Recovery of Pure and Alloyed Aluminum in Stages I and II after 2-MeV Electron Irradiation*

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Pure (99.9999%) aluminum and dilute alloys of aluminum were irradiated near helium temperature with 2-MeV electrons and the annealing of stages I and II studied. Five recovery substages are resolved in stage I with the lowest two ascribed to ⟨110⟩ close-pairs and I–*C* to ⟨110⟩ migration. The addition of 0.3 at.% of Zn, Cu, and Ge suppresses recovery as measured by percent of total recovery throughout stage I. Stage II is quite impurity-sensitive but is present in the pure aluminum, as evidenced by two annealing peaks. The results fit the framework of the two-interstitial model with few reservations.

INTRODUCTION

WITH the assumption of a reasonably strong attractive interaction between impurity atoms and interstitials, a dilute concentration of impurities may be expected to suppress the recovery of electrical resistivity following energetic-particle bombardment by means of a trapping mechanism. The first investigators to show that suppression is, indeed, induced because of these impurity additions were Blewitt, Coltman, Klabunde, and Noggle[1] who doped copper with various amounts of several impurities. Sosin and Neely[2] later showed that the amount of suppression in stage I increased with the percentage of solute with almost complete suppression for 1.0 at.% of solute in copper. These earlier works assumed that all of the suppression observed was due entirely to impurity trapping. With the advent of the two-interstitial model used to explain recovery in copper,[3,4] and later its applications to aluminum by Sosin and Rachal,[5] a better model for suppression came about involving a new mechanism in addition to the impurity trapping. It was pointed out[5] that in focusing collisions during irradiation the appearance of an impurity atom could perturb the propagation of dynamic crowdions and in so doing convert them to a second kind of interstitial, the ⟨100⟩ dumbbell. Since these dumbbells do not anneal out until early in stage III, the above conversion suppresses the earlier stages of recovery, namely those due to the ⟨110⟩ interstitials.

The research reported herein was made to investigate the behavior of pure aluminum in stages I and II and to compare it with copper in the light of the two-interstitial model. Also, we wished to investigate how the recovery in aluminum is affected by dilute alloying, with particular interest directed toward determining the relative importance of the two suppression mechanisms mentioned above.

EXPERIMENTAL

The pure aluminum was obtained from A. I. A. G. Metals, Inc., and is quoted as 99.9999% pure. The alloys, with the aluminum also quoted as 99.9999% pure, were obtained from Materials Research Corp. All samples were in the form of ribbons having a thickness of 0.002 in. and a width of 0.030 in. These ribbons were soft soldered to metallic bands which had been deposited on 0.180-in.-diam sapphire rods by Advanced Vacuum Products. There are 15 bands to a rod, each band 0.047 in. wide and spaced 0.047 in. apart. Two samples are mounted on a pair of rods, each with four complete turns of exposed sample and two complete turns of dummy. The Van de Graaff beam, swept both horizontally and vertically by a TV yoke coil, is defined by a rectangular, water-cooled aperture within the drift tube producing a swept area at the sample block of 0.75 in. width and 0.50 in. height. Thus each one of the two mounted samples has 4 in. of ribbon exposed to the beam. After mounting, the samples are annealed *in vacuo* for 36 h at 250°C, etched and washed thoroughly, and then bolted to the sample block.

Standard potentiometric measuring procedures were employed with platinum and carbon resistance thermometers used for temperature monitoring. The anneals are effected through the use of a resistance heater imbedded in the sample block in conjunction with a gas thermal switch. The measuring current through the sample is maintained at 0.2 A to within about 3 parts in 10^6 using an electronic servo. Reproducibility of resistance measurements is well within 0.5 $\mu\Omega$, or about 0.5% of the total resistivity change.

For the major part of the work irradiation was performed at about 6°K and isochronal anneals made up to 31°K, at which point liquid neon was substituted for the liquid helium for the remainder of the anneals. The neon gas was purchased commercially and liquefied in our Collins helium-hydrogen liquefier. A recovery system was used so that the neon gas could be reliquefied. Great pains had to be taken to keep the neon

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[1] T. H. Blewitt, R. R. Coltman, C. E. Klabunde, and T. S. Noggle, J. Appl. Phys. **28**, 639 (1957).
[2] A. Sosin and H. H. Neely, Phys. Rev. **127**, 1465 (1962).
[3] C. J. Meechan, A. Sosin, and J. A. Brinkman, Phys. Rev. **120**, 411 (1960).
[4] A. Seeger, *Radiation Damage in Solids* (International Atomic Energy Agency, Vienna, 1962).
[5] A. Sosin and L. H. Rachal, Phys. Rev. **130**, 2238 (1963).

gas pure. One set of data is reported in which the irradiation was performed at neon temperature.

