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THERMAL CONVERSION OF INTERSTITIALS IN ELECTRON IRRADIATED COPPER*

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Abstract

A study by internal friction measurements has been made on high purity copper of the effects of 1 MeV electron irradiation on the rate of addition of point defects to dislocations in the temperature range 78°K to 400°K . A distinct minimum in the point defect pinning rate is observed at about 160°K . It is also observed that a peak in the decrement as a function of irradiation time occurs, having a peak position time dependence which reflects the rate at which point defects arrive at dislocations. The above observations are discussed and taken as direct experimental evidence in support of the thermal conversion model. The maximum in internal friction and the minimum in the pinning rate are accounted for in a model of damping due to the dragging of points defects by dislocations.

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One of the outstanding controversies in the interpretation of radiation damage experiments centers around the identification of the defect which migrates in Stage I (around 45°K in copper) and in Stage III (around 275°K in copper). It is generally agreed that an interstitial defect migrates in Stage I, it has been proposed that this defect can thermally convert into another interstitial-type defect which migrates in Stage III.^{1,2} If such a mechanism occurs, then a process which depends on the time-rate at which interstitials diffuse through the lattice may reflect the importance of thermal conversion and provide further insight into its nature. For further details concerning thermal conversion, see Refs. 3 to 8.

Recently, Thompson and Buck⁹ and Roth et al.¹⁰ have used dislocation pinning studies to search for a thermal conversion process. Thompson and Buck irradiated a high purity single crystal of copper with Co⁶⁰ gamma rays; the sample was resonated at about 11 kHz. The observed changes in resonant frequency, due to corresponding changes in effective elastic moduli, and changes in logarithmic decrement were analyzed on the basis of the Granato-Lucke (G-L) model, although the data failed to show the agreement between the observed changes predicted by the G-L model. By using this model, Thompson and Buck deduced the number of pinning points (i.e., lattice defects) added to the dislocation segments as determined

independently by the two measurements. The rate of addition of pinners to dislocations derived from the decrement measurements were then plotted, at one hour exposure to gammas, as a function of temperature of the sample during irradiation. This plot shows a distinct minimum at about 180°K . The minimum value is lower than the rate at 80°K by a factor of about 20; it is lower than the rate near 400°K by a factor $> 10^6$. In turn, the rate at 400°K is greater than the one at 80°K by about 10^5 .

Thompson and Buck also noted the differences in the shapes of the curves of numbers of pinners vs. irradiation time in that from 81°K to below 162°K these curves begin as linear functions, then appear to tend toward saturation; the corresponding curve at 241°K is concave upward -- with no saturation tendency.

The minimum in pinning rate as a function of temperature, as seen in the decrement measurements, was taken as clear experimental evidence which selects uniquely between defect models and points to the conversion model. This conclusion may be slightly compromised in that their modulus measurements show substantially less of a minimum. Furthermore, Roth et al. have reported somewhat similar experiments in which polycrystalline, high purity copper was irradiated with 3 MeV electrons. Only a small pinning rate minimum -- a factor of about two or less between 80°K and 150°K -- was reported in both modulus and decrement measurements. Roth et al. used 5 kHz torsional oscillation.

According to Roth et al., their defect production rate, 7.4×10^{10} defect pairs/cm³-sec, was 185 times greater than the defect production rate used by Thompson and Buck. Accordingly, Roth et al. used initial pinning

rates as compared to the pinning rate at one hour, used by Thompson and Buck.

The differences between the results of Thompson and Buck and of Roth et al. might be attributed to several differences in experimental techniques: gammas vs. electrons, single crystals vs. polycrystals, differing excitation modes, etc. Thus a need exists for additional work in this critical area.

We have recently reported¹¹ results which show a peak in the decrement as a function of irradiation time, at fixed temperature, using high energy electrons. As described previously,^{11,12} we attribute this peak to the enhanced energy dissipated by point defects dragged by dislocations which oscillate in response to an external periodic stress. This description is accurate provided few -- of the order of one -- point defects are present on a vibrating dislocation segment. As the number of defects grows, the motion of the dislocation is sufficiently restricted that the energy dissipation becomes reduced, as is more commonly reported. Thus, the time dependence of the peak should reflect the rate at which point defects arrive at dislocations, and the peak position should serve as temperature dependent characteristic time, t_p , which may then be associated with thermal conversion.

For the work reported herein, 1 MeV electrons were used to bombard a 0.01 cm x 1 cm x 1/2 cm cantilevered beam (i.e., foil) in a configuration similar to that used by Sosin and co-workers.¹³ A defect production rate of approximately 1×10^{11} Frenkel pairs per cm^3 per sec was maintained for all runs. The material was high purity (99.999%) polycrystalline copper

obtained from ASARCO. An average strain amplitude of 5×10^{-6} was used for all runs. Although this value is slightly large and the decrement was somewhat amplitude dependent, reducing the strain by an order of magnitude did not change the character of the decrement vs. time plots. The resonance frequency was approximately 500 Hz. Decrement and modulus readings were taken every three seconds. These data were then fed directly into a computer plotter, whereby the data were plotted out point by point with straight lines connecting the points.

