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# Divacancies in Irradiated Copper

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The divacancy migration was ascribed to stage III of recovery process on the basis of the observation on the serrations and the bump in the stress-strain curve of low temperature irradiated copper crystal. The divacancies may be produced as the direct results of irradiation. The processes of divacancy formation were discussed referring to the machine calculation performed by Vineyard *et al.* Although the chance of divacancy formation depends on the direction of initial motion of the knock-on, sufficiently large probability is expected even in the irradiation by 1 MeV electrons.

## 1. Introduction

The radiation damage and the recovery processes in copper have been investigated extensively during the last decade, and the detailed mechanisms are now brought to light. There are, however, differences of opinion about the lattice defects responsible for the stage III of recovery process. Since Brinkman, Dixon and Meechan[1] proposed that this recovery step is due to the migration and disappearance of interstitial atoms, Seeger[2] and Meechan, Sosin and Brinkman[3),4)] have asserted the interstitial mechanism. Meanwhile, Corbett, Smith and Walker[3] proved that the single interstitial atoms in copper can migrate below 60°K with the activation energy of 0.12 eV. Meechan, Sosin and Brinkman[4] and also Seeger then insist that there are two types of interstitial atoms and one type can migrate in stage I, while the other type disappears in stage III.

Van Bueren[6] and Li and Nowick[7], however ascribed divacancy migration to stage III. Very recently Suzuki and Furusawa[8] also concluded from their measurements of stress-strain curves that divacancies are responsible for the stage III of recovery process. In this paper the reason to arrive at this conclusion is described briefly, and the processes of formation of divacancies are discussed.

## 2. Stress-Strain Curves of Low Temperature Irradiated Copper Crystals

Suzuki and Furusawa[8] have measured stress-strain curves of copper crystals irradiated at about 90°K in pile. The integrated dose was about $10^{16}$ fast neutrons/cm$^2$. The shear stress-shear strain curves measured at liquid nitrogen temperature are summarized in Fig. 1. The bump in the easy glide region was always observed provided that the low temperature irradiated crystals had not been warmed by more than 30 minutes at 0°C before the tensile test, as already

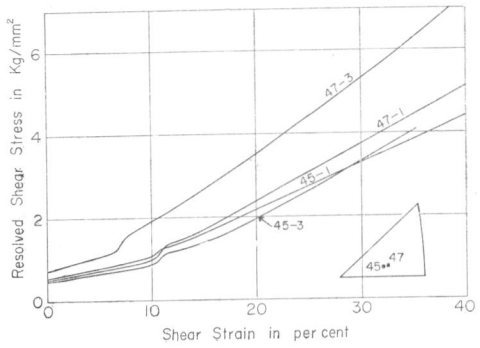


Fig. 1. The stress-strain curves of copper crystals irradiated at 90°K and tested at 78°K.

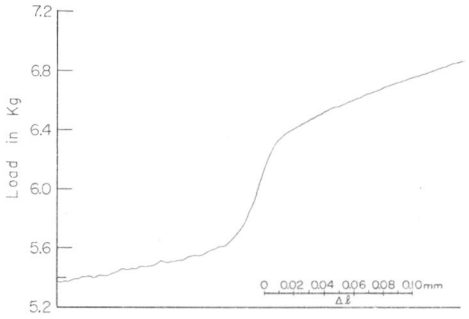


Fig. 2. A part of the recorded stress-strain curve in the vicinity of the bump. Serrations are observed before the bump, but the curve becomes smooth after the bump.

observed by Makin[9]. Small serrations in the stress strain curve were also observed in the easy glide region before the bump as shown in Fig. 2. These serrations disappeared under the same condition as the bump. The serrations and the bump in the stress strain curve, therefore, seem to be caused by the lattice defects which are responsible for the stage III of recovery process.

### 3. Origin of Serrations and Bump

Each serration in the stress-strain curve corresponds to an avalanche of slip, which is due to the decrease of frictional force for dislocations after the passage of a few preceding dislocations. In the case of room temperature irradiated copper[10], dislocation loops may be an important origin of the frictional force, while in low temperature irradiated copper, dislocation loops might be extremely rare, because the irradiation dose was as low as $10^{16}$ fast neutrons/cm$^2$ and also the irradiation temperature was about 90°K. Meanwhile, the isolated interstitial atoms and vacancies could not be the origin of the frictional force which decreases considerably after the passage of a few preceding dislocations. Thus the defects responsible for the stage III of recovery process should be clusters of vacancies or interstitials.

