Kinetic Study of Vacancy and Interstitial Annealing in Metals†

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The rate equations governing the annealing of vacancies and interstitials in irradiated and prequenched irradiated metals for stage-III recovery have been studied. Vacancies were considered to be the mobile defect for this recovery, and the effects of the formation and migration of small vacancy clusters were investigated. Interstitials, either in the form of single trapped interstitials or small interstitial clusters, were assumed to be immobile. This system gives rise to two annealing stages, one of which involves annihilation of vacancies and interstitials, and the other, at higher temperatures, arises from vacancy migration to permanent sinks such as dislocations or grain boundaries. The form of the interstitial, trapped or clustered, has little effect on the calculated results. Peak temperatures and calculated effective migration energies, however, are sensitive to the vacancy clustering parameters (migration and binding energies). The presence of small concentrations of mobile vacancy clusters can shift the low-temperature peak to lower temperatures without changing its magnitude, and give rise to low and variable measured activation energies. The recovery model suggested by these calculations ascribes stage III to interstitial-vacancy annihilation and stage IV to vacancy migration to sinks. Depending on the clustering parameters, the kinetics for stage III may be primarily related to single-vacancy migration or may be complicated by vacancy clusters. This latter case does not require any initial cluster concentration and does not require high cluster concentrations during the recovery process.

INTRODUCTION

THE nature of so-called stage III annealing in metals is the subject of a long-standing controversy.[1,2] It is commonly agreed that close-pair interstitial-vacancy recombination and free interstitial migration take place in stage I. Stage II is a relatively minor annealing stage without much clear structure and is normally associated with impurities. After quenching there is a major annealing stage called stage IV. Since quenching should not produce any interstitials, stage IV presumably arises from the migration and annealing of vacancies. In some quenching experiments[3–5] an annealing stage was found at lower temperatures than stage IV which might be called stage III and which was attributed to divacancy annealing. This stage was larger than expected from divacancies alone, and it has recently been suggested[6] that divacancies and small clusters may play a very significant role in the annealing of quenched materials. The rate equations for the annealing and clustering of vacancies were studied and showed that an annealing stage can occur in which the over-all effect is the elimination of immobile single vacancies. There must be a mobile defect for this process to occur and there must be a mechanism by which "local" equilibrium can be maintained between single vacancies and the mobile species, e.g., $V_2+V_1 \rightarrow V_3$, $V_3+V_1 \rightarrow V_4$, $V_4 \rightarrow V_2+V_2$, where both the divacancy and trivacancy are mobile.

The more "common" stage III is found in cases in which interstitials have been present. The question here is: If interstitials migrate in stage I and vacancies in stage IV, what is migrating in stage III? Numerous models have been proposed for this stage, but none have attained general acceptance. Perhaps the most widely advocated model[2] involves two interstitial configurations, one of which migrates in stage I, the other in stage III. Proposals have also been made for diinterstitial migration, release of interstitials from traps, breakup of interstitial clusters, and vacancy migration. Vacancy migration was the natural proposal before stages III and IV were delineated, but since then has never held much favor. Although the arguments against vacancy migration in stage III are straightforward and simply stated, they are not completely convincing, i.e., some workers have never been convinced that vacancies could not play some role in stage III. For example, Lwin *et al.*[7] found the stage III kinetics in aluminum after electron irradiation to be consistent with vacancy migration (in disagreement with other authors). Dworschak *et al.*,[8] using a somewhat indirect method involving damage rates, conclude that the vacancy is the most probable mobile defect for stage III in copper. Lee and Koehler[9] have interpreted annealing studies of quenched and irradiated gold in terms of a vacancy model. Corbett[1] has consistently felt that

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[1] For a complete review, see J. W. Corbett, in *Solid State Physics*, edited by F. Seitz and D. T. Turnbull (Academic, New York, 1966), Suppl. 7.
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stage III involves many complex interactions, including vacancy migration.

The most pertinent type of experiment for the present discussion involves the comparison of irradiation annealing for samples some of which have been prequenched and some of which have not. Budin and Lucasson[10] have performed such experiments for aluminum and found two distinct stages 70°C apart which they labelled III and IV. They conclude that interstitials must migrate in stage III and vacancies in IV. Bauer[11] recently has performed similar experiments but prefers a model in which interstitial migration, restricted by impurities, occurs in the lower temperature portion of stage III and the beginning of vacancy migration accounts for the higher-temperature portion of stage III. Duesing and Schilling[12] have recently reported corresponding experiments for platinum in which they found similar results. However, they explain their data in terms of single-vacancy migration and suggest the same interpretation for the aluminum experiments.