In dealing with dilute alloys a question that arises is the solubility of the solute in the solvent. Using our measured values of residual resistivity of the alloys, we have compared them with the values given by Vassel.[6] The residual resistivities are listed in Table I. The values for the Ge and the Zn alloys compare quite well with those of Vassel while the agreement for the Cu alloy is not as good. The resistivity of the Cu alloy yields a value of 0.15 at.% rather than the 0.3 at.% quoted, indicating that some agglomeration of the Cu may have taken place, possibly during the annealing before final mounting.

DAMAGE MEASURED AS A FUNCTION OF TEMPERATURE

Since the isochronal anneal data were obtained using two different base temperatures, a means of combining these data into a single, coherent picture was needed. Previous results by Herschbach[7] on the deviations from Matthiesson's Rule in aluminum and gold indicated that the amount of damage remaining in the samples as measured at neon temperature (27.4°K) would not be the same as that measured at liquid-helium temperature. Thus, to plot the two sets of data together, the neon data had to be corrected by the ratio of the damage measured at helium temperature to that measured at neon temperature. Also, any change in this ratio with the change in defect concentration must be taken into account.

To ascertain the above, first pre-irradiation measurements were made at both temperatures. Later, measurements at both temperatures were made following anneals at 31, 55, and 200°K. In all measurements the ratio of the damage remaining measured at 6°K to that at 27.4°K was 0.80±0.02 in the pure aluminum,

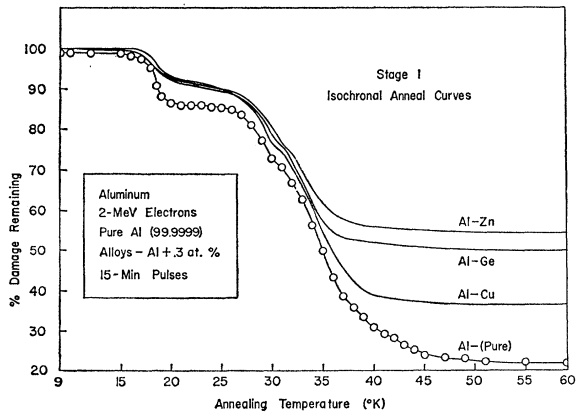

FIG. 1. Stage-I isochronal anneal curves for pure aluminum and three dilute alloys of aluminum. To avoid crowding, data points have not been plotted.

[6] C. R. Vassel, J. Phys. Chem. Solids **7**, 90 (1958).
[7] K. Herschbach, Phys. Rev. **130**, 554 (1963).

indicating that over the range of defect concentration present, the deviation is independent of the concentration. For the alloys the ratio was within 1.02±0.02 for all temperatures. Thus damage annealed out as measured at neon temperature was reduced by 0.8 in the pure aluminum as compared with helium based data, whereas no reduction was necessary in the alloy data.

We have attempted to compare our results with those of Herschbach which he interprets as being in qualitative agreement with the Sondheimer and Wilson theory for such deviations. An expression used by Herschbach obtained from the above theory gives for the deviation

$$\Delta R(T)=R_{\rm id}(T)R_{\rm res}/(aR_{\rm id}(T)+bR_{\rm res}), \qquad (1)$$

where $\Delta R(T)$ is the deviation in the resistance due to damage measured at helium temperature and at temperature T; $R_{\rm id}$ is the resistance at T before irradiation; $R_{\rm res}$ is the damage remaining at T as measured at helium temperature; and a and b are constants of order unity. Because we only measure the deviation at one temperature, we can only solve for one of the unknown constants. Herschbach obtains from his data, $a=4.65$ and $b=0.75$. Using his value for b we get a value of $a=2.53$, somewhat lower than the previous value. Since for sufficiently low temperature, for the helium base in the present case, $\Delta R(T)$ is zero, then $\Delta R(T)$ as a function of T will be expected to rise to some maximum value and then decrease as $R_{\rm res}/a$ according to the annealing behavior of the metal in question. The maximum lies at $R_{\rm id}(T)\simeq R_{\rm res}$. The corresponding temperature for the above maximal condition in the work of Herschbach occurs near 40°K, whereas in the present case it obtains near 30°K. Thus in the present work, $\Delta R(T)$ rises with increasing temperature below 30°K faster than in the former one. In a plot of $\Delta R(T)/[R_{\rm left}(T)/R_{\rm dam}(6°{\rm K})]$ versus temperature, Herschbach at 27°K gets a value of about 7.0 while in the present case this value is 18.0, very near the maximum value of the former case.

