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

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Samples of pure aluminum and aluminum alloyed with 0.3 at.% Zn, Cu, and Ge were irradiated by 2-MeV electrons to several widely differing doses and at a variety of temperatures. Isochronal annealing studies were performed with 30-min anneals spaced 5° apart from 60°K to the conclusion of stage III. In one experiment a pure aluminum and a zinc-alloy sample were exposed to air when at a temperature of 300°C prior to irradiation. The presence of the additional air impurities was found to impede the motion of the defect migrating in stage III. Impurity effects dominate the recovery through the stage-II region and extend into stage III, although the possibility of an intrinsic process near 73°K exists. From the results of this work, the stage-III recovery in pure aluminum can be explained in terms of a model where single vacancies migrate to clusters of interstitials that were formed during the preceding stages of annealing.

I. INTRODUCTION

It has been well established that impurities dominate the stage-II (60–170°K) recovery in aluminum.[1–3] Several experimenters have reported annealing behavior in the early part of stage II that suggests the possibility of an intrinsic process in this region.[3–5] Impurity effects have been found to extend into the stage-III region. Garr and Sosin[6] report a recovery substage near 190°K in pure aluminum that is influenced by the residual impurities in that it decreases as the purity of the sample increases. In studies with pure aluminum alloyed with 0.1 at.% Mg, Ag, or Ga they found appreciable substructure in the early part of stage III.

The identity of the defect(s) mobile in the stage-III region is still in doubt. The observation that stage-III recovery in a pure metal is governed by a unique activation energy and that the kinetics of the reaction is sensibly second order has led some experimenters to identify the mobile defect as the dumbbell interstitial.[4,6–8] A number of experiments have been done in which it has been argued that the defect which is mobile in stage III is responsible for the clustering of solute atoms in aluminum alloys,[5,9,10] indicating this defect to be the migrating vacancy. Other possibilities exist, such as the migration or breakup of interstitial agglomerates (e.g., dimers) or possibly deep-trap release of interstitials. Corbett[11] argues for a multiplicity of processes, rather than a unique process, in stage III. Herschbach and Jackson[8] believe that stage III in aluminum is composed of at least three different annealing processes. The introduction of impurity solute atoms into a "pure" metal has proved to be a useful tool in the search for the identity of the defects in the annealing of a specimen following irradiation.

The research reported in this paper was performed with both pure and dilutely alloyed aluminum samples in an effort to further investigate the recovery in stages II and III following 2-MeV electron irradiation. In particular, the recovery between pure aluminum samples and the alloys is compared for several different doses. In one experiment both a pure aluminum sample and one of the alloys were exposed to the atmosphere while at 300°C during the preirradiation treatment. The resulting diffusion of air into the samples was found to have a noticeable effect upon the recovery following a subsequent irradiation.

II. EXPERIMENTAL

The specimen materials used were identical to those reported by Snead and Shearin.[2] The pure aluminum was quoted as 99.9999% pure and the alloys were the same quoted purity of aluminum that had been doped with 0.3 at.% Zn, Cu, or Ge. All samples were in the form of foils with a thickness of 5.1×10^{-3} cm and a width of 7.6×10^{-2} cm. The samples were wound around two sapphire strips and then mounted onto a copper sample holder. The details of this sample holder and the mounting process have been fully described elsewhere.[12]

The preirradiation treatment of the mounted samples consisted of etching and washing the samples and then performing a furnace anneal at 300°C for 24 h in a vacuum of 10^{-5} Torr or better. Following a slow cool-down the sample holder was then mounted in the cryostat, described in detail elsewhere.[12] In the air-poisoned run a pure aluminum sample and a zinc-alloy

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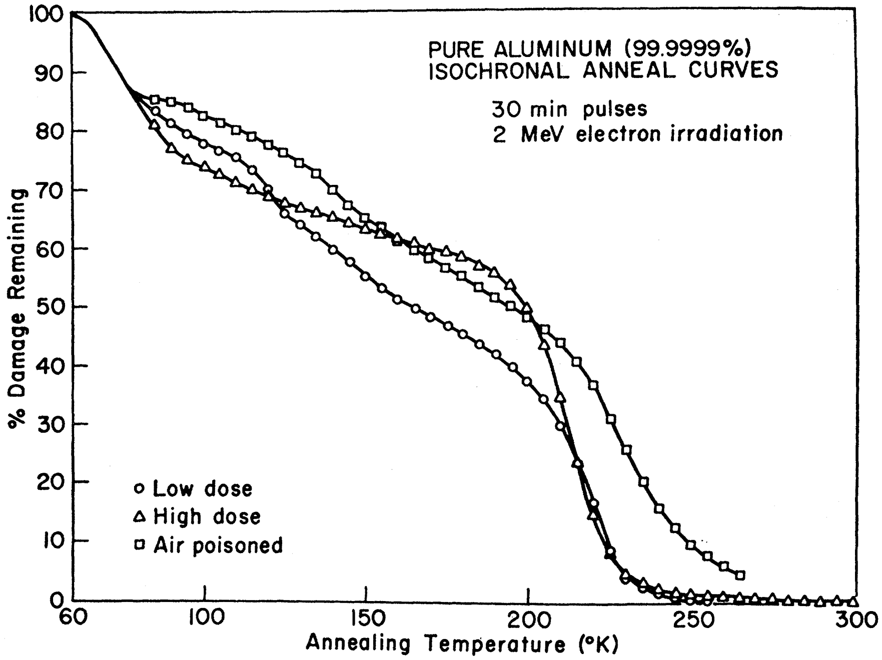

FIG. 1. Isochronal anneal curves for pure aluminum.

sample were exposed to air while at 300°C, as mentioned previously.