A mechanism by which single-vacancy migration may give rise to two distinct annealing stages involves two types of sinks: The low-temperature stage corresponds to sinks which require fewer vacancy jumps to reach than the high-temperature stage and which can be used as a sink only once. Since a large stage III is found only after interstitials have been present, it is natural to assume that this stage involves vacancy-interstitial annihilation at trapped interstitials or small interstitial clusters. Once the interstitials are eliminated, the remaining vacancies must make many more jumps to reach dislocations or grain boundaries. The appropriate rate equations for this mechanism are investigated in the present paper and compared with the experimental data.

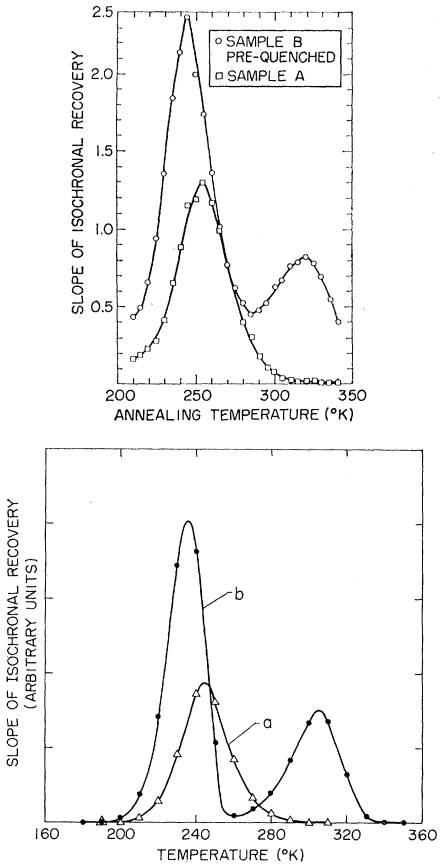

FIG. 1. Comparison of experimental and calculated annealing curves. The experimental results of Bauer (Ref. 11) for aluminum are shown on the top and the roughly comparable calculated curves, involving only single-vacancy migration to trapped interstitials and a fixed concentration of sinks, on the bottom. The curves represent the annealing behavior of a simply irradiated sample, run (a), and of a prequenced and irradiated sample, run (b). The experimental curves are courtesy of W. Bauer.

CALCULATIONS

Simple Model

The simplest possible reaction scheme for vacancy migration to interstitial sinks (trapped interstitials or small interstitial clusters) and to other sinks (dislocations, grain boundaries, or impurity traps) is given by

$$V+I \xrightarrow{K_1} \text{annihilation},$$
$$V \xrightarrow{K_2} \text{sinks},$$

and the associated rate equations are

$$\frac{dV}{dt} = -K_1VI - K_2V, \tag{1}$$

$$\frac{dI}{dt} = -K_1VI. \tag{2}$$

These equations can be solved for the relation between V and I but cannot be solved in closed form for V and I as a function of time.

A complete discussion of the application of rate theory to annealing in metals is given by Damask and Dienes[13] and will not be repeated here, but of primary importance is the assumption that all interacting species are randomly distributed at all times, i.e., no spacial correlations are considered. In the case given above, vacancies migrate to and annihilate at single immobile interstitials (presumably trapped) and migrate to other sinks. All more complex interactions such as vacancy cluster formation, divacancy migration, vacancy migration to interstitial clusters, or impurity effects are neglected for the present, but will be discussed later.