RESULTS

A. Stage I

The isochronal annealing in stage I following electron irradiation (2 MeV) near 6°K is shown in Fig. 1 for

TABLE I. Sample resistivity data.

Sample	$\rho_0(10^{-9}\Omega$ cm) (6°K)	$\rho_0(20°{\rm C})/\rho_0(6°{\rm K})$	Total$\Delta\rho$ ($10^{-10}\Omega$ cm)	$R_{\rm He}{}^c/R_{\rm Ne}$
Al (pure) run 1	2.60	1270.0	25.0[a]	···
Al (pure) run 2	2.19	1290.0	27.2[a]	···
Al (pure) run 3	1.77	1400.0	21.4[b]	0.795
Al 0.3 at.% Ge	154.0	22.5	36.8[a]	1.021
Al 0.3 at.% Cu	83.0	37.0	42.1[a]	···
Al 0.3 at.% Zn	150.0	27.0	40.1[a]	1.041
Al 0.3 at.% Zn	130.0	25.4	37.6[b]	1.014

[a] Irradiated at helium temperature.
[b] Irradiated at 27.4°K.
[c] After 29°K anneal.

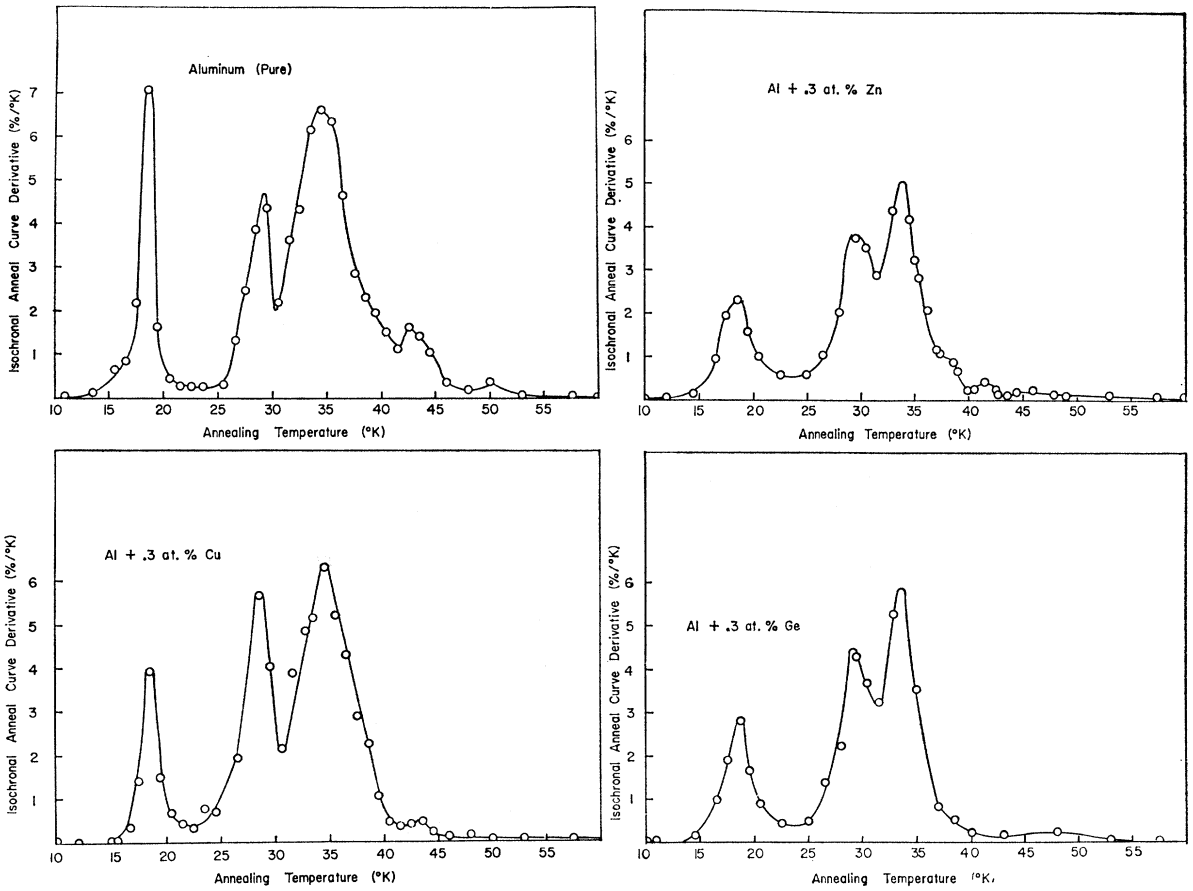

FIG. 2. The slope of the isochronal anneal curves for stage I. The irradiation was performed at 6°K.