The vacancy cluster can not decompose into single vacancies, because the migration of a single vacancy is frozen below room temperature. On the other hand, a vacancy cluster composed of three vacancies or more does not seem to migrate as a whole below room temperature. The divacancy is, therefore, the only possible defect among the vacancy clusters.

An interstitial cluster forms during the irradiation at liquid nitrogen temperature gathering single interstitials. Therefore, if there were sinks for interstitials such as dislocations, the number of interstitial clusters must decrease. According to Meechan, Sosin and Brinkman[4] the amount of recovery at the stage III of recovery process increased considerably by cold work before the irradiation. The interstitial clusters, therefore, are not responsible for the stage III of recovery process.

The divacancies, on the other hand, may disappear recombining with migrating interstitial atoms during the irradiation at liquid nitrogen temperature. If there were many dislocations, considerable part of interstitial atoms were absorbed into the dislocations and relatively larger amount of divacancies should be left after the irradiation. The divacancies are, therefore, the only lattice defects consistent with the above mentioned experiments.

The origin of the bump was illustrated as follows. The hardening in the region of easy glide is caused by the exhaustion of sources of dislocations. T. Suzuki[11] and the present author[12] have pointed out that there may be sources to multiply dislocations on successive atomic planes. The stress to continue the operation of the source for one atomic plane may be equal to the stress excluding the friction due to divacancies, because the majority of the dislocations are free from the friction and push the preceding dislocations. Meanwhile, the dislocations multiplied on the successive atomic planes are subjected to the friction due to divacancies. The bump takes place when the dislocation sources on one atomic plane has been exhausted.

### 4. Processes of Divacancy Formation

The divacancies responsible for the serrations and the bump in the stress-strain curve

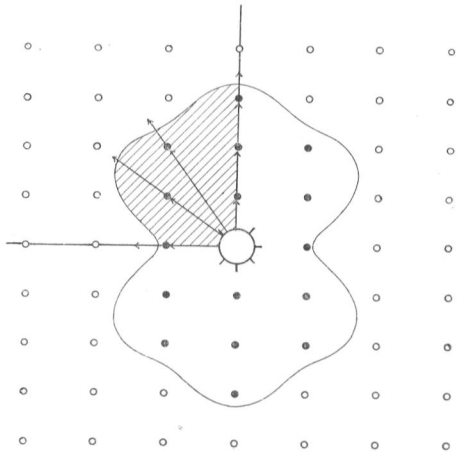

Fig. 3. Atomic displacements in (110) atomic plane. A vacancy is at the center. The open circles indicate the atoms which may be able to form a stable split interstitial with a knock-on. Four replacement collisions in the directions [100], [211], [111], [011] are possible in this atomic plane.

should be produced as the direct result of irradiation. The atomic displacement due to the irradiation depends on the initial direction of motion and the kinetic energy of the knock-on. The divacancies may be produced if the initial direction of knock-on is suitable. The machine calculation performed by Vineyard and his coworkers[13] indicates that there are limited number of processes of atomic displacements at rather low energy irradiation. Using the standard Born-Mayer potential, Vineyard *et al.* showed the limiting separation of the stable Frenkel pair. Figs. 3, 4 and 5 denote an alternate representation of the stable region of the separation, referring to the calculation by Vineyard *et al.*

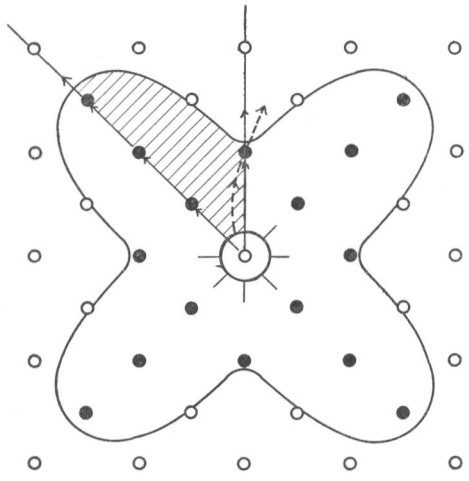

Fig. 4. Atomic displacements in (100) atomic plane. The dotted curve indicates the trajectory of the knock-on by the multiple process producing the divacancy.