Standard potentiometric measuring techniques were employed with the temperature being monitored by a platinum resistance thermometer. The measuring current through the samples was maintained at 150 mA to within about 5 parts in 10^6. The reproducibility of voltage measurements was better than 10^{-7} V, corresponding to an uncertainty in the resistivity of about 10^{-11} Ω cm. During the anneals the temperature could be maintained within ±0.2K° by means of a resistance heater mounted to the sample holder. The residual resistivity of the pure aluminum samples at 4.2°K was 1.74×10^{-9} Ω cm, which corresponds to a resistivity ratio ($\rho_{300°\mathrm{K}}/\rho_{4.2°\mathrm{K}}$) of about 1650. This resistivity ratio for the pure aluminum sample used in the air-poisoned run was 900, a significant decrease over the preceding value.

The irradiations were performed with a Van de Graaff accelerator. The samples were cooled by liquid neon during the irradiations. In some cases the sample temperatures were maintained below the suspected advent of I_E free migration while in others free migration was taking place during the irradiation. In the air-poisoned run the temperature of the samples during irradiation was near 80°K. The isochronal annealing schedule following irradiation consisted of points five degrees apart from 60°K to the conclusion of the experiment (>250°K), with 30 min being spent at each temperature.

III. RESULTS

A. Pure Aluminum

The isochronal anneal curves for the pure aluminum samples are shown in Fig. 1 with the corresponding derivative plots shown in Figs. 2 and 3. The recovery is measured relative to the damage remaining following an anneal to 60°K ($\Delta\rho_0$). The values of $\Delta\rho_0$ for each of the three runs are indicated on the derivative plots. Since the irradiation temperature during the air-poisoned run was near 80°K, the $\Delta\rho_0$ in this case refers to the damage remaining following an 80°K anneal. The various runs will hereafter be referred to as the low-dose, high-dose, and air-poisoned runs. It is seen that the initial defect concentration exceeds the impurity concentration in both the low-dose and the high-dose runs. Table I shows the percentages of damage annealing out in various temperature intervals. Over 50% of the damage anneals in the stage-III region (above 170°K).

Upon inspection of Figs. 1–3 several things are worthy of note:

(1) The fractional recovery below 80°K is essentially the same in both the low- and high-dose runs with a definite recovery substage occuring at 73°K in each case.

(2) The remainder of stage II appears to be impurity dominated with fractional recovery being suppressed in the high-dose run relative to the low-dose run.

(3) The stage-III region is dominated by a single peak that is dose-dependent, shifting its center temperature toward lower temperature as the dose increases.

(4) The latter part of the stage-III peak in the air-poisoned run does not appear as sharp as it does in the other runs.

The stage-III peak in the pure aluminum appears to be due to a single process. The order of kinetics for

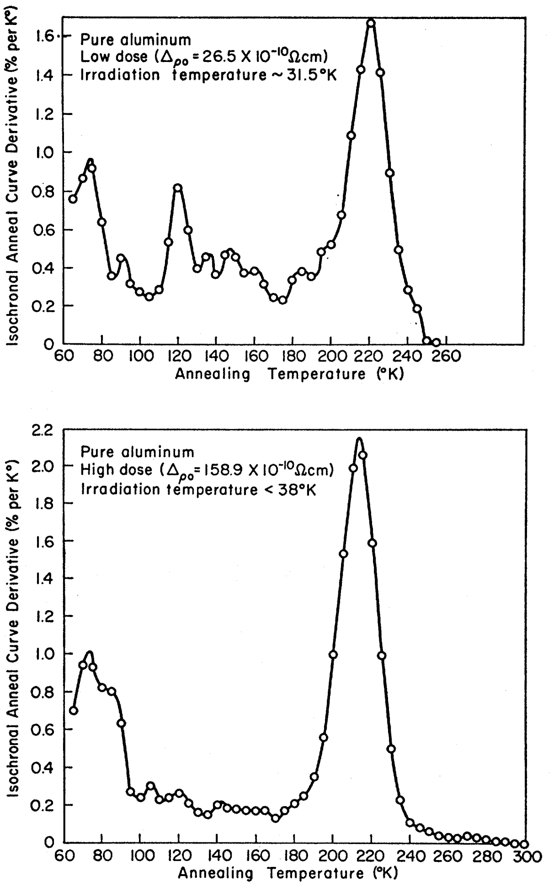

FIG. 2. The slope of the isochronal anneal curves for pure aluminum in the low-dose and high-dose runs.

this process is defined[13] by the expression

$$dn/dT=-(K/a)n^{\gamma}\exp(-E/kT),\qquad (1)$$

where n is the concentration of defects recovering, K is a constant involving the frequency factor, a is the warming rate ($\frac{1}{6}$K° per min in these experiments), γ is the order of kinetics, E is the activation energy, T is the absolute temperature, and k is the Boltzmann constant. When comparing the low- and high-dose runs with the pure aluminum, the shift in the center temperature of this stage-III peak is found to be 6.5°K. As a result of this dose-dependent behavior, the effective order of the kinetics for the process involved may be obtained from the expression

$$\Delta T_c=(\gamma_{\mathrm{eff}}-1)\frac{T_{c1}T_{c2}}{E/k}\ln\left(\frac{n_2}{n_1}\right),\qquad (2)$$

which can be derived by use of (1) for each of the two doses. In (2), γ_{eff} is the effective order of the kinetics, T_{c1} and T_{c2} are the center temperatures for the low and high doses, respectively, $\Delta T_c=T_{c1}-T_{c2}$, n_1 and n_2 are the concentrations of defects annealing in the low- and high-dose runs, and E and k are as defined in (1). If the order of kinetics for this process is dose-dependent, then γ_{eff} will be some average of the respective values of γ for the low- and high-dose runs. From the data, T_{c1}= 220°K, T_{c2}= 213.5°K, and n_2/n_1= 7.07. An activation energy of 0.60 eV is assumed, based on the results of Isebeck *et al.*[7] and Federighi *et al.*[5] Using these values an effective order of kinetics of 1.5 is obtained. This figure is significantly lower than the value of approximately 2 that has been reported by other experimenters[1,5,6] for the order of kinetics associated with this process.