The rate constants are given by $K_1 = C\nu e^{-E_V{}^M/kT}$ where $C=84$, $\nu=10^{14}$/sec, $E_V{}^M$ is the vacancy-migration

[10] C. Budin and P. Lucasson, in *Interaction of Radiation with Solids*, edited by A. Bishay (Plenum, New York, 1967), p. 497.
[11] W. Bauer, Radiation Effects 1, 23 (1969).
[12] G. Duesing and W. Schilling, Radiation Effects 1, 65 (1969).
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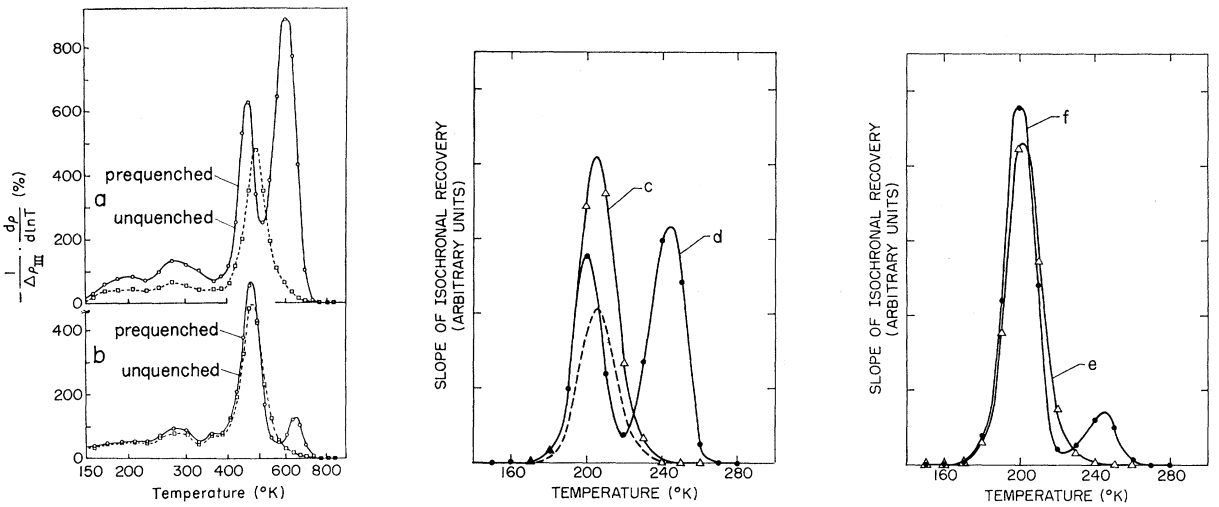

FIG. 2. Comparison of experimental and calculated curves. The experimental results of Duesing and Schilling (Ref. 12) for platinum are shown on the left and the roughly comparable calculated curves (with different scales), involving only single-vacancy migration to trapped interstitials and a fixed concentration of sinks, on the right. For the experimental results, the dashed curves represent simply irradiated runs and the solid curves represent prequenched and irradiated runs. More vacancies remained in the sample in prequenched case (a) than in prequenched case (b). For the calculated results, curves (c) and (e) represent simply irradiated runs (the initial total vacancy and interstitial concentrations are equal), and curves (d) and (f) represent prequenched and irradiated runs (the initial total vacancy concentration is greater than the initial total concentration). The dashed curve represents the normalization of curve (c) in relatively the same amount as used in the experimental plots. The experimental curves are courtesy of Duesing and Schilling.

energy, k is the Boltzmann factor, and T is the temperature, and $K_2=\alpha\lambda^2\nu e^{-E_V{}^M/kT}$, where the parameters α and λ are discussed by Damask and Dienes[13]: $\alpha\lambda^2$ may be thought of as an effective sink concentration. V and I are the vacancy and interstitial concentrations. The equations were solved by a self-consistent iterative technique in which the concentrations converge at a given time before each time step is taken to a new time. For comparison with experiment it has been assumed that vacancies and interstitials contribute equally to the resistivity.

For comparison with Bauer's data, run VI,[11] representing the annealing behavior of a simply irradiated sample run (a), and of a prequenched and irradiated sample run (b), the vacancy migration energy was taken as $E_V{}^M=0.6$ eV, an appropriate value for aluminum, and 10-min 10°K isochronal runs were made for initial concentrations (parts per million) of (a) $V_0=1.5$, $I_0=1.5$ and (b) $V_0=5$, $I_0=2.5$. $\alpha\lambda^2$ was taken as 10^{-7}, indicating a very low sink concentration. Bauer's results are shown on the left-hand side of Fig. 1 and the present results on the right. The peaks occur at a temperature about 10°K lower in the calculated runs, and run (b), correspondinging to the prequenched case, crosses below run (a) and is smaller between the peaks in the calculations than in the experiments. The first difference simply involves temperature scaling, and a slightly higher $E_V{}^M$ would bring about an appropriate match. The form of the calculated curves and the shift of the low-temperature peak with concentration certainly are in general agreement with experiment.