pure aluminum and three dilute alloys of aluminum. In this percentage of recovery plot, suppression by the alloying becomes quite evident at about 20°K. The relative amount of suppression among the alloys does not vary significantly, however, until the latter part of the stage, from 35°K on up. At the end of the stage the Zn alloy has been suppressed 27%, the Ge alloy 31%, and the Cu alloy has the least effect on the suppression of recovery of only 13%. For the pure aluminum 78% of total recovery is realized at the end of stage I. The corresponding value reported by Herschbach[7] using 21-MeV deuterons was 61% and the value given by Sosin and Rachal[5] for 1.0-MeV electrons is about 83%.

The annealing character of the four samples in stage I is depicted by the isochronal derivative curves shown in Fig. 2 in which three large peaks are clearly defined in all samples. A small peak is present at ~43°K except in the Ge alloy. A substage at 39°K found by Herschbach is not so well defined here, being resolved only for the Zn alloy. This peak is resolved also for pure aluminum in a later run (Figs. 5 and 6). Herschbach reports four substages in stage I and indicates the possibility of a fifth near 30°K. In the present case this peak is well defined and is centered at 29°K. In Table II it is seen that the center temperatures for I-*A* and I-*B* in the

TABLE II. Pertinent data regarding stage-I recovery.

Substage designation	Sample[a]	T_c (°K)	% Recovery due to substage	% R_p-R_a at end of substage	Activity
I *A*	Al (pure)	18.4	13.5	0.0	⟨110⟩
I *A*	Al+Cu	18.4	9.3	4.2	close
I *A*	Al+Ge	18.4	9.9	3.6	pairs
I *A*	Al+Zn	18.3	9.9	3.6	
I *B*	Al (pure)	29.2	16.0	0.0	⟨110⟩
I *B*	Al+Cu	28.7	16.0	4.0	close
I *B*	Al+Ge	29.2	14.7	4.8	pairs
I *B*	Al+Zn	29.3	13.5	6.0	
I *C*	Al (pure)	34.7	34.8	0.0	
I *C*	Al+Cu	34.2	32.4	6.4	mobile
I *C*	Al+Ge	33.8	19.6	20.0	⟨110⟩
I *C*	Al+Zn	33.8	22.4	22.5	
I *D*	Al (pure)	39.0	7.5	0.0	shallow
I *D*	Al+Cu	39.0	4.2	9.7	traps or
I *D*	Al+Ge	none	1.8	23.0	cluster
I *D*	Al+Zn	38.8	1.5	27.0	breakup
I *E*	Al (pure)	42.5	4.9	0.0	shallow
I *E*	Al+Cu	43.2	1.2	13.4	traps or
I *E*	Al+Ge	none	0.6	28.0	cluster
I *E*	Al+Zn	41.5	1.0	32.0	breakup

[a] Alloys 0.3 at.%.

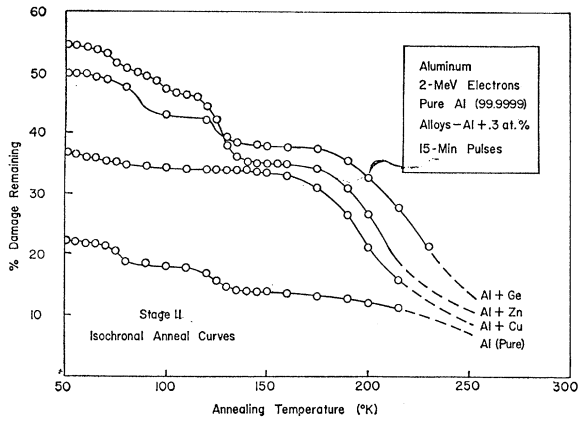

FIG. 3. Stage-II isochronal anneal curves for pure aluminum and three dilute alloys of aluminum. The irradiation was performed at 6°K.

four specimens are in good agreement, but the center temperature of I-*C* is higher for the pure sample than for any of the alloys. The center temperature obtained for I-*C* from Fig. 6 also confirms this trend. Since I-*B* and I-*C* overlap and their respective contributions to the recovery as given in Table II are difficult to separate, the values listed are only estimates. The sum of the two, however, is accurate.

It should be noted here that in all runs made on the pure aluminum, annealing of about 2% was found below 9°K.