B. Alloys

Most of the work done with the alloys was done using the zinc alloy. Both a low- and a high-dose run were performed using this alloy in order to provide a direct basis of comparison with the pure aluminum. For the same reason a zinc-alloy sample was used in the air-poisoned run. In addition a low-dose run was performed using both a copper- and a germanium-alloy sample.

The isochronal anneal curves for experiments using the zinc alloy are shown in Fig. 4 with the corresponding

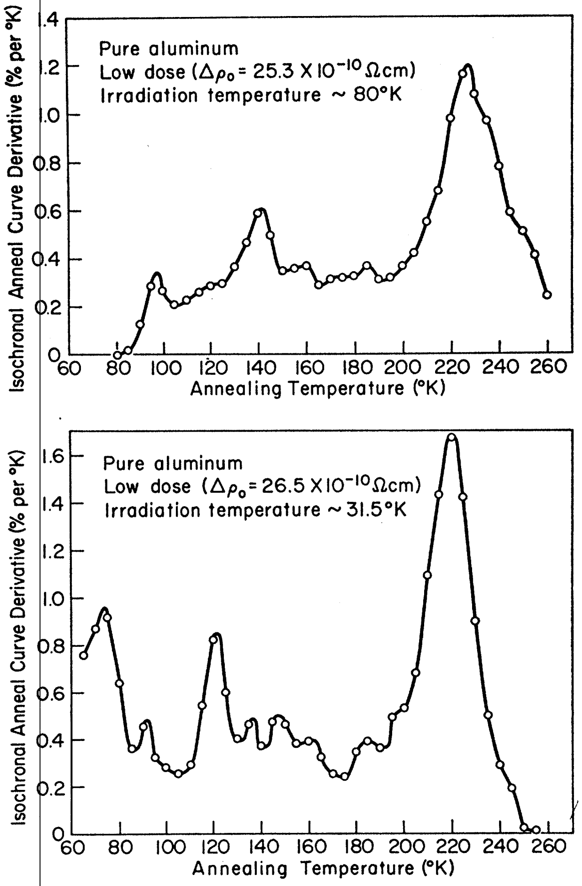

FIG. 3. The slope of the isochronal anneal curves for pure aluminum in the air-poisoned and low-dose runs.

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TABLE I. Comparison of the recovery of pure aluminum and zinc alloy in certain temperature regions for the low-dose, high-dose, and air-poisoned runs.

Pure aluminum

Treatment	$\Delta\rho_0$ ($10^{-10}\ \Omega$ cm)	% recovery (60–80°K)	% recovery 60–100°K	% recovery 100–170°K	% recovery 170–260°K	% damage remaining at 260°K
Low dose	26.5[a]	13.5	20.3	28.1	51.6	0.0
High dose	158.9[a]	15.2	26.1	14.1	59.1	0.7
Air-poisoned low dose	25.7[b]	...	...	24.2	52.1	5.9

Al+0.3 at.% zinc

Treatment	$\Delta\rho_0$ ($10^{-10}\ \Omega$ cm)	% recovery 60–80°K	% recovery 60–110°K	% recovery 110–150°K	% recovery 150–260°K	% damage remaining at 260°
Low dose	104.7[a]	5.5	13.6	22.7	56.2	7.5
High dose	696.6[a]	6.1	16.6	23.8	58.7	0.9
Air-poisoned low dose	43.2[b]	...	...	22.6	35.9	29.2

[a] Following an anneal to 60°K.
[b] Following an anneal to 80°K.

derivative plots shown in Fig. 5. The values of $\Delta\rho_0$ and the respective sample temperatures during irradiation are indicated in Fig. 5. As in the studies with the pure aluminum, the recovery below 80°K is seen to be relatively independent of dose. However, Table I shows that the recovery in this region is definitely suppressed in the zinc alloy relative to the pure aluminum. A closer inspection of the low- and high-dose runs in Fig. 5 shows that a recovery peak occurs at about 73°K in each case. Since the magnitude and position of this peak are essentially the same in both of these runs, this peak appears to be a first-order peak. Figure 2 shows that a dose-independent peak likewise occurs at 73°K in the pure aluminum. Garr and Sosin[3] reported a recovery substage centered at 73.5°K in their pure aluminum samples which was observed to increase with increasing sample purity. They mentioned that this peak may possibly be due to an intrinsic process.

Comparison of Figs. 2 and 5 shows that it is possible to identify a recovery peak in the region 80–100°K for both the pure aluminum and zinc-alloy samples. This peak is also present in the air-poisoned run in each case. In the zinc alloy this substage appears to be relatively dose-independent with a center temperature near 100°K. In the pure aluminum, however, this peak is definitely not independent of dose, with a shift of its center temperature of over 6K° lower in the high-dose run compared to the low-dose run.