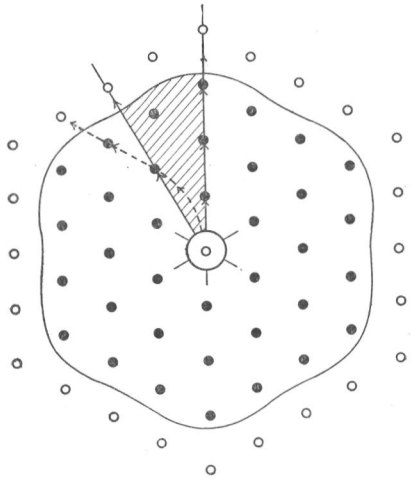

Fig. 5. Atomic displacements in (111) atomic plane.

The displacement events are classified as follows:

I. Simple processes
   (1) Focussing collision along ⟨100⟩
   (2) Focussing collision along ⟨110⟩
   (3) Focussing collision along ⟨111⟩
   (4) Replacement collision along ⟨211⟩
   (5) Replacement collision along ⟨321⟩

II. Multiple processes
   (6) Two replacement collisions along ⟨110⟩
   (7) One replacement collision along ⟨110⟩ and one replacement collision along ⟨100⟩

(1) and (2) have been discussed in detail by Vineyard *et al.* and are known that the threshold energies in these directions are nearly equal to the minimum value of about 25 eV. Meanwhile, the threshold energy along ⟨111⟩ direction was about 90 eV. The replacement collisions in the direction of ⟨211⟩ and ⟨321⟩ have not been calculated by Vineyard *et al.*, but the knock-on should be subjected to higher repulsive potential than in the direction ⟨111⟩ and the threshold energy should be higher than 90 eV. Besides these simple processes there may be multiple processes. The primary knock-on may induce two simple processes of formation of displaced atoms. Since the interest is limited to rather low energy collisions, the possible simple processes of atomic displacement should be along ⟨110⟩ and ⟨100⟩. Two ⟨100⟩ processes are impossible, because they make an angle

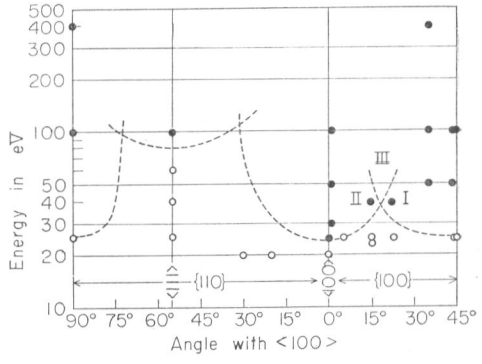


Fig. 6. Schematic representation of the orientation dependence of the threshold energies for various displacement processes. The points in this figure were taken from the calculation by Vineyard *et al.*

of 90 degrees. The two possible multiple processes are represented in Figs. 4 and 5. The multiple process (6) can be discussed in detail using the calculation by Vineyard *et al.* The simple process in the direction of ⟨100⟩ takes place in the vicinity of ⟨100⟩ and the process of ⟨110⟩ in the vicinity of ⟨110⟩, the former takes place in the region I in Fig. 6 and the later in the region II in the figure. The interference between two simple processes is supposed to be very small, except that those are induced by the same knock-on. The region III is, therefore, denotes the conditions of multiple process (6). The threshold energy of the process is almost 40 eV or slightly larger than this value. The extension of this region depends on the shape of the dotted curves limiting the range of ⟨110⟩ and ⟨100⟩ replacement collision in Fig. 6.

The other multiple process takes place in (111) atomic plane as shown in Fig. 4. The machine calculation by Vineyard *et al.* has not been extended to this direction. We may, however, suppose the threshold energy is almost equal to 50 eV.