A similar comparison can be made with the experiments of Duesing and Schilling[12] for platinum. No attempt was made to match the temperature scale and therefore a vacancy migration energy of 0.6 eV was maintained for 10-min 10°K isochronal runs. However, the effective sink concentration $\alpha\lambda^2$ was increased to 5×10^{-5} and the initial concentrations (parts per million) were taken as (c) $V_0=500$, $I_0=500$, (d) $V_0=1000$, $I_0=250$, (e) $V_0=1000$, $I_0=1000$, and (f) $V_0=1300$, $I_0=1000$, values much higher than the previous cases but which should be roughly equivalent to the experiment situation. The measured curves are shown on the left of Fig. 2 and the corresponding calculated curves on the right. At first glance the (c) and (d) curves do not appear to be in agreement with experiments, but this is caused by the normalization procedure used by Duesing and Schilling. With roughly the relative normalization used by the authors, run (c) is given by the dashed curve and curves (c) and (d) give satisfactory correspondence with the experimental results. The unnormalized calculated curves were plotted to emphasize that the amount of annealing in run (c) is greater than in the low-temperature peak of run (d) but occurs at a higher temperature. This point will be discussed in greater detail later. The crossing of the curve for the prequenched case below the other peaks is seen to be in agreement with the platinum experiments, whereas this effect was not seen in the aluminum experiments.

Since the high-temperature peak involves primarily vacancy migration to sinks, varying the sink concentration $\alpha\lambda^2$ shifts the peak temperature in a predictable way but has little effect on the low-temperature peak.

All the above calculations involve a singly-activated process, and therefore the effective activation energy obtained by standard methods (e.g., change of slope for isochronal runs) is in agreement with the input value $E^M=0.6$ eV at all temperatures.

Effects from More Complex Reactions

A great variety of reactions more complex than simple vacancy migration to immobile or trapped single interstitials are possible, but in general the rate equations for these cases require further approximations. The presence of small mobile vacancy clusters and small immobile interstitial clusters will be considered.

If all the interstitials are in the form of immobile diinterstitials, the reaction $V_1+I_2\rightarrow I_1$ will be of primary importance. However, the single interstitial released by this reaction will presumably be very mobile and therefore the reactions $I_1+V_1\rightarrow$ annihilation, $I_1\rightarrow$ sinks, and $I_1+I_2\rightarrow I_3$ will also occur (the I_1 concentration will always be so small that $I_1+I_1\rightarrow I_2$ can be neglected). Then $V_1+I_3\rightarrow I_2$, $I_1+I_3\rightarrow I_4$, $I_1+I_4\rightarrow I_5$, etc. are also possible reactions. In order to reduce the number of independent differential equations to be solved and in view of the high mobility of single interstitials, the approximation was made in the case in which initially all interstitials are in the form of diinterstitials that an I_1 released by a V_1+I_2 interaction instantaneously partitions itself among the vacancies, diinterstitials, and sinks in accordance with their effective concentrations. The interstitial is removed by the V_1 and sink interactions, but remains in solution in the I_2 reaction. The equations are so written that, although the overall interstitial concentration increases by this reaction, all interstitials remain in the form of diinterstitials. In these diinterstitial cases, reactions such as $V_2+I_2\rightarrow$ annihilation, and $V_3+I_2\rightarrow V_1$ were also included.

Since the mobility of multiple interstitials decreases with number of interstitials in the aggregate, if the assumption is made that all interstitials initially are in the form of tetrainterstitials, single, di-, and tri-interstitials are assumed to be infinitely mobile and, for example, the diinterstitial released by the interaction $V_2+I_4\rightarrow I_2$ is partitioned among sinks, all the vacancy species present, and the remaining tetrainterstitials according to their respective concentrations. As before, this last interaction increased the concentration of the largest interstitial species assumed to be immobile, in this case tetrainterstitials, rather than creating different size clusters. Thus the immobile interstitial cluster used in a given calculation can be thought of as an average or a representative cluster. It will be shown that the results are not very sensitive to this approximation.

