PROCEEDINGS OF THE INTERNATIONAL CONFERENCE ON CRYSTAL LATTICE DEFECTS, 1962, CONFERENCE
JOURNAL OF THE PHYSICAL SOCIETY OF JAPAN VOL. 18, SUPPLEMENT III, 1963

Radiation Effects in Metals at Low Temperatures*

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An extensive study has been and is being made of radiation damage by electrons and post irradiation annealing in pure and alloyed copper and aluminum. Copper+0.1 atomic percent silver and beryllium and copper+0.03, 0.1, 0.3, and 1.0 atomic percent gold have been investigated. Presently, we are examining copper+0.1 atomic percent zinc, nickel, gallium, and aluminum. The recovery data are reasonably consistent with a model due to Hasiguti and Martin. Aluminum+0.1 atomic percent copper and zinc also have received attention, but some discrepancy is noted. A qualitative model, invoking migration and trapping of crowdions, appears to fit the recovery data. Stage III in aluminum is governed by second-order kinetics with an activation energy of 0.45 ev. Thus copper and aluminum possess the same "Stage III dilemma".

This paper is a report of continuing studies of radiation effects in pure and alloyed copper and aluminum. We shall describe our observations on pure polycrystalline copper only briefly since they have been reported recently. Preliminary data pertaining to oriented copper single crystals will be presented. We shall concentrate primarily on the effects of solute atom additions in copper. Turning to aluminum, some results pertaining to Stage I will be given but more attention will be directed to Stage III. Finally, some effects of solute addition in aluminum will be discussed.

Our observations on pure polycrystalline copper[1] may be summarized briefly as follows. From measurement of electrical resistivity following electron irradiation near 4.2°K, we have plotted the damage rate (resistivity increase per unit integrated flux) as a function of electron energy in the range from about 450 Kev to 1000 Kev. The shape of the curve can be adequately described by a theory which ascribes the displacements entirely to ejections in directions near to ⟨110⟩ directions. Following this procedure, the minimum displacement energy, T_o, for copper is fixed at about 19—20 ev. While the theory developed in this work is rather arbitrary and approximate, it is useful in affording a consistent manner in which to extrapolate our data to yield a value of T_o since the lowest energy behavior is insensitive to the details of the calculation.

* This research supported by the United States Atomic Energy Commission.

The character of the substages of Stage I (below 60°K) is unexpectedly complex. Substage I_A (14—24°K) decreases, I_B (24—28.5°K) increases slowly, and I_C (28.5-33°K) increases rapidly, respectively, in relative importance as the electron energy is reduced to a value scarcely above the minimum required to achieve displacements (~400 Kev). These observations appear to indicate that directionality effects are significant. To determine the effects of directionality, we have prepared single crystals of copper. The crystals are oriented for electron incidence along ⟨100⟩ and ⟨110⟩ directions. In order to avoid excessive angular beam spread on traverse through the sample, we are attempting to limit the thickness of the sample to less than about 0.013 cm. Two experiments have been performed under these conditions but both experiments were complicated by extensive experimental difficulties. Significantly different damage rates *versus* electron energy were observed but the results of the two experiments were sufficiently inconsistent that the observation must be treated as entirely preliminary. In neither case did the experiment proceed sufficiently far to allow a study of recovery following irradiation. At the moment it appears that the threshold energy is lower in the ⟨100⟩ direction but that the damage rate for displacements in near-⟨110⟩ directions becomes larger near 1 Mev.

We turn now to a discussion of the effects of different solute additions on the recovery of resistivity following electron irradiation.

Among the solute atoms we have investigated, beryllium (0.1 at.%) is particularly effective in suppressing recovery. Only about 45% of the irradiation-induced resistivity increment recovers below 110°K, irrespective of the electron energy. The resistivity then decreases, but subsequently increases, as the temperature of annealing is raised. A large decrease then sets in at about 230°K. These observations are in good qualitative agreement with the observations of Martin[2]. We have not made any detailed study of this solute atom.