B. Stage II

Stage II was investigated in some detail since it is in this stage that the damage suppressed in stage I due to impurity trapping is expected to anneal out. The isochronal annealing plot of the specimens for stage II is shown in Fig. 3. In the pure sample two distinct annealing peaks are found (see Fig. 4), one centered at 126°K and the lower one at 78°K. The 126°K peak is also present in the Al-Zn and the Al-Ge alloys, but the lower peak has divided into two at 75 and 97°K in the zinc alloy. This lower peak in the Al-Ge is very broad and is centered at 83°K. We feel that more careful investigation of this peak will show it made up of more than one peak, similar to the Al-Zn alloy.

The behavior of the copper alloy in stage II is of great interest. For Al+0.1 at.% Cu, Sosin and Rachal[5] found that there was no definable annealing peak in stage II. This they attribute to an inability of the copper impurities to trap crowdions. This leaves the problem of explaining why the recovery seen in the pure sample is not seen in the Al+0.1 at.% Cu. This they explain using the mechanism for the production of static crowdions as due to propagation of dynamic crowdions down ⟨110⟩ chains. With the addition of impurities in the lattice, the range of these propagating defects is restricted with also some conversion of the dynamic crowdions to ⟨100⟩ dumbbells. These two effects decrease the probability of a thermally migrating ⟨110⟩ interstitial meeting an impurity other than copper and being trapped. We find essentially the same results as above for Al+0.3 at.% Cu. Only 3% of total recovery is accomplished in this state, and this occurs below 80°K. The 126°K peak seen in the other three samples is completely missing for the copper alloy.

In Table III are listed some of the pertinent facts regarding stage II recovery. Note that the damage suppressed in stage I has not fully annealed out at the end of this stage, indicating that either there are higher activation energy traps yet to release trapped crowdions above this stage or that some mechanism other than impurity trapping is at work suppressing stage I recovery. In the Ge alloy almost one-fourth of the total damage still remains, which in the pure sample was annealed out at the end of the stage. Similar results are seen for the other two alloys in Table III.

TABLE III. Pertinent data regarding stage II recovery.

Substage designation	Sample[a]	T_c (°K)	% Recovery due to substage	% R_p-R_a at end of substage	Activity
II *A*	Al (pure)	78	5.5	0.0	impurity
II *A*	Al+Cu	none	2.5	16.4	trap
II *A*	Al+Ge	83	8.0	24.6	release of
II *A*	Al+Zn	75 and 97	8.3	28.2	crowdions
II *B*	Al (pure)	126	3.8	0.0	impurity
II *B*	Al+Cu	none	0.7	19.5	trap
II *B*	Al+Ge	126	4.3	24.1	release of
II *B*	Al+Zn	126	11.3	21.4	crowdions
III	Al (pure)	...	...		
III	Al+Cu	~190	>25		dumbbells
III	Al+Ge	~200	>29		
III	Al+Zn	...	...		

[a] Alloys 0.3 at.%.

DISCUSSION

We propose to explain the previous results within the framework of the two interstitial model first proposed to account for recovery in copper[3,4] and later applied to aluminum by Sosin and Rachal.[5] In this model the ⟨110⟩ split interstial, the static crowdion, is expected to become mobile in Stage I, where five annealing peaks were found. First we wish to identify the close-pair recovery substages associated with this interstitial. One expects that for increasing energy transfer from the bombarding particle to the lattice sites, the range of the interstitials will increase, thereby decreasing the relative concentrations of close-pairs to long range migrating interstitials. For heavy-charged-particle irradiation, then, one expects the close-pair substages to be suppressed with respect to electron produced damage and conversely for the peak (or peaks) due to the long-range migrating ⟨110⟩ to be less significant for electron irradiation with respect to heavy ion bombardment.