The most general case which was run involved mobile single, di-, and trivacancies and single, di-, and tri-interstitials and immobile tetravacancies and tetrainterstitials. The rate equations are then given by

$$\frac{dV_1}{dt}=-K_1V_1-2K_{11}V_1V_1+2K_{11}'V_2-K_{12}V_1V_2+K_{12}'V_3-K_{13}V_1V_3$$
$$+K_{13}'V_4-K_{14}V_1I_4\left(1+\frac{3V_1}{\Sigma}\right)-K_{24}V_2I_4\left(\frac{2V_1}{\Sigma}\right)-K_{34}V_3I_4\left(\frac{V_1}{\Sigma}\right),$$

$$\frac{dV_2}{dt}=-K_2V_2+K_{11}V_1V_1-K_{11}'V_2-K_{12}V_1V_2+K_{12}'V_3-2K_{22}V_2V_2+2K_{22}'V_4$$
$$-K_{14}V_1I_4\left(\frac{3V_2}{2\Sigma}\right)-K_{24}V_2I_4\left(1+\frac{V_2}{\Sigma}\right)-K_{34}V_3I_4\left(\frac{V_2}{2\Sigma}\right),$$

$$\frac{dV_3}{dt}=-K_3V_3+K_{12}'V_1V_2-K_{12}V_3-K_{13}V_1V_3+K_{13}'V_4-K_{14}V_1I_4\left(\frac{V_3}{\Sigma}\right)-K_{24}V_2I_4\left(\frac{2V_3}{3\Sigma}\right)-K_{34}V_3I_4\left(1+\frac{V_3}{\Sigma}\right),$$

$$\frac{dV_4}{dt}=K_{13}V_1V_3-K_{13}'V_4+K_{22}V_2V_2-K_{22}'V_4-K_{14}V_1I_4\left(\frac{3V_4}{4\Sigma}\right)-K_{24}V_2I_4\left(\frac{V_4}{2\Sigma}\right)-K_{34}V_3I_4\left(\frac{V_4}{4\Sigma}\right),$$

$$\frac{dI_4}{dt}=-K_{14}V_1I_4\left(1-\frac{3I_4}{4\Sigma}\right)-K_{24}V_2I_4\left(1-\frac{I_4}{2\Sigma}\right)-K_{34}V_3I_4\left(1-\frac{I_4}{4\Sigma}\right),$$

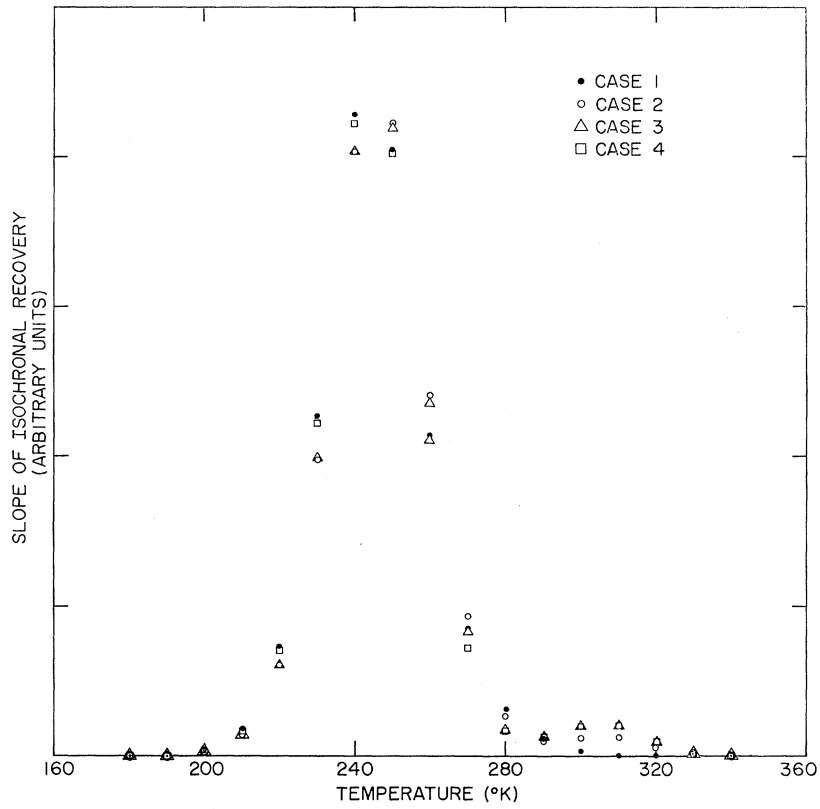

FIG. 3. Comparison of four runs in which single vacancies are mobile and do not cluster, there is an equal initial total concentration of vacancies and interstitials, and the interstitials are in the form of (1) single interstitials, (2) diinterstitials and (3) and (4) tetrainterstitials. In cases (2) and (3) the interstitials released by vacancy-interstitial reactions interact with sinks, vacancies, and interstitial clusters, while in case (4) the reactions with interstitial clusters are removed.

