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Atomic mechanisms during the annealing of irradiated metals*

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Abstract: The still unresolved problems associated with annealing stages I and II are described. The evidence which supports the assignment of stage III annealing in irradiated gold and aluminum to vacancy migration is described. Shimomura's electron microscope pictures of interstitial clusters in electron irradiated gold observed below stage III are described. It is shown that the interaction between interstitial clusters and migrating vacancies reduces the number of jumps to annihilation by a factor of thirty to sixty in aluminum and gold. Possible reasons for the second order annealing kinetics are examined. Remaining problems in copper and silver are mentioned.

By now most research workers have agreed on the major outlines of what happens during stage I annealing. The small subpeaks in stage I, which obey first order annealing, are ascribed to close interstitial vacancy pair recombination. Then at a temperature near the upper end of stage I a second order peak is seen. This results from the long range three dimensional migration of an interstitial to vacancies, to impurity traps, to interstitial clusters, to surfaces, to grain boundaries, or to dislocations.

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There are a few questions which remain. They are:

1. What is the geometrical structure of the interstitial in fcc and also in bcc crystals?
2. Why is the annealing peak structure so different in gold from its appearance in stage I from copper, silver, nickel, platinum, and aluminum?
3. Is stage I_D in copper a collection of overlapping close pair peaks or is it correlated recovery of the free interstitial with its close vacancy?

Koehler and Leibfried³⁾ suggest that questions 1 and 2 have the following answers: The stable form of the interstitial in most fcc crystals is the cube centered interstitial. This gives the I_A , I_B , I_C , I_D close pair recombination peak structure easily. In gold they propose that the split $\langle 100 \rangle$ interstitials are the stable interstitials which are easily seen to give a more complicated close pair recovery structure. Snead, Wiffen, and Kauffman⁴⁾ give stage I annealing data on gold irradiated to low dose with 2MeV electrons which shows features resembling copper. They claim that I_E occurs at 21°K in gold. It is clear that impurity interstitial interaction can give rise to discrete annealing peaks in stage II. However, in neutron irradiated metals and in heavily damaged specimens prepared by electron, proton, or deuteron irradiation a large essentially continuous stage II annealing is observed. This might possibly arise as follows: During the stage I_E annealing the freely migrating interstitials form clusters which are interstitial platelets on the (111) planes. These clusters have been observed below stage III in gold⁵⁾. The interstitial clusters have a large strain field and it is possible that the strains may lower the vacancy migration energy into the stage II region.

Let us next consider stage III annealing. First we make some general remarks. All metals if irradiated at 4°K show a prominent low temperature annealing which has in many metals been shown to be associated with long range defect migration. Long range migration has been demonstrated in aluminum, copper, silver, and gold mainly by showing that the damage production rate at 100°K is larger in impure samples⁶⁾.

Both experiment and theory⁷⁾ unite in saying that the migration energy associated with interstitials in fcc metals is small, of the order of 0.1eV. Moreover, existing theory does not suggest that a metastable interstitial exists which under very special circumstances can be converted into the stable interstitial. M. Doyama and I tried to produce such a metastable interstitial. We used one of five fold symmetry hoping that its unusual symmetry and complexity would prevent its relaxation into one of the simpler types of interstitial. However, it did relax into a split <100> interstitial with a continuous decrease in the energy of the system. The Morse potential appropriate for copper was used for atom atom interaction. This is not a proof, of course, but it does indicate that some new physical reason for metastability will be needed.

It is fairly evident also that vacancies and divacancies migrate at temperatures which are approximately the temperatures associated with stage III annealing. Thus it seems that the simplest model one could propose would be that interstitials migrate in stage I and vacancies migrate in stage III. In fact, this is what we shall contend happens in aluminum, gold, and platinum. Shilling and Beukel will present the evidence for platinum. Let us consider the evidence for aluminum and gold.

