\sim4\times10^{-6}$. The impurity atoms which are effective in trapping vacancies are the same order of magnitude or more than the vacancies for the cases under consideration.[9] Therefore, a considerable number of vacancies may be associated with impurity atoms before meeting other vacancies. However, if the increase in resistivity is due only to vacancy-impurity association, the time to reach the maximum in resistivity should be sensitive to the concentration of impurities and hence to the resistivity ratio, whereas, this time is found not to depend on this ratio for the range of ratios of the specimens used. It is possible, however, that some impurities are important as nucleating sites for the formation of vacancy clusters; further work is required to determine the precise role of impurity-vacancy interactions.

For quenches above 500°C the number of jumps a vacancy makes during the quenching process becomes comparable to that during the aging time required to reach the maximum resistivity. Therefore, some vacancy clusters should have been formed during the quenching process and hence no further increase in resistivity should occur for quenches made above this temperature.

A simple model can explain the variation in time to reach maximum resistivity with quenching temperature. Assuming that for quenches below 500°C the quenched-in defects are primarily single vacancies, essentially randomly distributed, then, the rate controlling process for the formation of clusters should be the formation of divacancies as a result of single vacancy migration. If X is the average distance between vacancies distributed randomly, then $X=C^{-\frac{1}{3}}$ and in addition we have $tD/X^2=\text{const}$, where D is the diffusion constant for vacancies. The temperature dependence of D does not enter into the method of plotting in Fig. 4. Therefore τ, the time to reach maximum resistivity, is proportional to $e^{+2E_f/3kT_q}$, where E_f is the vacancy formation energy and T_q is the temperature from which the quench was initiated. The proportionality between τ and $\exp(1/T_q)$ is seen in Fig. 4. From the straight line slope of this curve the energy of formation can be calculated and is found to be $E_f=1.0$ev. The falloff observed for quenches approaching 500°C should be expected because of the approach to quenching temperatures where clustering can occur during the quenching process.

B. The Variation of Reaction Times for Quenches from above 500°C

If vacancy clusters are formed during the quenching process for quenches made above 500°C, then these vacancy clusters can act as sinks for migrating vacancies and hence should play an important role in determining the annealing kinetics. A simple qualitative model may be helpful in describing this process. We make the simplest possible assumptions: (1) The number of clusters to which vacancies migrate is proportional to the quenched-in resistivity, (2) the vacancies migrate to the clusters in a random walk fashion, and (3) the clusters formed are sufficiently large so that they can be regarded as vacancy sinks. This final assumption will be valid only for high-temperature quenches, that is, for quenches above 600°C. It follows from the above assumptions that the ratio of the reaction times for two different quenching temperatures above 600°C should be proportional to the ratio of the quenched-in resistivity to the $-\frac{2}{3}$ power. This is found to be obeyed by the present data as well as those of previous workers. Consider for example the data of Bauerle and Koehler[10]: They find reaction time for 50 and 19 hr for quenches from 600° and 700°C, respectively, giving a ratio of 2.6. The corresponding ratio of quenched-in resistivity obtained was 0.244. Taking this to the $-\frac{2}{3}$ power we obtain 2.56, which agrees with the above measured ratio of 2.6.

APPENDIX. CALCULATION FOR FIG. 1

The average number of jumps made by a vacancy during quenching can be written as

$$N=\int_{T_q}^{T_r} K\exp(-E_1/kT)dt,$$

[9] The impurities detected by spectrographic analysis are copper and silver. All other elements are checked for and are less than 10^{-6}.

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

where T_q=temperature where quench initiated, T_r =temperature of lowest limit (taken as 300°K), K=jump frequency coefficient (10^{13}/sec), E_1=migration energy of a vacancy (0.8 ev), R=quenching rate (taken as 2.5×10^4 °K/sec), k=Boltzmann constant, T=temperature (°K), and t=time (sec). Substituting the linear cooling velocity

$$T=T_q-Rt,$$

one obtains

$$N=\int_{T_q}^{T_r}\left(-\frac{K}{R}\right)\exp(-E_1/kT)dT.$$

Introducing a parameter Y as $Y\equiv E_1/kT$, then

$$dT=-(E_1/k)dY/Y^2$$
$$Y_q=E_1/kT_q,$$
$$Y_r=E_1/kT_r.$$

Therefore

$$N=\frac{KE_1}{kR}\int_{Y_q}^{Y_r}\frac{\exp(-Y)}{Y^2}dY$$
$$=\frac{KE_1}{kR}\left\{\left[-\frac{\exp(-Y)}{Y}\right]_{Y_q}^{Y_r}-\int_{Y_q}^{Y_r}\frac{\exp(-Y)}{Y}dY\right\}$$
$$=\frac{KE_1}{kR}\left\{\left[-\frac{\exp(-Y)}{Y}\right]_{Y_q}^{Y_r}-\int_{Y_q}^{\infty}\frac{\exp(-Y)}{Y}dY+\int_{Y_r}^{\infty}\frac{\exp(-Y)}{Y}dY\right\}.$$

An approximate solution has been given to the above integration[11] as

$$\int_Z^{\infty}\frac{\exp(-Y)}{Y}dY\cong[\exp(-Z)]\left[\frac{1}{Z}-\frac{1}{Z^2}+\frac{2!}{Z^3}-\frac{3!}{Z^4}+\cdots\right].$$

Therefore,

$$N\cong\frac{KE_1}{kR}\left\{-[\exp(-Y_q)]\left[-\frac{1}{Y_q^2}+\frac{2!}{Y_q^3}-\frac{3!}{Y_q^4}\right]+[\exp(-Y_r)]\left[-\frac{1}{Y_r^2}+\frac{2!}{Y_r^3}-\frac{3!}{Y_r^4}\right]\right\}.$$

Since $\exp(-Y_r)$ is negligibly small with respect to $\exp(-Y_q)$ for the present case, we get

$$N\cong\frac{KE_1}{kR}\left[\exp\left(-\frac{E_1}{kT_q}\right)\right]\times\left[\left(\frac{kT_q}{E_1}\right)^2-2!\left(\frac{kT_q}{E_1}\right)^3+3!\left(\frac{kT_q}{E_1}\right)^4\right].$$

The average number of jumps necessary to meet another vacancy was computed from

$$\tfrac{1}{12}C\cong\tfrac{1}{12}\exp(-E_f/kT_q),$$

where C=fractional concentration of vacancies at the quenching temperature and E_f=formation energy of a vacancy (1.0 ev).

[11] National Bureau of Standards, Applied Mathematics Series **51**, VII (1958).