The orientation dependence of the formation of mono- and divacancies are shown schematically in Fig. 7, where the initial direction of motion of knock-on is shown in standard stereographic projection, and the energy of the knock-on was assumed to be 50 eV. The probability of formation of divacancies seems to be of the order of 10 per cent of single vacancies under the irradiation of about 1 MeV electrons.

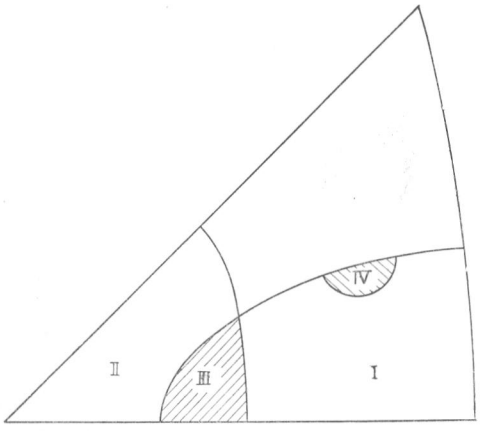


Fig. 7. Schematic representation of the orientation dependence of the displacement events:
I Focussing collision along [110] direction.
II Focussing collision along [100] direction.
III Divacancy formation through the displacements in (100) atomic plane.
IV Divacancy formation through the displacements in (111) atomic plane.

## 5. Formation and Migration Energy of Divacancies

The binding energy of divacancies in copper was estimated by Seeger and Bross[14] as 0.3 eV, and the revised theoretical value by Corless and March[15] was repulsion. These calculations, however, did not take into account the relaxation around the divacancy. It seems to be reasonable to believe that the lattice relaxation increases the binding energy significantly. Kimura, Maddin and Kuhlmann-Wilsdorf[16] assumed there are repulsive force between two vacancies within the distance of several atomic spacing, and estimated from the probability of divacancy formation the repulsive potential to be 0.23 eV. And they also assumed the binding energy in gold as 0.4 eV. These values give 0.6 eV for the energy required to cut a divacancy by a dislocation. This energy is correlated to the stress increase at the bump, and we have the concentration of divacancies of $10^{-7}$ for 100 g/mm$^2$ of stress increase. This value of divacancy concentration does not seem to be unreasonable.

The activation energy of the stage III of recovery process is known to be between 0.6 and 0.7 eV. The divacancy mechanism of stage III of recovery process predicts the migration energy of divacancy should be between 0.6 and 0.7 eV. Damask, Dienes and Weizer[17] calculated the migration energy of divacancies in copper assuming the Morse potential between atoms, and obtained the value of about 0.2 eV. Their calculation, however, neglected the lattice relaxation around the divacancies. The lattice relaxation around the divacancy may be considerably larger than the single vacancy, while the lattice relaxation around the single vacancy was estimated to lower the formation energy by about 0.4 eV[18]. In the calculation of the formation energy of the divacancy[19] it was shown that the lattice relaxation around the stable divacancy lowered the energy by about 1.0 eV compared with the unrelaxed configuration. The intermediate configuration of

migration of the divacancy, however, should change the relaxed configuration and increase the migration energy than in the unrelaxed case.

Meanwhile, we have an experimental information of the migration energy of divacancies in quenched gold, and it seems to be about 0.6 eV[20]. The migration energy of divacancies in gold is, therefore, believed to be only of the order of 0.1—0.2 eV less than that for a single vacancy. This situation may not be changed considerably in the case of copper. Thus the activation energy of the stage III recovery seems to be the migration energy of divacancies.

## 6. Discussion

Seeger and his school[2] insist that the stage III of recovery process takes place by means of the migration of interstitial atoms which are in different configuration than those migrating at stage I. Brinkman, Meechan and Sosin[1),3),4)] are also of the same opinion. The possibility of single interstitial mechanism seems to be excluded by the observation of serrations and bump in the stress-strain curve in the low temperature irradiated copper single crystal.

Meechan, Sosin and Brinkman[4] excluded the possibility of divacancies because of the magnitude of the recovery in stage III relative to that in stage I. The ratio was almost the same for the change of electron energy in the range from 1.0 to 1.4 MeV, while they believed the ratio should increase with increasing energy. The probability of formation of divacancies, however, does not seem to be sensitive to the energy of electron provided that the energy is larger than 1 MeV.