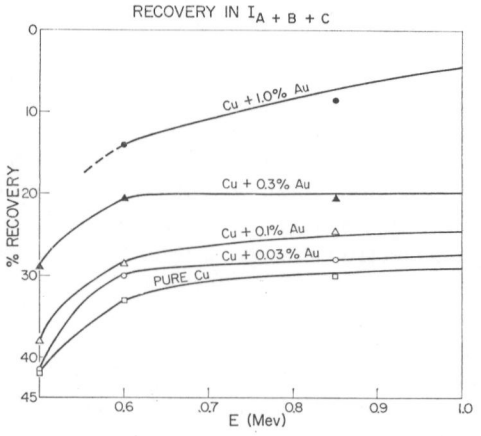

Fig. 1. Resistivity recovery in the "close pair" substages as a function of incident electron energy, E, for several different concentrations of gold in copper.

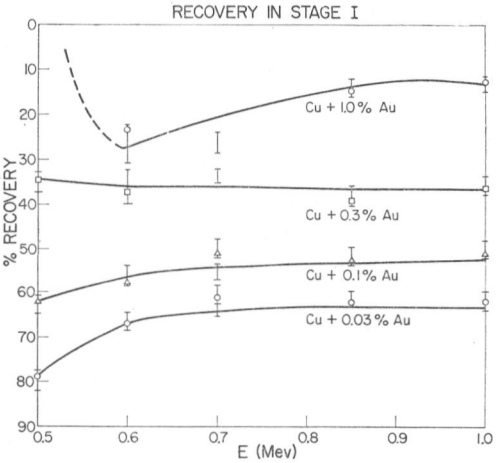

Fig. 2. Resistivity recovery in Stage I as a function of incident electron energy, E, for several different concentrations of gold in copper.

The effects of additions of silver or gold are more straightforward; their effects appear to be quite similar. We have studied these effects for a number of gold concentrations —0.03, 0.1, 0.3, and 1.0 at.%—and as a function of electron energy. The case of Cu+ 1.0 at.% Au is somewhat different than the others; we return to this shortly. In the case of the other materials, it is observed that the extent of Stage I suppression is only slightly dependent on the electron energy above 600–700 Kev. The data are shown in Figs. 1 and 2.

We have attempted to analyze the concentration dependence in the range above 700 Kev, where the energy dependence is small. In the model which we have constructed, each jump of the interstitial is considered. The probability that an interstitial is trapped in its initial position is $P_1 \approx gc$, where c is the concentration of solute atoms and g is a factor introduced to account for the extended interaction between interstitials and solute atoms (*i.e.*, g is a measure of the number of trapping sites around a solute atom). If the interstitial is not trapped in its initial position, its first jump will take it to a new site which may serve as a trap. The probability that an interstitial is not trapped on sampling $(i-1)$ new sites is $(1-gc)^{i-1}$. Then the probability that the interstitial is trapped on sampling its i th new site is, approximately, $P_i \cong gc(1-gc)^{i-1}$ and the probability that an interstitial is trapped on sampling n new sites is $P=\sum_i^n P_i$.

Applying this model to the data of Fig. 1, we deduced that $n=2$ and $g \approx 70$. The model does not fit the data of Fig. 2 as well, presumably because the final position of an interstitial immediately following irradiation is not random with respect to the spatial distribution of solute atoms but is determined to some extent by the impurity content. Furthermore, the concept of a simple average number of sites, n, is probably not entirely justifiable since a large range of values of n is involved. Nevertheless, a reasonable fit can be made by taking $n \cong 24$ and $g \approx 70$.

These values are qualitatively consistent with any simple model of recovery in Stage I. The details of the models will be published soon[3].