The evidence for aluminum and gold is mainly based on the fact that the activation energy observed in stage III annealing is the same as that seen in the annealing of a specimen quenched from low temperature. In aluminum Federighi⁸⁾ and coworkers observed $E_{III} = 0.61 \pm 0.03 \text{ eV}$ after neutron irradiation and $E_V^M = 0.62 \pm 0.04 \text{ eV}$ in a specimen quenched from 600°C . For quenched specimens Zamboni and Federighi determined the activation energy by plotting $\log t_f$ versus the reciprocal of the absolute temperature. t_f is the time to anneal out a fraction f of the damage. The slope of the line gives the migration energy. For neutron irradiated specimens they used slope change, Meehan Brinkman, and the above method. Doyama and Koehler⁹⁾ using the slope change method observed $E_V^M = 0.60 \pm 0.04 \text{ eV}$ in a pure aluminum specimen quenched from 300°C . Sosin and Garr¹⁰⁾ obtained a low migration energy in stage III for electron irradiated aluminum. They use a second order method to determine the activation energy. W. Bauer¹¹⁾ in this conference shows that the second order method leads to erroneous activation energies. Lwin Doyama and Koehler¹²⁾ irradiated high purity aluminum at 100°K using 2MeV electrons. They determined the stage III migration energy using slope change and also by using Primak (second order) analysis. They find that $E_{III} = 0.62 \pm 0.04 \text{ eV}$. Their long isothermal runs at 223°K are observed to follow second order annealing kinetics.

It is therefore clear that the same defect as revealed by activation energy migrates in quenched and in irradiated aluminum. If isochronals are done on quenched and on irradiated specimens one observes that the temperature associated with most rapid annealing is lower in an irradiated specimen than in a quenched specimen if both start with the same Δp at -150°C .

To say it in another way, the number of jumps that a defect makes before annihilation is anomalously small in an irradiated specimen. If a frequency factor is used which gives about the correct number of jumps n_j in a quenched specimen (i.e. n_j is approximately the reciprocal of the vacancy concentration) and the same frequency factor is then used for an irradiated specimen the calculated rate of annealing will agree with experiment only if the number of jumps made by a vacancy until its annihilation is too small by at least a factor of thirty. We believe that this results from the interaction between the vacancies and the interstitial clusters present in the irradiated aluminum below stage III. We shall discuss this discrepancy more quantitatively in gold where the interstitial clusters have been observed and measured below stage III.

In the case of gold Sharma, Lee, and Koehler¹³⁾ have shown that the same defect (as distinguished by energy of migration) is observed during the annealing of very pure gold which has been (a) lightly deformed (b) fast quenched from 700°C and (c) irradiated with 3MeV electrons at 100°K. The activation energy was determined by the slope change method. The activation energies observed by Lee and Koehler¹⁴⁾ were for 3MeV electron irradiation at 100°K.

$$E_{III} = 0.85 \pm 0.02\text{eV}$$

$$\rho_{4.2^\circ\text{K}} \cong 0.5 \times 10^{-9} \text{ ohm cm}$$

and for the fast quenched specimens (quenched from 700°C with $\frac{dT}{dt} > 4 \times 10^4 \text{ }^\circ\text{C/sec}$)

$$E_v^M = 0.86 \pm 0.02\text{eV}$$

$$\rho_{4.2^\circ\text{K}} \cong 0.5 \times 10^{-9} \text{ ohm cm}$$

Kino and Koehler¹⁵⁾ got after a fast quench from 700°C

$$E_V^M = 0.90 \pm 0.05 \text{ eV}$$

$$\rho_{4.2^\circ\text{K}} < 0.56 \times 10^{-9} \text{ ohm cm}$$

Sharma and Koehler¹⁶⁾ found, on gold fast quenched from 700°C

$$E_V^M = 0.87 \pm 0.04 \text{ eV}$$

$$\rho_{4.2^\circ\text{K}} < 0.5 \times 10^{-9} \text{ ohm cm}$$

The $\rho_{4.2^\circ\text{K}}$ was the residual resistivity of the 5mil thick gold strip before quenching. It provides a measure of the purity. The above values of $\rho_{4.5^\circ\text{K}}$ were not corrected for size effect. Such a correction would give

$$\rho_{4.5^\circ\text{K}}^{\text{Corr}} \cong 0.13 \times 10^{-9} \text{ ohm cm} \quad (\text{for } \rho_{4.5} = 0.5 \times 10^{-9} \text{ ohm cm and assuming diffuse reflection of the conduction electrons at the specimen surface}).$$