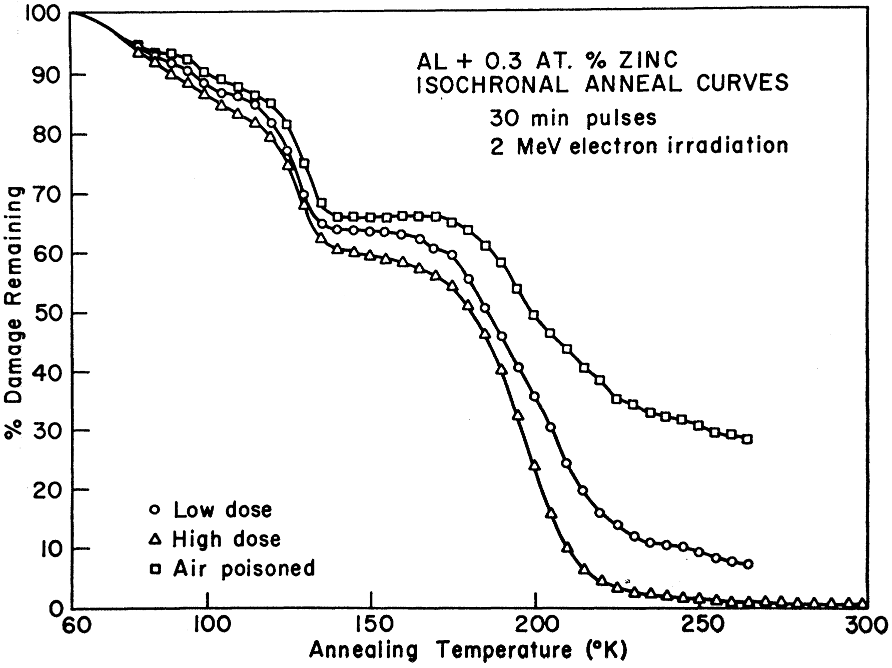

FIG. 4. Isochronal anneal curves for the zinc-alloy samples.

A prominent recovery peak in the zinc alloy occurs at approximately 128°K in all three runs. This peak recovers between 21.5 and 23.1% of the damage. This is clearly a first-order peak and is believed due to the release of interstitials from the zinc-impurity traps.

Recovery in the stage-III region in the zinc alloy is seen to be more complicated than it is in the pure aluminum. The low-dose run seems to indicate that there are *at least two* distinct overlapping recovery processess taking place in stage III. Evidence for this is also seen from the results of the air-poisoned run, although the latter part of stage III is further complicated by the additional air impurities. This behavior in the latter part of stage III was also observed in the pure aluminum sample used in the air-poisoned run, as seen in Fig. 3. Although the stage-III peak in the high-dose run appears to be due to a single-recovery process, it must be realized that the defect concentration is very much higher in this run than in the others. Thus, if the latter part of stage III is due to a dose-dependent process and the initial part is not, we might expect a complete overlapping of these two peaks at a sufficiently high dose.

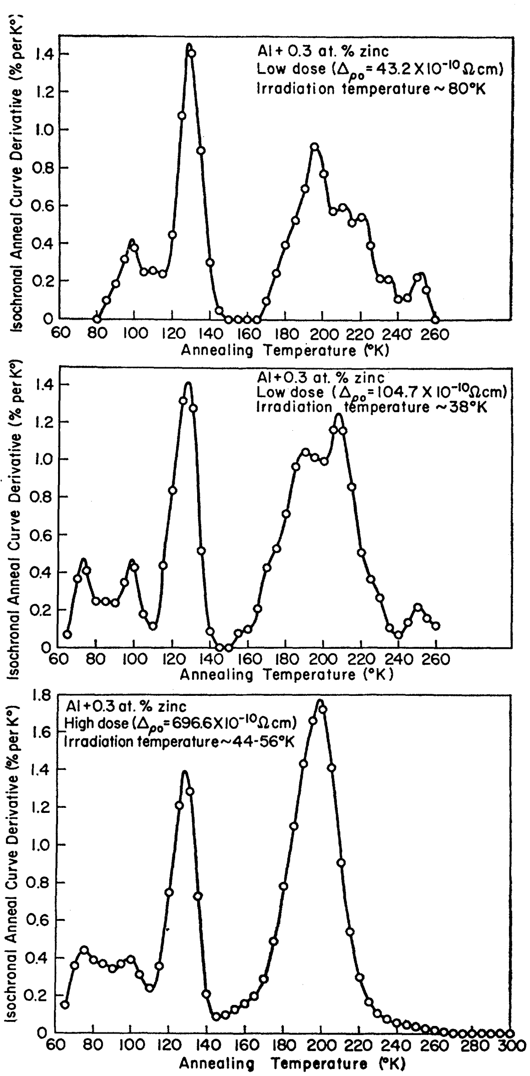

FIG. 5. The slope of the isochronal anneal curves for the zinc-alloy samples in the air-poisoned, low-dose, and high-dose runs.

Concentrating on the air-poisoned run, it is seen from Table I that the presence of the additional air impurities serves to delay the diffusion of the defect(s) recovering in stage III, particularly the latter part of this region. This suppression is much more noticeable in the case of the zinc alloy than it is in the pure aluminum, with nearly 30% of the initial damage still remaining at 260°K in the former case and 5.9% in the latter.

The isochronal anneal curves depicting the recovery of resistivity in the copper and germanium alloys are shown in Fig. 6 along with the comparable low-dose runs with the pure aluminum and the zinc alloy. It is seen that these curves reflect quite different regions of recovery. The copper alloy, for example, shows almost no recovery until stage III. Figure 7 shows the corresponding derivative plots. It is apparent that most, if not all, of the stage-II region is dominated by impurities. It is also clear that, at least for the alloys, a strong argument for several distinct processes in stage III can be made. The fact that the copper alloy had little recovery prior to 160°K suggests that the big peak in the early part of stage III in this alloy is due to impurity-trap release. Other experimenters[1,2] have reported that copper impurities do not trap interstitials in aluminum samples. In each of these cases this statement concerned the fact that no recovery peak was observed in stage II in copper-doped aluminum. The present results likewise show no trap-release peak in stage II, but the large peak occuring during the early portion of stage III is attributed to interstitials released from copper-impurity atoms rather than the migration of a second interstitial.