If we assume that there are of the order of 70 trapping sites around each gold atom, it appears reasonable, based on the recovery data, that there are perhaps an order of magnitude more trapping sites around each beryllium atom. Then in the case of Cu+0.1 at.% Be and Cu+0.1 at.% Au, the product gc approaches unity. Since resistivity increases are observed directly in both materials—in Stage II in the former and in Stage I in the latter—we suggest that resistivity increases may be observed when interstitials are trapped in sites which are in the overlap "region of influence" of two solute atoms. Furthermore, the failure of the resistivity of Cu+0.3 at.% Au to show directly any recovery at the lowest energies used (see Fig. 2) is probably due to similar effects.

We are presently engaged in studies of the nature of the substages of Stage II in order to attempt to fix the configurations of interstitial and solute atom which lead to trapping. In the case of Cu+Au, a model which incorporates suggestions due to Hasiguti[4] and Martin[2] will be considered here, at least for purposes of discussion. We take the gold atom to be located at the origin, (000). We next assume, following Hasiguti, that the normal interstitial position is in the center of the elementary cube and that the interstitial moves only by ⟨100⟩-type motions (except, perhaps, very close to the solute atom). Both of these assumptions are open to criticism. First, there is no agreement that the normal position of what we may call a collapsed interstitial is in the center of the cube rather than in a slightly more extended form, namely, as an interstitialcy shared by two atoms centered on a normal lattice position and oriented along a ⟨100⟩ direction. In fact, we consider the latter more likely. Furthermore, it is implicitly assumed that the crowdion is not stable; we have favored models which include crowdions. Second, Hasiguti's assumed motion of an interstitial may be broken down into two consecutive jumps, each of distance a, where $2a$ is the cube edge distance, and each jump is along the same direction. It seems quite possible that the two jumps could be at right angles to each other, although both are along ⟨100⟩ directions. The resulting jump, however, would be along a ⟨110⟩ direction.

Putting aside these criticisms, Hasiguti has calculated the stable configurations for a solute atom-interstitial pair. As a result of the assumption concerning the nature of the interstitial jump, Hasiguti found four nonequivalent stable configurations around an oversized atom and calculated the interaction energy for the case of gold solute atoms in copper, based on quasi-continuous elasticity theory and a previous theory due to Eshelby[5]. His tabulated results are given in Table I. Note that there are four possible stable configurations in this model. Two of these configurations are characterized by such low interaction energy that we doubt that they could be easily resolved in our measurements. Based upon this model, we expect two annealing substages in Stage II, with activation energies of approximately 0.15 and 0.28 ev.

To complete the model, we also accept the suggestion of Martin that still deeper trapping sites may be associated with lattice positions which are simultaneously next to

Table I

Interstitial Position*	E (interaction) ev	E (activation) ev
(111) Stable	0.16	0.28
(122) Stable	0.03	0.15
(230) "Stable"	0.003	0.12
(322) → (122)		
(133) "Stable"	0.01	0.13
(430) → (230)		
(333) → (133)		
(342) → (322) → (122)		

* in units of $\frac{1}{2}$ a, where a is the lattice constant (cube edge)

two solute atoms. In an alloy with $c \approx 10^{-3}$, one expects a concentration of such sites of about $\sim 10^{-5}$. Since this is the magnitude of the interstitial-vacancy concentration in most irradiations, it is quite reasonable to expect that an appreciable fraction of the interstitials will be trapped in such sites.

Fig. 3 shows the three substages which have been observed in the Stage II temperature range. The details of the substages vary with gold concentration; we are presently exploring these details. However, the most striking feature of the data is that the magnitudes of the two lower temperatures substages (II_A and II_B) are only slightly dependent on gold concentration (in the range of concentrations studied) whereas the magnitude of the highest temperature substage (II_C is extremely dependent on concentration. The concentration dependence of substage II_C led Martin to suggest that this substage should be ascribed to release of interstitials from gold-gold traps. The relative independence of concentration of the other substages is consistent with this suggestion and with the hypothesis that they should be ascribed to release from traps near single gold atoms, since the concentration of gold is in each case well in excess of the defect concentration.