Figures 1-5 show three features which are particularly important:

1. The initial curvature of the normalized inverse modulus defect vs. time plots are negative for the temperature range from 78°K to 110°K but positive for temperatures above 180°K . This is in agreement with the reports of Thompson and Buck but not with the data of Roth et al.
2. The pinning rate curve of Fig. 5 goes through a minimum near 160°K . This is in general agreement with the results of Thompson and Buck although their minimum appeared to be located between 170°K and 180°K . In fact, Thompson and Buck did not investigate the pinning rate at any temperature above 160°K and below 240°K so that the apparent difference in position of the minimum probably is no cause for concern. Furthermore, the position of the minimum depends on the defect production rate, dislocation density, and time at which the pinning rate is calculated so some difference is to be expected. Our position of the minimum agrees with Roth et al. This is comforting since the experimental conditions were similar in production rate, polycrystalline material, etc.

The depth of the minimum is of equal interest with its position. Our data is in better agreement with those of Thompson and Buck than of Roth et al. since the ratio of pinning rates at 78°K and 160°K is about six in our observations; there is an apparent substantial disagreement in depth with the observation of Roth et al. We shall return to this below. Note, however, that we have accepted a different measure of pinning than either Thompson and Buck or Roth et al. Both of these groups follow a standard Granato-Lucke treatment. In this treatment, the normalized inverse modulus defect is generally taken as proportional to $(1 + n)^2$, whereas in our treatment a proportionality to $(1 + n)^1$ is adopted. The justification for this approach has been presented in a previous reference.¹² This difference has no apparent effect on the position of the minimum and only a minor effect on the amplitude.

3. Fig. 5 also demonstrates the effect of temperature on the value of the decrement peak characteristic time, t_p . It is obvious that the curve of t_p vs. temperature can be viewed as a faithful "reflection" of the curve of normalized inverse modulus defect vs. temperature. This observation concerning t_p is reported for the first time here. In fact, we were unaware of any previous observation of this peak effect in the decrement until very recently -- after our early report of this effect. We have now found that J. R. Nielsen¹⁴ observed this peak effect during proton irradiation of copper, even at 20°K, but was unable to present an explanation for its origin.

The three observations are, in all probability, related and due to a common cause. Prior to our own experimental program, we accounted for the

observations of Thompson and Buck -- the first two observations discussed above -- in a model for thermal conversion. This model extends directly to the decrement peak effect when we adopt the position that the decrement peak is due to the dragging of defects by oscillating dislocations and is, therefore, dependent on the number of defects on dislocation lengths. In fact, this is the universal hypothesis which binds all three observations -- the time dependence of each observation is a reflection of the rate of arrival of interstitials at dislocation.

With the above hypothesis, the kinetics of arrival of interstitials at dislocations becomes of central importance. Therefore, we reproduce here the major features of our model on these kinetics, presented earlier.⁴

The rate equations which describe the model are

$$\frac{dn_I}{dt} = \phi' - n_I[K_c + (4\pi r_c I_o + N_o)D_I] \quad (1)$$

$$\frac{dn_{III}}{dt} = n_I[K_c + 4\pi r_c I_o D_I] - n_{III}D_{III}N_o \quad (2)$$

$$\frac{dn_\delta}{dt} = \ell_o[n_I D_I + n_{III} D_{III}] \quad (3)$$

where n_I is the concentration of Stage I interstitials,

n_{III} is the concentration of Stage III interstitials,

K_c is the rate constant for thermal conversion of Stage I interstitials to Stage III interstitials,

I_o is the impurity concentration,

r_c is the radius for capture of interstitials by impurities,

D_I is the diffusion coefficient for the Stage I interstitials,
 D_{III} is the diffusion coefficient for the Stage III interstitials,
 n_δ is the number of interstitials trapped at dislocations on dislocation segments of average length ℓ_o ,
 N_o is the dislocation density, and t is time.

We also have the relations

$$K_c = \nu \exp (-E_c/kT) \quad (4)$$

$$D_I = D_{Io} \exp (-E_I/kT) \quad (5)$$

$$D_{III} = D_{IIIo} \exp (-E_{III}/kT) \quad (6)$$

where ν is the defect jump frequency,

E_c is the energy for thermal conversion of the Stage I interstitial to a Stage III interstitial,

E_I and E_{III} are the migration energies of the Stage I and Stage III interstitials, respectively,

D_{Io} and D_{IIIo} are the appropriate diffusion constants,

k is Boltzmann's constant and T is temperature.

In writing these rate equations, (1) to (3), we have made the following approximations:

1. Interstitial recombination with vacancies is included in a constant numerical factor in ϕ' , of about 1/4. The vacancy concentration is always small in any experiment under consideration.

2. Interstitial-interstitial reactions are ignored for reasons similar to that of the previous point.

3. The impurity trapping term -- $4\pi r_c I_o D_I n_I$ -- is a term which truly describes conversion of interstitials by impurities. To introduce trapping without conversion would merely complicate the equations without any significant effect on the conclusions.