Several interesting things happen at the end of the stage-III recovery in the alloys (Fig. 7). The slope of the isochronal-anneal curve changes its sign after 235°K in the copper alloy, indicating that the resistivity contribution due to defects in this sample *increases* as the temperature of the sample is raised. This behavior is not observed in the other alloys. Evidently G.P. zone formation is taking place with the copper atoms being transported to zones rich in solute atoms. Evidence of G. P. zone formation in aluminum alloys has been previously reported by others.[3,5,9,10] In the zinc and germanium alloys a small recovery peak occurs near 250°K, following the large peak near the end of stage III. This peak is also distinguishable in the zinc alloy in the air-poisoned run (Fig. 5). Since such a peak is not prominent in the pure aluminum samples, it seems reasonable to associate it with the impurities in the alloys.

Concerning the region between 60 and 80°K in the copper and germanium alloys (Fig. 7), there is evidence for a recovery peak at about 73°K in the copper alloy, as was found in the pure aluminum and the zinc alloy.

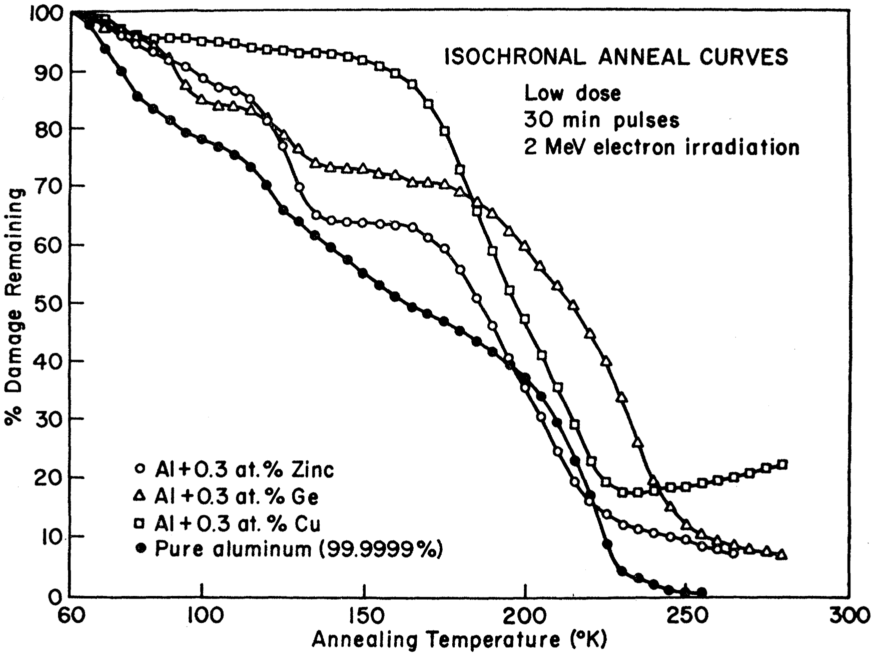

FIG. 6. Isochronal anneal curves for pure aluminum and all three of the alloys used in the low-dose runs.

However, this peak is not well defined in the germanium alloy. The recovery between 80 and 100°K is quite different in all three alloys, which would seem to reflect differing trapping characteristics among the dopants.

IV. DISCUSSION

The recovery in the stage-II region (60–170°K) is governed by the impurities in the sample, with the possibility of an intrinsic process near 73°K. Several experimenters in the past[4,5] have felt that free interstitial migration occurs in the region from 60 to 100°K. As recently reported by Garr and Sosin[3] there is still considerable doubt concerning the nature of this recovery in the early part of stage II. The results of this research do not appreciably clarify the situation.

It seems clear from the results of this research that impurity effects extend well into the stage-III region. Several shoulders are seen on the low-temperature side of the main stage-III peak in the low-dose run with the pure aluminum (Figs. 2 and 3). The low-dose runs with each of the alloys (Fig. 7) show a prominent recovery peak on the low-temperature side of the "main" stage-III peak. In the case of the copper alloy, as mentioned before, this peak must certainly be due to trap release by the copper impurities. It seems likely that this is the case in the zinc and germanium alloys also. In the high-dose run with the zinc alloy, only one recovery peak in the stage-III region is distinguishable. This is reasonable since trap release in this region could well be a first-order process and the migration of a defect in the latter portion of the stage is definitely not a first-order process. Thus, these two substages could completely overlap for a sufficiently large defect concentration. In fact, the trap-release peak may not exist at all for large defect concentrations. If the dose-dependent peak is due to the migration of vacancies, for example, the trapped interstitials may be able to combine with vacancies at a temperature below where the impurities would release them.

Federighi *et al.*[5] found a shoulder on the low-temperatude side (near 200°K) of the main stage-III peak in aluminum of 99.995% purity which had been doped with vacancies (via quenching from 600°C) and then irradiated with fast neutrons. This shoulder was not present in their pure aluminum sample that had been annealed at 600°C and then neutron irradiated. They interpreted the shoulder as being due to correlated recombination of vacancies in regions of concentrated defects (depleted zones) produced by the neutron irradiation.

Garr and Sosin,[6] in studies using 99.995% pure aluminum, also found a distinct shoulder on the low-temperature side of the main stage-III peak. This small peak was influenced by the impurities in their samples, with its magnitude decreasing with increasing sample purity. In studies using several dilute alloys of aluminum they found similar peaks which were larger than in the case of their pure aluminum samples. They feel that this stage-III shoulder is due to impurities.