We have made a few other observations on the characteristics of substages II_A and II_E. Fig. 4 gives the results for II_C of three experiments. The first was a conventional isochronal experiment with points at 55, 61, and 74°K. In the second experiment, points at several different time intervals were made at a series of temperatures: 56, 59, 62, and 66°K. The third experiment was a conventional isothermal experiment, carried out at 62.5°K. All three sets of data can be made to coincide using a time correction procedure, assuming an activation energy of about 0.18± 0.03 ev. This energy is also consistent with

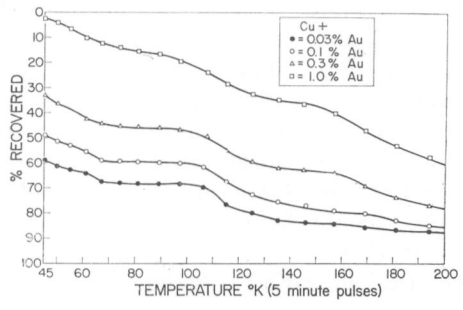

Fig. 3. Resistivity recovery in Stage II. The samples had been irradiated with 1.1 Mev electrons at 4.2°K prior to annealing.

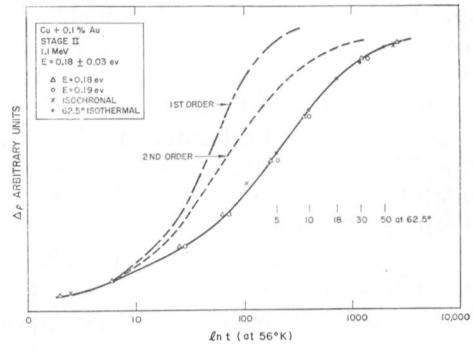

Fig. 4. An analysis of annealing in substage II_A. A time correction has been applied $\tau = \tau_0 \exp(E/kT)$.

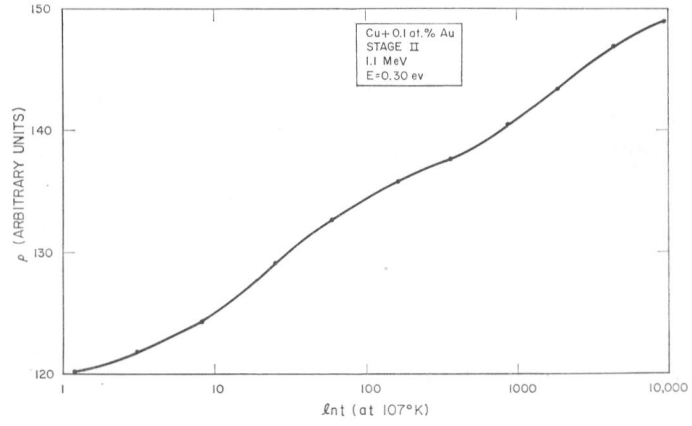

Fig. 5. An analysis of annealing in substage II_B. A time correction has been applied, as in Fig. 4.

the energies calculated from the second experiment, using the slope-change method of calculation. There is reasonable agreement with Hasiguti's value of activation energy associated with the (122) configuration. Fig. 5 gives somewhat similar results (for a single experiment) for II_B. The energy used for time correction, 0.30 ev, is in reasonable agreement with Hasiguti's value of 0.28 ev associated with the (111) configurations.

Further possible confirmation of the model can be obtained from Fig. 4. The curve which has been drawn through the experimental (time-corrected) points is calculated on a model in which the interstitial undergoes a somewhat extensive amount of diffusion before reaching its final location—a sink or another trap. The data are not consistent with either simple first or second order reaction rate theory. Assuming that an interstitial is released from a shallow trap in this substage and is later captured at a deeper trap or annihilated at a vacancy, the data implies that the interstitial cannot leave a trapping site associated with a particular gold atom and move directly to a different trapping site associated with the same gold atom. This is exactly what Hasiguti's model suggests.