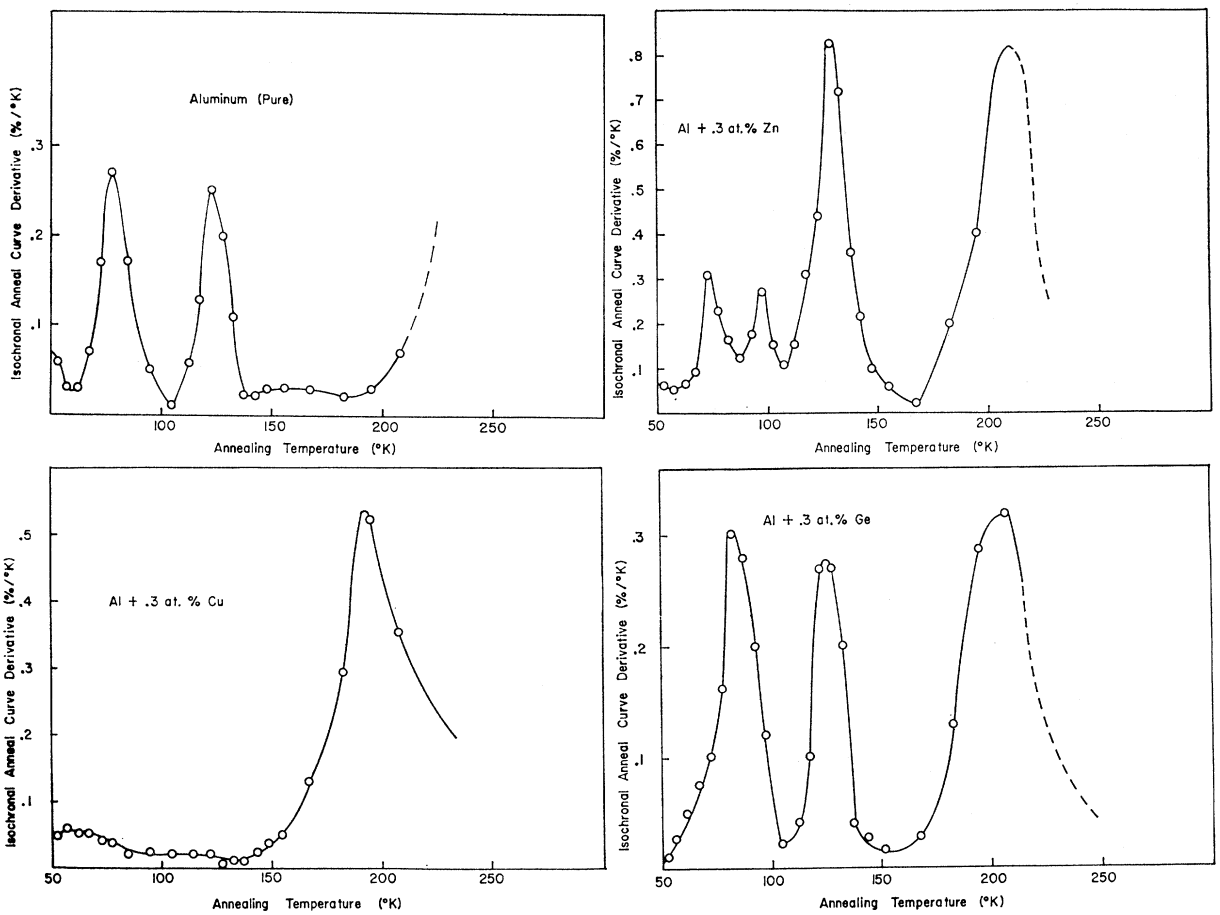

FIG. 4. The slope of the isochronal anneal curves for stage II. The irradiation was performed at 6°K.

The above can be investigated by comparing the present results with those of Herschbach[7] in which he irradiated pure aluminum with 21-MeV deuterons. We compare peaks I-*A*, I-*B*, and I-*C*, the three lowest peaks in stage I as listed in Table II.

The recovery due to I-*A* in the deuteron case is about 5% of the total recovery, while 13.5% is evidenced in the present case. Likewise more recovery is seen in I-*B* after electron irradiation with approximately 16% of total recovery, whereas in the deuteron case no estimate can be made because this peak was not resolved, indicating a large degree of suppression. Thus, for I-*A* and I-*B*, recovery is suppressed in the heavy ion bombardment relative to electron irradiation at 2 MeV. Just the opposite result is found for I-*C*. I-*C* accounts for over 40% of the total recovery in the work of Herschbach but is about 35% in the present results. The implication is that a different process is needed to explain annealing in I-*A* and I-*B* as compared with I-*C*. It should be noted here that the above argument should be interpreted on the assumption that there is another process at work that tends to change the recovery seen due to different irradiating mechanisms. It is the differing production rates for crowdions and dumbbells for the two cases. With heavy ions more ⟨100⟩ interstitials will be formed initially than with electrons, thus suppressing ⟨110⟩ recovery in the former case. However, suppression of the ⟨110⟩ recovery as a whole should result from this mechanism, and it is hard to imagine how it could suppress a given ⟨110⟩ annealing process more than another.

Another key to the identity of an annealing process is the annealing kinetics obeyed, with close pairs having first-order kinetics and freely migrating interstitials second. An indication of the kinetics associated with a given annealing peak is the behavior of the center temperature of the peak as a function of the concentration of the defects giving rise to the peak. For first order there is no change in the center temperature with the concentration, but for higher orders there is a temperature shift. For I-*A* and I-*B* it was seen that the T_c for all four samples was in fairly good agreement for differing defect concentrations in the samples. The difference in concentrations of crowdions does not fully determine the temperature shift, however, due to the excess concentration of vacancies present in the alloys.