The dose-dependent behavior of the main stage-III peak indicates the free migration of a defect. There is still considerable controversy as to the nature of this defect. The large percentage of the initial damage annealing in this region in the pure aluminum would seem to rule out deep trap release of interstitials since the defect concentration is often many times the impurity

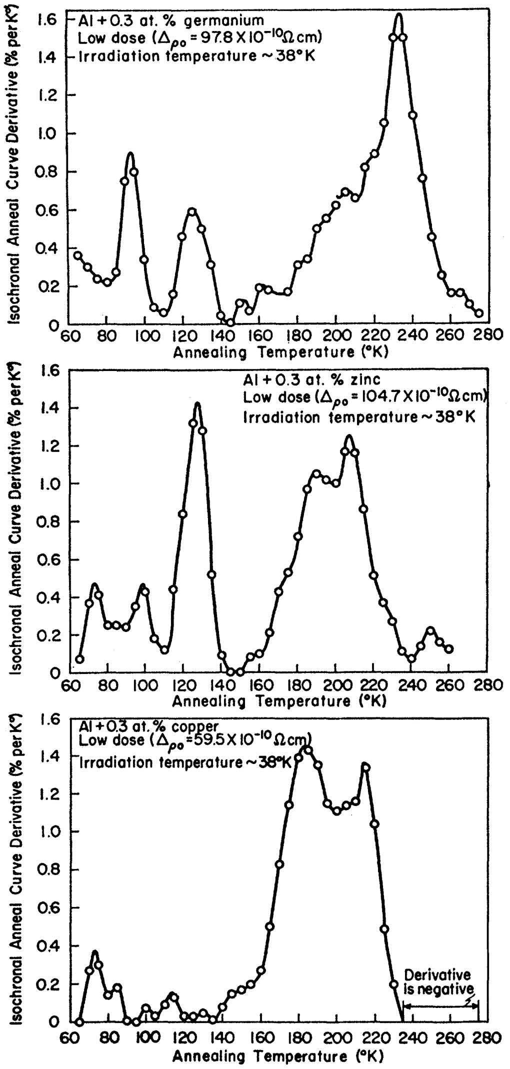

FIG. 7. The slope of the isochronal anneal curves for all three alloys in the low-dose runs.

concentration. Burger *et al.*[4] found that stage III in pure aluminum was essentially the same (percentagewise) when the defect concentration was varied over a hundredfold. In their high-dose runs the defect concentrations were well in excess of the impurity concentration.

If the interstitials are not in a trapped state in the latter part of stage III, then they must either exist in interstitial clusters or they must exist as so-called dumbbell, or converted, interstitials. In view of the one-interstitial model of recovery[11] it would appear that the agglomeration of migrating interstitials must be considered. Corbett, Smith, and Walker[14] state that the cross section for interaction between two interstitials is comparable with that for the annihilation interaction between an interstitial and a vacancy. Federighi *et al.*[5] believe that interstitial clustering takes place during stage-I free migration.

Snead, Wiffin, and Kauffman[13] have recently studied the stage-I recovery in fcc pure metals following 2-MeV electron irradiation and have found that recovery in the I_E substage (free-interstitial migration) in copper is dose-dependent. In particular, the fraction of I_E recovery increases as the defect concentration approaches, and then passes, the impurity concentration. As the dose increases further, the fraction of I_E recovery passes through a plateau and then begins to decrease. If the dose is sufficiently high they find, with the aid of a data point obtained by Dworschak *et al.*,[15] that almost complete suppression of I_E results. This suppression for the high doses they explain on the basis of dimer formation (primarily). At very low doses the competition for a migrating interstitial is dominated by the impurities, with the result that most interstitials are trapped. As the dose increases, the lattice vacancies and the interstitials themselves offer competition for the migrating interstitial. For sufficiently high doses the interstitials produced by the irradiation are close enough to each other so that no migration occurs in I_E due to the attraction of the interstitials for each other, causing dimer formation from close interstitial pairs. The defect levels investigated in the present research, even for the low-dose runs, are such that a large number of dimers should be formed during the free migration of interstitials in stage I.

It has been widely claimed that few dimers should be formed during an irradiation which is performed at a temperature above I_E. Several experimenters have performed studies where the recovery spectrum following a high-temperature irradiation (above I_E) was compared with one following a low-temperature irradiation (below I_E). Bauer and Sosin[16] have performed an experiment in which they irradiated copper with 1.3-MeV electrons. One sample was irradiated at 70°K and another was irradiated at 10°K and then warmed to 70°K. The resistivity increments in the two samples (at 70°K) were nearly equal in order to avoid any concentration-dependent effects. They found closely identical annealing in stage III for each of the samples and concluded from this that dimer migration or breakup could not account for the recovery in stage III. From inspection of the data presented in their paper it is seen that their defect concentrations at 70°K were considerably less than the impurity concentration in their samples. Thus, as explained by Snead *et al.*,[13] the interstitial migration in stage I is governed by the impurities and no dimer formation would be anticipated.

It seems reasonable to expect some dimers to be formed during the irradiation, regardless of the tem-

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[16] W. Bauer and A. Sosin, Phys. Letters **24A**, 193 (1967).

perature at which the irradiation takes place. The damage-production–versus–electron-flux curves associated with this work have been discussed elsewhere.[17] These curves, for the pure aluminum, were interpreted in light of an unsaturable trap model, where a given impurity atom could accomodate more than one interstitial. Thus, trapped dimers may be formed during a high-temperature irradiation. Also, the likelihood of dimers being formed as a result of multiple displacements (even by electrons) cannot be ignored.

If dimers can be formed during free-interstitial migration in stage I, then it seems plausible that they can also be formed when the impurity traps release their interstitials. It would seem that other interstitials, as well as the vacancies, can compete as a sink for any particular migrating interstitial following its release from an impurity trap. This, of course, assumes that the dimer formation is stable up to, and possibly beyond, the stage-III region. Thus, dimers could be formed by any of the annealing processes involving free migration of an interstitial prior to stage III, and experiments in which high- and low-temperature irradiations are performed would not be expected to show much difference in stage-III recovery.