There appears to be some difficulty with the Hasiguti's model, however. Fig. 5 suggests that substage II_B is not a single substage but rather a doublet. There appears to be no simple explanation for this in Hasiguti's model. This discrepancy must be regarded as particularly important and leads us to seek an alternate model. We would like to suggest a model which, at least qualitatively, appears to be able to account our observations. In this model, the interstitials which are released from traps are in a crowdion configuration, aligned along a ⟨110⟩ direction. Fixing our attention on a particular gold atom, each of the nearest neighbor positions is an incipient trapping site for a crowdion. However, eight of these twelve positions are equivalent to each other (for a particular ⟨110⟩ direction); the remaining four are equivalent among themselves. We expect a slight difference in binding energy for these two classes of deep traps, thereby explaining the II_B doublet. In this model, II_A is associated with the next more distant parallel ⟨110⟩ direction around the gold atom, providing shallower traps, and II_C is still identified with traps near two gold atoms.

We turn now to aluminum. Fig. 6 presents the recovery spectrum following irradiation with electrons at 1.0 Mev. The spectra following irradiation at 0.7 and 0.4 Mev are quite similar. A first order recovery process with energy of 0.064 ± 0.004 ev occurs, centered at about 19°K. This is certainly due to close pair recombination. The large recovery which occurs between about 27 and 55°K is composed of more than one

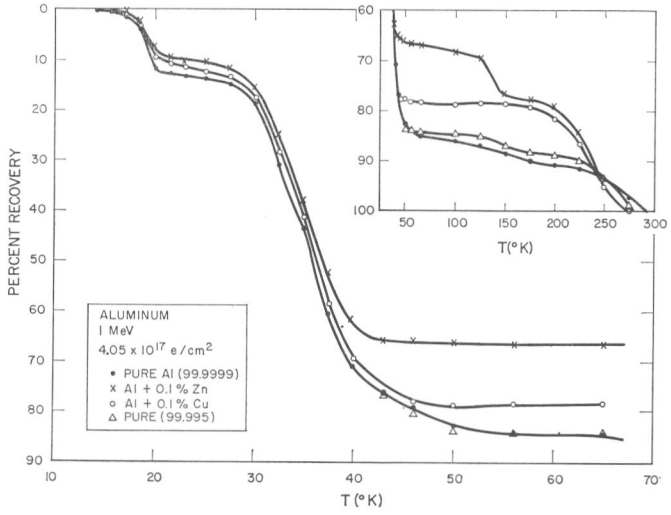

Fig. 6. Resistivity recovery in aluminum and dilute aluminum alloys following irradiation with electrons at 4.2°K.

substage, but has not yet been studied in detail by us.

Note that 0.1 at.% Cu or Zn again causes suppression of recovery in Stage I. About 1/3 of the resistivity which persists in Al+ 0.1 at.% Zn recovers at about 135°K—Stage II. There is also some recovery in the pure aluminum samples but there does not appear to be any significant Stage II recovery in Al+0.1 at.% Cu. Finally, the resistivity recovers fairly completely in Stage III—about 275°K.

We have studied the recovery in Stage III in detail in several isochronal and isothermal annealing experiments. The annealing process is accurately second-order; the activation energy is 0.448 ± 0.009 ev. The results are summarized in Fig. 7. In this experiment, measurements were made at several time intervals at each of succeedingly increasing temperatures. The data are plotted against the equivalent time at 213°K, with a time correction procedure using the above energy. The slope of this curve, which extends over more than three decades of time, is unity, indicating second order kinetics.

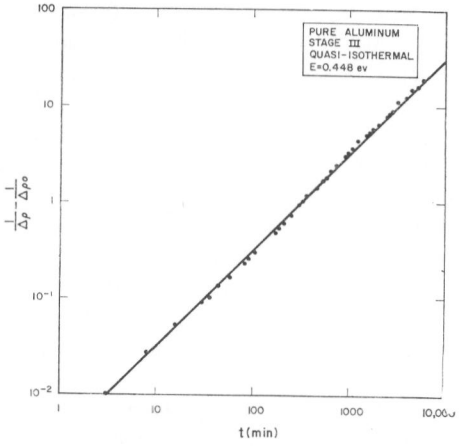

Fig. 7. An analysis of a pulsing experiment in the Stage III temperature region of aluminum. Measurements started at −60°C with subsequent measurements at five degree intervals. Several measurements were made at each temperature following different lengths of time at temperature. The time correction is of the same form as used in Fig. 4.