Because of this and because of the inherent inaccuracies in derivative plots, we can only accept the apparent upward temperature shift of T_c of I-C in the pure specimen as an *indication* of possible higher order kinetics for substage I-C rather than a definitive argument. From the above we conclude that I-A and I-B are due to close-pair recovery, and I-C is assigned tentatively to ⟨110⟩ free migration. Recent measurements of the annealing kinetics of substage I-A at the Atomics International Laboratory[8] indicate that this substage is, indeed, first order, in support of the above conclusion. Final judgment of the kinetics of I-B and I-C await future measurement.

Substages I-A and I-B can be further characterized. In high-energy deuteron irradiation with the attendant large energy transfer, dynamic crowdions are produced with energy too high to allow long range focusing and these are quickly defocused giving a higher ratio of ⟨100⟩ defects to ⟨110⟩ defects. The greater recovery in stage I in the present work than in that of Herschbach[7] supports this. Thus in deuteron irradiation we expect the ⟨100⟩ process to be enhanced when compared with electron irradiated recovery. Since the opposite obtains for substages I-A and I-B, we characterize these two substages as due to ⟨110⟩ close-pair recovery. A similar argument applied to the results for the alloys yields the same conclusion. As discussed later, conversion of dynamic crowdions to dumbbells changes the concentrations of defects in favor of the ⟨100⟩ processes. Thus in the alloys there should be more ⟨100⟩ close-pairs with an enhancement of the associated recovery. In the alloys, I-A and I-B are suppressed with respect to the pure specimen, supporting the conclusion above.

In the helium-based data, I-D was resolved for only the Zn alloy, and I-E was resolved for all but the Ge alloy. From the run in which two samples were irradiated at neon temperature (see Figs. 5 and 6), the I-D peak in the pure aluminum was resolved with a center temperature of 39.0°K. Herschbach[7] has credited these two peaks to either shallow trap release or cluster breakup. For clusters, we expect greater recovery for the deuteron case. I-D in the results of Herschbach is larger than in the present case, lending some credence to the clustering idea, but for I-E there appears no significant difference in the magnitudes of the two results. Herschbach does find I-E about 2°K higher than ours.

As Sosin and Rachal[5] have shown, the suppression of recovery in aluminum alloys is due to two effects: the trapping of ⟨110⟩ interstitials by impurity atoms and the conversion of ⟨110⟩ defects to ⟨100⟩ defects through defocusing of dynamic crowdions during irradiation. Since the suppressed damage due to impurity trapping is expected to anneal out in stage II, the suppressed damage remaining at the end of that stage is due to the defocusing mechanism. From Table III it is seen that in the Al-Ge alloy 24% of total recovery is suppressed at the end of stage II. Since the total suppression of the sample at the end of stage I was 28%, then 14% of the suppression would appear to be due to impurity trapping and 86% due to the defocusing mechanism. For the zinc alloy the defocusing mechanism accounts for 67% of the suppression, while in the copper alloy there is actually more suppression at the end of stage II than at the end of stage I, implying 100%+suppression due to defocused crowdions.

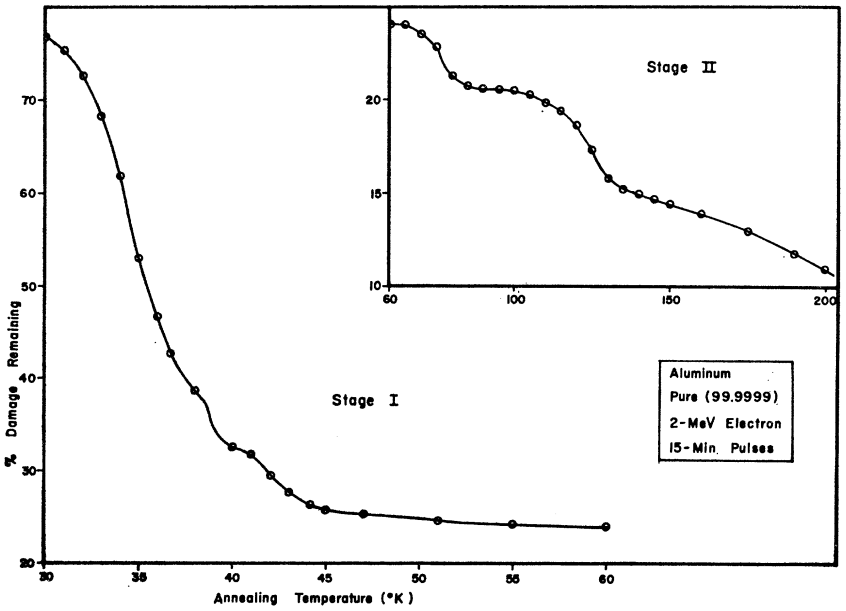

FIG. 5. Latter stage-I isochronal anneal curve for pure aluminum with stage-II isochronal anneal curve for pure aluminum in insert. Irradiation was done at 27.4°K and the anneals were for 15 min at each temperature.