where

$$\Sigma \equiv V_1+V_2+V_3+V_4+I_4+\alpha\lambda^2,$$
$$K_1=\alpha\lambda^2\nu_1\exp(-E_1^M/kT),$$
$$K_2=\alpha\lambda^2\nu_2\exp(-E_2^M/kT),$$
$$K_3=\alpha\lambda^2\nu_3\exp(-E_3^M/kT),$$
$$K_{11}=84\nu_1\exp(-E_1^M/kT),$$
$$K_{11}'=14\nu_1\exp[-(E_1^M+E_2^B)/kT],$$
$$K_{12}=36\nu_1\exp(-E_1^M/kT)+144\nu_2\exp(E_2^M/kT),$$
$$K_{12}'=27\nu_1\exp[-(E_1^M+E_3^B-E_2^B)/kT]+18\nu_2\exp[-(E_2^M+E_3^B-E_2^B)/kT],$$
$$K_{13}=9\nu_1\exp(-E_1^M/kT)+32\nu_3\exp(-E_3^M/kT),$$
$$K_{13}'=36\nu_1\exp[-(E_1^M+E_4^B-E_3^B)/kT]+16\nu_3\exp[-(E_3^M+E_4^B-E_3^B)/kT],$$
$$K_{22}=10\nu_2\exp(-E_2^M/kT),$$
$$K_{22}'=30\nu_2\exp[-(E_2^M+E_4^B-2E_2^B)/kT],$$
$$K_{14}=32\nu_1\exp(-E_1^M/kT),$$
$$K_{24}=48\nu_2\exp(-E_2^M/kT),$$
$$K_{34}=48\nu_3\exp(-E_3^M/kT),$$
$$\nu_1=10^{14},$$
$$\nu_3=\tfrac{1}{5}\nu_2=(1/25)\nu_1,$$

E_i^M is the migration energy of a cluster of i vacancies, E_i^B is the binding energy of a cluster of i vacancies, and $\alpha\lambda^2$ is the effective sink concentration as discussed by Damask and Dienes.[13]

In the first set of runs to be discussed, E_1^M was taken as 0.6 eV with di- and trivacancies immobile, $\alpha\lambda^2$ equals 10^{-7}, V_1 (initial) $=1.5\times10^{-6}$, and the total interstitial content I_1 (initial) $=1.5\times10^{-6}$ (e.g., if all the interstitials are tetrainterstitials, $I_4=3.75\times10^{-7}$). In case 1 all the interstitials are I_1, i.e., the case discussed in the previous section. In case 2 all the interstitials are I_2, in case 3, I_4, and in case 4, I_4 but with the mobile-interstitial–immobile-interstitial reaction removed, i.e., the mobile interstitials are only partitioned among the sinks and vacancies.

The results of 10-min 10°K isochronal runs are shown in Fig. 3. The curves for all four cases are similar: There is no indication of a high-temperature stage in case 1 because no interstitials have been able to reach sinks and so the one to one ratio of vacancies to interstitials is always maintained. Cases 1 and 4, neither of which involve interstitial-interstitial interactions, are very similar, and cases 2 and 3 are very similar but are slightly slower than 1 and 4 because mobile interstitials can return to interstitial clusters. Vacancy migration is the rate-controlling process in all cases and so the effective migration energy (obtained by the change-of-slope method) is E_1^M. A corresponding set of runs was made with V_1 (initial) $=4.5\times10^{-6}$ and I_1 (initial)

$=3.0\times10^{-6}$ which led to the same conclusions: The over-all annealing curves are not very sensitive to the form of the immobile interstitial or to the approximations made in fitting the rate equations to a particular situation.