4. No reactions are presumed to occur once an interstitial has reached a dislocation line.

The solution to our rate equations for the rate of arrival of pinners -- interstitials -- at dislocations is ($N_o < 4\pi r_c I_o$).

$$\begin{aligned} \frac{dn_\delta}{dt} = & \frac{\phi' D_I \ell_o}{K_c + 4\pi r_c I_o D_I} \{1 - \exp [-(K_c + 4\pi r_c I_o D_I)t]\} \\ & + \phi' D_{III} \left\{ \frac{1 - \exp[-D_{III} N_o t]}{D_{III} N_o} \right. \\ & \left. + \frac{1 - \exp[-(K_c + 4\pi r_c I_o D_I)t]}{D_{III} N_o - K_c - 4\pi r_c I_o D_I} \right\} \end{aligned} \quad (7)$$

We have shown in Ref. 4 that this simple kinetic formulation describes the pinning rate data reported by Thompson and Buck, derived from damping measurements. It also accounts for some of the details of pinning at a particular temperature, best appreciated by an approximation to Eq. (7):

$$\frac{dn_\delta}{dt} = \phi' \ell_o \left\{ \left[\frac{K_c}{D_I} + 4\pi r_c I_o \right]^{-1} + D_{III} t \right\} \quad (8)$$

From Eq. (7) or Eq. (8), it can be seen that the positive curvature of the high temperature curves is predicted since D_{III} becomes the

controlling term in this range. Furthermore, it is predicted that the pinning rate should be proportional to the defect creation rate, ϕ' .

This is demonstrated by the insert plot in Fig. 2. An additional run was performed at 160°K with a defect production rate, $\phi' = 5 \times 10^{11}$ Frenkel pairs per cm³ per sec. A well defined peak (peak height 1.2) resulted for a time of approximately 30 minutes. Assuming that the decrement roughly scales with production rate, this is in agreement with the other curve at 160°K in Fig. 2.

Still another feature which must be accounted for by a complete kinetic analysis is the initial curvature behavior described above. In fitting the data of Thompson and Buck, the parameters which were used were chosen to correspond to accepted values. Only the energy for thermal conversion was left as a free parameter and the value of about 0.20 eV was deduced. With the adoption of these parameters, given in Ref. 4, it can be shown that the pinning rate should increase linearly at low temperatures instead of showing any significant saturation. Tendency towards saturation could be accounted for by the inclusion in the kinetic analysis of the loss of interstitials from dislocations, presumably by diffusion down the dislocation lines toward common nodal points and, possibly, aggregation into multi-interstitial clusters. We have not included such loss terms into the analysis, pending further detailed experimental observation.

This apparently simple picture is complicated somewhat by a feature of the data in Figs. 1-3, which we have thus far failed to mention -- the amplitude of the peak in the decrement during irradiation. In the model proposed elsewhere and sketched briefly above, this amplitude should be

quite independent of temperature of bombardment, depending only on the number of point defects on dislocation segments. Instead a notable variation in amplitude is observed. Two effects apparently are responsible for this variation.

First, the presence of the Bordoni peak, BP, with its maximum near 80°K and effective below about 200°K , complicates matters. There is a paucity of information concerning the effect of radiation on the BP. Thompson and Holmes¹⁵ found only a 20% diminution in the BP after rather heavy neutron bombardment. In contrast, Nielsen¹⁴ observed that the BP was eradicated after proton bombardment. The results from our work are more consistent with the latter.

A second complication has been noted in our own experiments. We have found that the initial value of the decrement (i.e., after a high temperature annealing treatment and prior to irradiation) and the amplitude of the maximum in decrement are highly structure-sensitive. Although a single sample was used throughout this study, differences in cooling rate, from annealing temperature to irradiation temperature, are amazingly important. For example, the amplitude of the peak, at 160°K was 1.03 and 1.20 in two different runs; note also the variation in values of initial decrement shown in Figs. 1-3. We believe that this high structure sensitivity is related to the character of the BP, at least in part. Obviously, further study of the BP, as effected by irradiation, is needed.

We further suggest that sensitivity to structural details accounts for much of the differences in the results reported by Thompson and Buck, Roth et al., and ourselves.

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FIGURE CAPTIONS

- Figure 1 The decrement normalized to its value at time, $t = 0$, and plotted as a function of time for the indicated temperatures. The initial decrement, $\Delta_0 \times 10^3$, is given in parenthesis beside each temperature.
- Figure 2 The decrement normalized to its value at time, $t = 0$, and plotted as a function of time for the indicated temperatures. The initial decrement, $\Delta_0 \times 10^3$, is given in parenthesis beside each temperature.
- Figure 3 The decrement normalized to its value at time, $t = 0$, and plotted as a function of time for the indicated temperatures. The initial decrement, $\Delta_0 \times 10^3$, is given in parenthesis beside each temperature.
- Figure 4 The normalized inverse modulus defect plotted as a function of time for the indicated temperature. The 78°K curve represents the raw data.
- Figure 5. The time rate of change of the normalized inverse modulus defect evaluated at a time, $t = 1$ minute, and plotted as a function of temperature. The peak time evaluated from the data of Figs. 1, 2, and 3 plotted as a function of temperature.