Shimomura⁵⁾ thinned electron irradiated gold at +2°C and in some cases at -30°C and examined the specimens using a cold stage (100°K) in the electron microscope. An example of his pictures is shown in fig. 1 obtained on 99.9999% pure gold. The number per cm³ and the size distributions associated with various values of integrated flux are given in figs. 2 and 3. Examination of high magnification pictures taken with different diffraction vectors operating shows that the clusters are platelets on the (111) planes. A gold specimen quenched from 900°C to -20°C and thinned at 2°C shows no clusters. However, if the specimen is quenched from 900°C annealed at 20°C for ten days and then thinned one sees the usual vacancy tetrahedra. Thus the clusters are interstitial clusters. Annealing in the stage III region causes the interstitial clusters to shrink. Figure 4 shows the size distribution after irradiation and then after subsequent annealing. Thus in gold the vacancies migrate to interstitial clusters in stage III causing them to shrink. Note that in electron irradiated pure

gold and pure aluminum essentially all of the damage anneals out during stage III. Lee and Koehler¹⁴⁾ found that the purer the gold the less remains after stage III. For a specimen having $\rho_{4.5^\circ K}^0 \cong 0.5 \times 10^{-9}$ ohm cm less than 3% of the resistance put in by irradiation at 100°K remains after stage III. A similar result was found in the case of aluminum¹¹⁾ where 1% or less remains after stage III.

There is a difficulty in reconciling Shimomura's electron microscope data with the resistivity data. Consider 6N pure gold irradiated with 6.0×10^{18} electrons/cm². If one uses the size distribution observed after irradiation and assumes that for each interstitial in a platelet there is a lattice vacancy present then one can calculate the resistivity increase expected. One uses the measured edge dislocation resistivity and the observed stacking fault resistivity and the observed resistivity of lattice vacancies. For the case in question one predicts $\Delta\rho = 2.58 \times 10^{-9}$ ohm cm. However, one observes $\Delta\rho = 13.9 \times 10^{-9}$ ohm cm which is five times larger. In this case, Shimomura's size distribution of loops drops to zero at 25Å for small loops (see fig. 3). He believes that he does not miss very many of such loops. It is possible that there are a large number of very small interstitial clusters each containing only one or two interstitials trapped at some impurity. Further work is needed.

There is, however, another problem associated with stage III. If vacancies migrate to interstitial clusters how is it that one observes second order annealing kinetics? Let us examine this problem. Lee and Koehler¹⁴⁾ write the following rate equations during annealing:

$$\dot{c}_v = -K_1 c_v^2 - \sum_{n=1}^{\infty} K_{1n} c_{in} c_v \quad (1)$$

$$\dot{c}_{2v} = +\frac{1}{2} K_1 c_v^2 - \sum_{n=1}^{\infty} K_{2n} c_{in} c_{2v} \quad (2)$$

$$c_v + 2c_{2v} = \sum_{n=1}^{\infty} n c_{in} \quad (3)$$

$$\Delta\rho = f_v c_v + (2f_v - \Delta f) c_{2v} + f_i' \sum_{n=1}^{\infty} n c_{in} \quad (4)$$

or

$$\Delta\rho = (f_v + f_i')(c_v + 2c_{2v}) - \Delta f c_{2v} \quad (5)$$

where c_v is the vacancy concentration, c_{2v} is the divacancy concentration, $\Delta\rho$ is the resistivity associated with defects, c_{in} is the concentration of interstitial clusters containing n interstitials, $f_v/100$ is the resistivity of one percent vacancies, $f_i'/100$ is the resistivity of 1% interstitials in clusters, $(2f_v - \Delta f)/100$ is the resistivity of one percent divacancies. Let us assume that the rate of capture of vacancies by interstitial clusters is proportional to the cluster size. Thus

$$K_{1n} = K_{1\bar{n}} n \quad (6)$$

so that

$$\sum_{n=2}^{\infty} K_{1n} c_{in} = K_{1\bar{n}} \sum_n c_{in} = K_{1\bar{n}} (c_v + 2c_{2v}) \quad (7)$$

Similarly, we put

$$K_{2n} = K_{2\bar{n}} n \quad (8)$$

so that

$$\sum K_{2n} c_{in} = K_{2\bar{n}} \sum_n c_{in} = K_{2\bar{n}} (c_v + 2c_{2v}) \quad (9)$$

If we neglect Δf in eq. (5) we get

$$\Delta \dot{\rho} = (f_v + f_i')(c_v + 2c_{2v})$$

or

$$\Delta \dot{\rho} = - (f_v + f_i')(c_v + 2c_{2v})(c_v K_{1\bar{n}} + c_{2v} K_{2\bar{n}}) \quad (10)$$