A series of runs were made to study the effects of vacancy clustering. The vacancy binding energy values were patterned after those used earlier[6] to study vacancy clustering and annealing. For a low–binding-energy case, $E_{1v}{}^{M}=0.90$, $E_{2v}{}^{M}=0.75$, $E_{3v}{}^{M}=0.80$, $E_{2v}{}^{B}=0.10$, $E_{3v}{}^{B}=0.20$, and $E_{4v}{}^{B}=0.35$ eV; and for a medium–binding-energy case, $E_{1v}{}^{M}=0.90$, $E_{2v}{}^{M}=0.75$, $E_{3v}{}^{M}=0.85$, $E_{2v}{}^{B}=0.20$, $E_{3v}{}^{B}=0.40$, and $E_{4v}{}^{B}=0.70$ eV. The initial concentration of single vacancies was taken as 10^{-5}, of tetrainterstitials as 10^{-6}, and $\alpha\lambda^2=10^{-6}$.

First a comparison run was made with only single vacancies mobile ($E_{1v}{}^{M}=0.90$ eV) and the results of a 10-min 10°K isochronal run are shown in Fig. 4 by the curve through the closed circles. The results of the low–binding-energy case are shown by the open circles and the values are so close to the single-vacancy case that a separate curve was not drawn. There is a slight peak shift to lower temperatures. The results of the medium–binding-energy case are shown by the Δ's, and here there is a significant peak shift of 35–40°K for the low-temperature peak.

These three cases were also investigated for concentration effects, effects of varying V_1/I_4 ratios, and of varying $\alpha\lambda^2$. No unexpected results were found: Increasing the concentration of vacancies and interstitials lowered the temperature of the low-temperature peak and increasing the concentration of sinks lowered the temperature of the high-temperature peak, all in a regular manner.

Change of slope calculations for the effective activation energy were made for all these runs. When only single vacancies were mobile the single-vacancy migration energy was reproduced, $E_{1v}{}^{M}=0.90$ eV. For the low–binding-energy case the effective migration energy started slightly above 0.8 eV, rose to 0.86 eV at the top of the low-temperature peak, dropped to 0.84 eV between the peaks, and then rose to 0.89 eV for the high-temperature peak. For the medium–binding-energy case the effective migration energy again started slightly above 0.8 eV, decreased quickly to about 0.75 eV for the low-temperature peak, dropped further to about 0.72 eV between the peaks, and then rose to about 0.85 eV for the high-temperature peak.

For these effective migration energy calculations, the resistivity was assumed to be proportional to the total defect concentration. If each component defect in a cluster is assumed to contribute less to the resistivity than when isolated, striking decreases in the effective migration energy were found. When the temperature is instantaneously raised, the first effect is to alter the relative cluster concentrations by increasing the single vacancy and smaller cluster concentrations at the expense of the larger clusters. This gives rise to an increase in resistivity, so the initial resistivity value for annealing at the new temperature is effectively higher than the final value at the old temperature. For $\rho(V_2)=(15/8)\rho(V_1)$, $\rho(V_3)=(21/8)\rho(V_1)$, and $\rho(V_4)=(26/8)\rho(V_1)$, effective migration energies in the medium–binding-energy case could easily be lowered by several tenths of an eV: If the resistivity change in the last 10 sec of the old temperature and the first 10 sec of the new temperature are used, negative effective migration energies are found. This effect is important for the low-temperature peak where clusters play a major role, but had little effect on the high-temperature peak.

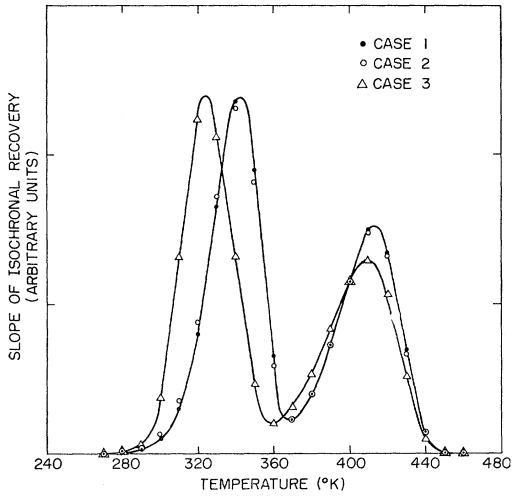

FIG. 4. Comparison of three runs illustrating the effect of vacancy clustering on isochronal annealing curves. The initial vacancy concentration is solely in the form of single vacancies and is 2.5 times the initial total interstitial concentration, which is in the form of tetrainterstitials. Only single vacancies are mobile in case (1), di- and trivacancies are also mobile in case (2) but have "small" binding energies (thus their concentrations remain small), and di- and trivacancies are again mobile in case (3) but have "medium" binding energies. In both cases (2) and (3) tetravacancies are allowed to form but are not mobile.