The recovery observed in stage III in a pure metal must then be due to one (or possibly more) of the following processes:

(1) migration of vacancies to interstitial agglomerates and impurity-trapped interstitials formed during the preceding stages of recovery;

(2) di-interstitial migration or dissociation followed by single-interstitial migration;

(3) migration of dumbbell interstitials which were formed by conversion of stage-I interstitials.[18]

The migration of single vacancies in stage III in aluminum has been proposed by several investigators. Federighi *et al.*,[5] in their neutron studies of pure and alloyed aluminum, have found that stage III is governed by a single activation energy of 0.60±0.04 eV, which is close to the value reported by De Sorbo and Turnbull[19] for the migration of single vacancies in aluminum. In addition they found that the activation energy in stage III following quenching from 600°C, with no subsequent irradiation, was 0.62±0.02 eV. This value was interpreted as the migration energy of single vacancies. Panseri and Federighi[20] reported that the defects which were mobile in stage III in aluminum were responsible for the clustering of the zinc solute atoms in an Al–10%Zn alloy (G.P. zone formation). Horak[9] has also performed neutron-irradiation experiments with pure aluminum and aluminum-zinc alloys. The solute concentrations in his zinc alloys were considerably higher than those used in the present research, employing impurity concentrations of 1.70, 3.41, and 5.27% of the atomic concentration in 99.9999% Al. He observed G.P. zone formation in all of these alloys, both after neutron irradiation following quenching from 555°K and after quenching and no irradiation. The temperature where the zone formation began was determined primarily by the concentration of vacancies and was found to be relatively insensitive to the impurity concentration over the range studied. He found that the formation and growth of these zones began at about the same temperature as the start of stage-III recovery in pure aluminum and thus concluded that the same lattice defect was responsible for both processes. This defect is widely believed to be the lattice vacancy.

One of the arguments against assigning the stage-III peak in pure aluminum to the migration of vacancies is that the activation energy for this recovery peak following electron irradiation was reported to be much less than that found in the neutron experiments. Sosin and Rachal[1] reported a value for the activation energy of the stage-III peak in pure aluminum of 0.45±0.01 eV. In work recently published, Lwin *et al.*[21] have found this activation energy to be 0.62±0.04 eV following 2-MeV electron irradiation. From the fact that this value agrees well with that observed after quenching, they concluded that stage III in aluminum occurs by vacancy migration.

Pieragostini *et al.*[10] used an Al–4%Cu alloy and performed a series of neutron-irradiation and quenching experiments to study the relation of stage-III recovery in pure aluminum to the vacancy-assisted clustering of copper atoms. In one copper-alloy sample, they treated the sample in such a way that the copper atoms were homogeneously distributed in the matrix and the vacancy concentration prior to irradiation was small. This sample was then irradiated at 80°K and the recovery spectrum studied. The resistivity was observed to decrease during the first part of stage III and then observed to increase at about 230°K. They interpreted the initial decrease as due to the annealing of vacancies to interstitial clusters, without producing diffusion of copper atoms. The increase of resistivity was attributed to G.P. zone formation. Sosin and Garr[22] have criticized the interpretation given by Pieragostini *et al.* to their results. They maintain that the initial decrease of resistivity in stage III, as reported above, is due to a defect that does not produce clustering, since no clustering is observed in the early part of stage III. They point out that stage III in the Al–4%Cu alloy is too broad to be attributed to a single defect. Their interpretation is that interstitial migration occurs initially in stage III, with vacancy migration occurring later. They also point out that vacancy migration occurs at a lower

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temperature in pure aluminum than in pure copper, for example, and that it may actually overlap into the region of the migrating interstitial. Ceresara *et al.*[23] have replied to this criticism by Sosin and Garr. They point out that the possibility of *two* migrating defects in stage III was disregarded since the whole stage appears to be controlled by a single activation energy. They reiterate that the initial decrease in stage III can be attributed both to the elimination of vacancies and their combination with copper atoms, without producing any clustering until about 230°K.

The controversy over the nature of stage III has been fueled by discussions about the kinetics of the stage III recovery peak in a pure metal. One of the primary reasons for advocating interstitial migration in stage III, by partisans of that model, has been the observed unique process (and activation energy). In addition, this process has been reported to follow second-order kinetics.[1] Burger *et al.*[4] have found that the initial part of the stage followed an order of kinetics that was *less* than 2, but the latter part followed second-order kinetics. The initial behavior they attribute to the correlated recombination of interstitials with vacancies since it is believed that neutron irradiation produces zones with a high local concentration of an equal number of interstitials and vacancies. Within these zones partial correlation is possible. Isebeck *et al.*[7] observed the same type of behavior following their neutron-irradiation experiments. They found that the last half of stage III followed second-order kinetics, while the first part did not.

If the vacancy model for stage-III recovery in pure aluminum is considered, at the beginning of stage III there would be n single vacancies and n/b sinks for these vacancies, in the form of agglomerated interstitials, where b is the average number of interstitials per cluster (probably very close to 2). Thus there is not a one-to-one correspondence between the number of migrating vacancies and the number of available sinks, and the recovery would not be second order. The kinetics will be something less than second order and will gradually approach this condition as the annealing proceeds. If the impurity concentration in the material is not negligible, then the kinetics of this process will be further complicated. Impurities can likewise serve as sinks for migrating vacancies as well as merely delay their diffusion. Thus it would appear that the order of kinetics will depend upon the relation between the defect concentration and the impurity concentration. In other words, the order of kinetics of the stage-III process in an impure sample should be dose-dependent. Analysis of the peak shift in stage III for the pure aluminum samples used in this research, as reported previously, yielded a value $\gamma_{\mathrm{eff}}=1.5$. Although this is not the method generally used to analyze the kinetics of a certain process it is felt that the value of 1.5 obtained signifies that the stage-III peak is not a pure second-order process. In fact, it appears that a value of $\gamma_{\mathrm{eff}}=1.5$ is a quite reasonable qualitative-quantitative result in light of the vacancy model.