The divacancy concentration is initially very small in comparison with the single vacancy concentration. If it remains small then (10) gives second order annealing and the rate constant $K_{1\bar{n}}$ is associated with vacancy migration. The rate eqs. (1) and (2) can be written:

$$\dot{c}_v = -K_1 c_v^2 - K_{1\bar{n}} c_v (c_v + 2c_{2v}) = -K_1 c_v^2 - K_{1\bar{n}} c_v z \quad (11)$$

$$\dot{z} = -K_{1\bar{n}} c_v z - K_{2\bar{n}} z (z - c_v) \quad (12)$$

where:

$$z = c_v + 2c_{2v}$$

Dividing eq. (12) by (11) and integrating the result one finds:

$$z = c_v \left[\frac{K_{2\bar{n}} + K_1 - K_{1\bar{n}}}{K_{2\bar{n}} - K_{1\bar{n}}} - \left(\frac{K_1}{K_{2\bar{n}} - K_{1\bar{n}}} \right) \left(\frac{c_v}{c_{ov}} \right)^{\frac{K_{2\bar{n}} - K_{1\bar{n}}}{K_{1\bar{n}}}} \right] \quad (13)$$

where c_{ov} is the initial vacancy concentration. Experiment shows that the number of jumps of a vacancy to annihilation in stage III in gold is 30 to 50 times smaller in an irradiated specimen than it is in a quenched specimen. We therefore expect $K_{1\bar{n}}$ and $K_{2\bar{n}}$ to be much larger than K_1 . When $t = 0$ the square bracket in eq. (13) is unity. At $t = \infty$ it is very nearly unity since the second term is zero. Equation (11) becomes therefore:

$$\frac{\dot{c}_v}{c_v^2} = - (K_1 + K_{1\bar{n}}) \quad (14)$$

Thus the vacancy annealing obeys a second order annealing equation with a rate constant which is determined by vacancy migration to interstitial clusters. From eq. (13) one sees that $\Delta\rho$ will also obey second order annealing kinetics.

One can also get second order annealing kinetics if most of the interstitial clusters are small ones not seen in Shimomura's experiments. If so, the vacancy interaction with the cluster must still be large since the frequency factor observed in stage III annealing in gold is 40 times that found in quenched gold.

The main point of this discussion is that the interaction of the lattice vacancies with the interstitial clusters is important for both aluminum and gold. It is the fact that $K_{1\bar{n}} \approx 40K_1$ in eq. (14) which in isochronals causes the irradiation peak to occur at a lower temperature than the quench peak for similar defect concentrations.

The situation in copper and silver is not clear. The stage III annealing obeys second order annealing kinetics and is associated with an activation energy which is smaller than the vacancy migration energy. (i.e. $E_{III} = 0.70 \pm 0.04\text{eV}^{17})$, $E_V^M = 0.88 \pm 0.1\text{eV}^{18})$ in copper; $E_{III} = 0.67 \pm 0.04\text{eV}^{17})$, $E_V^M = 0.83 \pm 0.05\text{eV}^{19})$ in silver.). At present, it is not clear what these differences mean. It is possible that the strain field of the interstitial cluster reduces the vacancy migration energy by 0.1 to 0.2eV. It could be that divacancies take part in the annealing. Grenning and Koehler²⁰⁾ used small atomic core impurities to immobilize interstitials in copper, silver, and gold. In copper and in silver containing small amounts of beryllium they found the same.

activation energy and the same frequency factor as Dworschak, Herschbach, and Koehler¹⁷⁾ observed for the pure metals. The annealing kinetics was second order for both the pure and the alloyed metals. This raises questions concerning the reason for second order kinetics in gold. In these copper and silver experiments the fractional impurity concentrations were 10^{-4} or larger. Therefore, the probability of forming large clusters of interstitials is small since most of the migrating interstitials will encounter an impurity before they meet an impurity interstitial complex. Thus, in this case the second order annealing kinetics results from small sized clusters.

In summary, we can say that Stage III annealing in aluminum, gold, and platinum results from vacancy migration. At present it is not clear whether the great majority of the interstitials present are in small clusters (containing one to three interstitials) or in large clusters (containing several hundred interstitials). It is clear that the interaction between the migrating vacancy and the interstitial clusters is important in aluminum, gold, and platinum.

The situation in copper and in silver is not clear. The activation energies seen in irradiated silver and copper are not the vacancy migration energy.

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Figure Captions

- fig. 1 High magnification picture of defects observed before stage III annealing in pure gold irradiated with 3MeV electrons observed from [112] direction.
- fig. 2 Density of defects in irradiated samples versus total flux. This figure shows that number of defects are constant for electron dose between 1.2×10^{18} and 6.0×10^{18} e/cm²
- fig. 3 Measured defect size distribution. Size of defects increases with increasing electron dose.
- fig. 4 Defect size distribution during stage III annealing