It is the significant characteristic of stage III of recovery process that the process obeys second order kinetics. The major part of divacancies will disappear combining with clusters of interstitials, other divacancies, single vacancies and also with clusters of vacancies. The number of them are almost proportional to that of divacancies during the recovery step, except the single vacancies and the clusters of vacancies. The absorbing probability by these latter two, however, may be much smaller than those by the former two. The kinetics of divacancy annihilation is, therefore, almost the second order.

If there are a sufficient number of dislocations, greater part of divacancies are absorbed into the dislocations, then the annealing kinetics tend to the first order. Meechan, Sosin and Brinkman[4] have observed the change of annealing kinetics just as mentioned.

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## DISCUSSION

**Brandon, D. G.**: It seems fairly clear that the serrations observed in the stress-strain curve are directly related to the pick-up of defects by dislocations, analogous

to the sweeping out of the defects observed by Wilsdorf and Greenfield in neutron irradiated thin films. I don't see how the possible diffusion events involved in this kind of pick up process can be related to the diffusion of individual defects to stationary sinks.

**Suzuki, H.**: The serrations observed in our experiment are different completely from those observed by Greenfield and Wilsdorf. Their specimens were irradiated at reactor temperature and tested at room temperature. The serrations in our experiments were observed in specimens irradiated at liquid nitrogen temperature and tested at liquid nitrogen temperature without heating up to room temperature before the test.

**Seeger, A.**: I should like to point out that our school of thinking agrees of course that divacancy may migrate in the general temperature range corresponding to stage III. Our point is that there are well-defined phenomena in stage III that cannot be explained by divacancies but are very satisfactorily accounted for by interstitial migration.

**Sosin, A.**: I should like to reconsider each of the main points made by Professor Suzuki. First, Professor Suzuki makes quite a bit of use of certain characteristics observed in plastic deformation after neutron irradiation. This is, I feel, somewhat dangerous since the theory of deformation is really not adequate to allow conclusive statements to be made about point defects. Furthermore, since neutron irradiation is involved, several mechanisms may be possible—for example, dispacement spikes or diluted zones. Finally divacancies could indeed be playing a role but this has little bearing on the Stage III dilemma.

As a second point, Professor Suzuki's arguments on the mode of divacancy production based on the calculations of Vineyard *et al.* is, I believe, incorrect. The curve from Vineyard *et al.* relates to the ease of creating a single displacement. The mechanism Suzuki suggests—one displacement created in a direction about half way between the ⟨110⟩ and ⟨100⟩ direction and another along the ⟨100⟩, say—would require, as a threshold, some 60 eV which implies that electron with energy of about 1 MeV are required. However, in our experiments we have observed essentially complete resistivity recovery in copper at room temperature or below when bombarding with electrons of much less energy—say 0.6 MeV.

In this connection, as Brinkman remarked previously, we have published a calculation of the cross-section for divacancy production by electrons in the proceedings of the Berkeley Conference. The calculation overestimates the cross-section since a step probability ejection function was used—it was assumed that the probability for ejection of an atom rose abruptly from zero to unity at the threshold energy. Even then, only small concentrations of divacancies were predicted even up to 2 MeV.

Third, I would like to emphasize the importance of the second order kinetics observed in Stage III in Cu, Ni and Al. Professor Suzuki assumes that we enter Stage III with divacancies, single vacancies and clustered interstitials. Under these conditions and if only the divacancies are mobile, the kinetics will not be second order but will start out looking like some order between one and two and end as a first order process. Furthermore, one would expect most of the interstitials and vacancies to persist beyond Stage III. The observed fact is that almost all of the damage in electron bombardment is eliminated by the end of Stage III.

Summarizing, it is possible, though not necessarily proven, that divacancies are responsible for the deformation effects discussed by Professor Suzuki but this does not appear to relate in anyway to the identification of the mobile defect of Stage III.

**Suzuki, H.**: I would like to reply to the first comment. Mechanical properties of crystals provide different informations on the nature and distribution of defects than those obtained from other measurements. The mechanical properties, therefore, may be useful in assignment of lattice defects responsible for the annealing stages.