Some more information can be obtained by focusing attention on the high temperature side of the main stage-III peak. It is seen from the data presented in this paper that evidence for additional recovery processes in this region exists. This is particularly noticeable in the low-dose runs for the alloys (Fig. 7). As mentioned previously it is apparent that vacancy-assisted clustering of copper atoms is taking place above 235°K in that alloy. A small peak occurs at about 250°K in the low-dose run with the zinc alloy. It is also present in the air-poisoned run (Fig. 5) with that alloy. The germanium alloy likewise shows a small recovery peak near 265°K. These peaks could well be due to the release of vacancies from impurity traps. Furthermore, the presence of the additional air impurities in the zinc alloy in the air-poisoned run completely destroys the unique nature of the stage-III recovery process. The recovery curves for the pure aluminum (Fig. 3) do not indicate a prominent peak after the stage-III peak, but evidence for a small recovery process is seen above 240°K.

Finally, we consider the center temperatures of the main recovery process in stage III for the various samples. In the case of the pure aluminum the presence of the additional air impurities shifts this peak upward by about 7°K, in spite of the fact that the defect concentration at 200°K in the air-poisoned run is greater than in the low-dose run at the same point. For the low-dose runs with the alloys, the center temperatures for this peak vary widely between the alloys. On concentration grounds alone we would expect this peak in an alloy to occur at a lower temperature than the corresponding peak in the low-dose run with the pure aluminum, since the defect concentrations prior to this recovery process in the alloys were much larger than in the pure aluminum. This is not what is observed in the case of the germanium and copper alloys. These apparent impurity effects throughout the entire stage-III region of recovery are consistent with the idea of impurity-delayed migration of vacancies in stage III in aluminum.

V. CONCLUSIONS

The recovery in the stage-II region (60–170°K) in aluminum is governed by the impurities present with the possible exception of a recovery peak at about 73°K, which may be intrinsic. The effect of these impurities is also felt in the stage-III recovery. The prominent recovery peaks in the three alloys on the low-temperature side of the main peak in stage III seem to be due to the release of interstitials from deep impurity traps. It is proposed that the main peak in

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stage III in aluminum is due to the migration of single vacancies to interstitial agglomerates formed during the preceding stages of recovery. These interstitial clusters must be stable at least beyond the point where the deepest of the impurity traps release their interstitials. The impurity atoms can delay the diffusion of a vacancy migrating through the lattice by causing the defect to make more jumps, on the average, before annihilation. The presence of the impurities does not affect the activation energy for the onset of vacancy migration. Impurities can also trap the migrating vacancies and subsequently release them at a temperature well above that where the initial vacancy migration occurs. In light of the data presented in this research it is felt that the introduction of a second type of interstitial that moves in stage III is not necessary to explain the results.

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Lattice Thermal Conductivity, Nernst-Ettinghausen Effect, and Specific Heat in Antimony at Low Temperature*

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The lattice thermal conductivity, the high-field Nernst-Ettinghausen thermoelectric coefficient, and the specific heat of antimony have been determined in the temperature range 0.4–2.4°K. Thermal-conductivity results confirm the predominance of phonon-electron normal scattering in the lowest range of temperatures with the expected T^2 law. The dramatic increase in the lattice thermal conductivity above 1.5°K is thought to be due to the inability of the electrons to scatter phonons with wave numbers $q>2k_F$, where $2k_F$ is the diameter of a charge carrier's Fermi pocket. An effective scattering Debye temperature of $\Theta^*=(2k_F/q_D)\Theta \approx 25°\mathrm{K}$ is in good agreement with experimental results. Nernst-Ettinghausen results give the total electronic density of states $Z=(1.10\pm0.07)\times10^{33}$ erg^{-1} cm^{-3}; the presence of a phonon-drag contribution is confirmed and discussed. The specific-heat results, $C=(116.5\pm6.4)T+(211.0\pm5.3)T^3+1.97\pm0.23)T^{-2}$ in μJ (mole °K)$^{-1}$, are compared with the results of transport measurements and with recent specific-heat determinations.

I. INTRODUCTION

PART of this work is an extension to lower temperatures of Long, Grenier, and Reynolds's[1] study of the transport properties of antimony with the purpose of clarifying the nature of the scattering mechanisms.

A case in point relates to the Nernst-Ettinghausen (NE) effect and how precise a determination of the electronic density of states, Z, can be achieved from it. Their results indicated the existence of a strong superimposed phonon drag which prevented the electronic term from being determined with sufficient accuracy. To improve on this point, measurements of the transport effects were extended down to 0.4°K. Also, an independent determination of the density of states was made through specific-heat measurements in this same range of temperature.

Another point pertained to the inability to work out a scheme which would explain most properties related to the phonon system. For example, the magnitude and temperature dependence of the lattice thermal conductivity λ_g and the ideal electronic conductivity σ_i were found to disagree with Makinson's[2] and with Debye, Grüneisen, and Bloch's[3] formulas for metals, but the ratio between these two quantities agreed remarkably well with Ziman's T^7 law,[4] strongly indicating the predominance of phonon-electron scattering. Even though this conclusion seems reasonable, the strong three-phonon normal process implied in Ziman's theory is not very likely at these low temperatures. For that reason the extension of the measurement of λ_g down to 0.4°K was desirable in order to better understand the phonon scattering processes. A better understanding of the phonon drag also can be attained.

Section II presents briefly the pertinent details of the experimental procedure; Sec. III presents the results and discussion of the thermal-conductivity measurements, the NE effect, and the specific heat. Section IV

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