It appears that the "Stage III dilemma" which exists in copper is also present in aluminum. The migration energy of vacancies in aluminum is reasonably established—0.65 ± 0.06 ev[6]. While some divacancies may be present following 1.0 Mev electron irradiation, few, if any, can be produced by electrons with 0.4 Mev energy. Furthermore, it seems certain that some interstitial migrates in Stage I. It is likely, therefore, that basically the same process occurs in Stage III in aluminum and copper.

References

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DISCUSSION

Vineyard, G.H.: In reference to the dependence of suppression on bombarding energy—Do you explain this by the assumption that the impurity atom terminates a collision chain, resulting in trapping of an interstitial, and the assumption that collision chains are longer at higher energy?

Sosin, A.: No. To the contrary the assumption was made that the impurity atom did not influence the final position of the interstitial atom immediately after ejection. This model adequately explains the observed concentration dependence of suppression in the close pair stages. However, the model is less satisfactory in the latter part of Stage I where long initial interstitial-vacancy separation will occur. Certainly taking into account the effect of the impurity atom on the initial position of the interstitial would improve matters.

Elbaum, C.: Would you care to comment on the initial increase of the resistivity in copper containing gold (1%)?

Sosin, A.: I can only offer a partial answer to the question of the origin of the

resistivity increases which were observed. These increase effects become observable in Cu+0.3 atomic percent Au and obvious in Cu+1.0% Au. Similar effects are noted at higher temperatures in Cu+0.1% Be. The correlation which is suggested is that when the product of the concentration of solute atom times the number of incipient trapping sites begins to approach unity, resistivity increases occur. This suggests that if interstitials are trapped in the overlap region of the spheres of influence of two impurity atoms, its resistivity may actually be greater than when free in the lattice.

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Volume Changes Induced by Radiation in Copper and Aluminum

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The volume change associated with low temperature reactor bombardments have been studied for aluminum and for copper. In each of these cases the volume change-dose relationship was determined as well as isochronal annealing curves.

Both materials were made utilizing a bimetallic strip. The bimetal consisted of a pure metal, either copper or aluminum, with the other half being the same pure metal with a small amount (0.1 atomic percent) of fissile material. During the bombardment, the neutrons present in hole 12 facility cause defects to be produced with the same density in both parts of the bimetal so that no bending is produced from these neutrons. On the other hand, the thermal neutrons produce fission and these energetic fragments produce many displacements. The doped sample will thus expand at a greater rate than the pure sample, and the bimetal strip will bend in accordance with the laws of elementary physics. The deflection of the bimetal strip will only be a function of the fission damage. In the case of aluminum the fissile impurity was U^{235}, and in the case of copper it was boron 10. The selection of these doping materials was determined by their solubility.

Consider now the results of the copper study. The bimetal strip was fabricated from pieces of .010″ thick by .250″ wide and 4″ long. The two pieces were sweated together with soft solder. The top end of strip was clamped and the bottom free to move with an iron core attached to this lower end. This core entered a coil and the deflection of the strip thus changed the magnetic induction of the coil. The deflection was then measured by the changes in magnetic induction. This method was selected as a relatively small deflection was expected, and there is no mechanical coupling between the strip and the detector. This assembly was then mounted in a can with heater so that isochronal annealing studies could be made. Also included in the sample can was a strip of doped material cut adjacent to that used in the bimetal strip. Potential probes and current leads were attached to this so that resistivity measurements could be made simultaneously with the length change.

During the bombardment the can was filled with helium and the change in resistivity and the change in length were measured as a function of dose. Three different runs were made. The results are shown in Fig. 1.