It is important to note that since all the interstitials are removed during the low-temperature peak, its magnitude does not depend on vacancy clustering. Furthermore, the effects of vacancy clustering do not require any initial cluster concentration or a large buildup of clusters during annealing. In case 2 the maximum di-, tri-, and tetravacancy concentrations were 3.2×10^{-8}, 1.3×10^{-10}, and 3.7×10^{-12}, respectively, and in case 3 they were 4.9×10^{-7}, 5.4×10^{-8}, and 4.3×10^{-8}, respectively. The single-vacancy concentrations at the times the divacancy concentrations were at their maxima were 9.9×10^{-6} and 8.0×10^{-6} for cases 2 and 3, respectively.

SUMMARY AND CONCLUSIONS

Within the framework of an annealing model in which single vacancies and small vacancy clusters are

mobile and in which single interstitials or small interstitial clusters are immobile, (1) two annealing peaks are found, a low-temperature peak which involves annihilation of vacancies and interstitials and a high-temperature peak which involves vacancy migration to sinks; (2) the results of the calculations are not very sensitive to the form of the interstitial (single-, di-, or tetra-interstitial). (3) The results of the calculations, especially for the low-temperature peak, can be quite sensitive to the vacancy-clustering parameters (migration and binding energies) both in shifting the peak temperature and in the calculation of the effective migration energy. The low-temperature peak can be primarily either a single vacancy or a divacancy peak (even if the initial divacancy concentration is zero).

Many reactions were not included in the present study. Certainly if interstitial clusters are present there will be a spectrum of cluster sizes and it will change during the annealing process. Different cluster sizes will have varying migration and binding energies. Earlier studies[6] showed that under many conditions large vacancy clusters will form. These effects will alter the details of the annealing curves but should not materially alter the over-all structure.

In view of the close similarity of the annealing curves with the experiments of Duesing and Schilling[12] for platinum, it is reasonable to assume that clustering plays a minor role and the peak labeled stage III by the authors is basically a vacancy stage, in agreement with the conclusion by the authors. Duesing and Schilling suggest that either the mechanism investigated in the present paper or a mechanism involving vacancy clustering which delays resistivity recovery until large clusters are formed may be operative. However in the latter case mobile vacancies are rapidly taken out of solution during the clustering process and the peak shifts reported by the authors and shown in Fig. 2 are difficult to explain. This reaction should occur to some extent, but should not play a dominant role. The authors prefer the former model and proposed the latter because it was not clear at that time that the former could give rise to an appropriate peak separation.[14]

The fit of the calculated curves to the aluminum results reported by Bauer[11] is not as good. A very low sink concentration was required to give an appropriate peak separation and the calculated curves dip lower between the peaks than the experimental curves. However the published effective migration energies for stage III in aluminum (summarized by Bauer) have quite a considerable spread, indicative of the situation in which divacancies and vacancy clusters play an important role. If this is the case the peak temperatures would be matched with a slightly higher single-vacancy migration energy and a higher sink concentration.

In an earlier paper it was pointed out that vacancy clustering *should* affect annealing after quenching, depending upon the clustering parameters. Similarly, the effects reported in the present paper *should* be present, the detailed form again depending upon the specific clustering parameters. The data, including, for instance, the peak shifts in platinum discussed above, can be fitted equally well with the two-interstitial model. However, that model not only requires the existence of two interstitials but requires that radiation damage only create the metastable interstitial, and that the stable interstitial migrates with just a slightly lower activation energy than vacancies in all metals for which there is sufficient data. The vacancy-clustering model appears capable of explaining the data in a straightforward and natural manner. A more detailed analysis than that given here is required to extract the maximum information from any given experiment, not only by including more reactions, but also by considering impurity effects and spacial effects, but such an analysis should not alter the basic mechanisms in the vacancy model.

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[14] W. Schilling (private communication).