[8] A. Sosin (private communication).

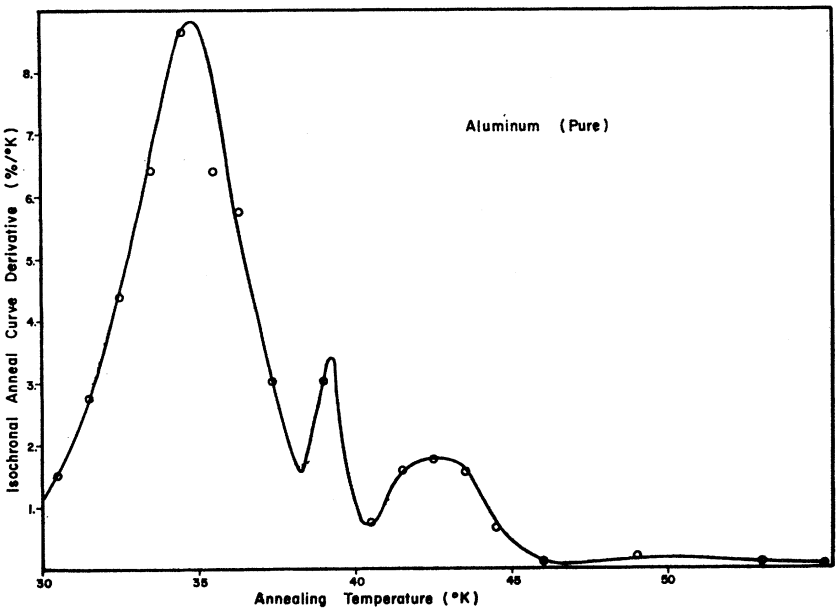

FIG. 6. The slope of the isochronal anneal curve for stage I, the irradiation performed at 27.4°K.

From the behavior of the copper alloy in stage II we reach the same conclusion that Sosin and Rachal[5] did for Al+0.1 at.% Cu, namely, that copper impurities do not trap crowdions. The suppression of the recovery seen in pure aluminum by the copper additions was discussed earlier. We attribute the peak at 126°K as due to impurity trap release. The lower peaks appear to be very impurity-sensitive, with activation energies apparently dependent upon the kind of impurity in the aluminum lattice, which is opposite from the behavior of the 126°K peak. The model for impurity trap release that seems to fit the best would assign the 126°K peak as release from a trapping site corresponding to the position of closest approach of a crowdion to the solute trapping atom, with the lower temperature peaks due to longer ranged trapping sites. More work must be done, however, on stage II before a complete model for trapping can be formulated.

CONCLUSIONS

From the results of the present work we draw the following conclusions:

(1) Stage I in aluminum is evidenced by five recovery substages, the lowest two attributed to ⟨110⟩ close-pairs with I-*C* assigned tentatively to the freely migrating crowdion.

(2) Suppression of the percentage of total recovery in stage I in the alloys is accomplished through impurity trapping of crowdions and by the alteration of the concentration ratios of the two species of defects present, with the latter process contributing from 67 to 100% of the suppression in the three alloys.

(3) Stage II in the pure aluminum is evidenced by two distinct peaks attributed to unspecified impurity traps; stage II in the alloys is similar to that of the pure but quite impurity sensitive. Copper impurities do not trap crowdions.

(4) The resistivity due to damage remaining in the pure aluminum as measured at neon temperature is 25% higher than the same damage measured at 6°K. This deviation from Matthiesson's rule is in qualitative agreement with similar measurements made by Herschbach. No deviation was found in the alloys.

(5) No substage corresponding to ⟨100⟩ close-pair annealing has been identified. We expect such substage(s) to be masked by the big recovery peak early in stage III previously attributed to ⟨100⟩ free migration. Thus this peak is expected to resolve into peaks due to both dumbbell close pairs and freely migrating dumbbells similar to the results of stage I for crowdions. There is some evidence that this may be the case.[9]

We feel that the results and conclusions herein reported can be interpreted within the framework of the two-interstitial model. There is still too much conjecture and too much to explain, however, to consider the story by any means complete.

ACKNOWLEDGMENT

We gratefully acknowledge the helpful discussions and suggestions of Dr. A. Sosin.

[9] F. Dworschak and J. S. Koehler, Bull. Am. Phys. Soc. **10**, 361 (1965).