Relationship between Neutron-Produced Prismatic Dislocations and the Change in Volume during Annealing in Copper*

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Two groups of copper single crystals of various orientations were irradiated with neutrons in the BNL reactor between 50°C and 70°C; one group was exposed to 0.53×10^{18} *nvt* (total epicadmium flux) and the other 1.1×10^{18} *nvt* (total epicadmium flux). An irradiated and a nonirradiated crystal of each orientation were isothermally annealed in a specially constructed dilatometer at temperatures ranging from 75°C to 350°C, and the irreversible differential changes in length were measured. In addition, electron microscope studies were made of the size distribution of irradiation-produced prismatic dislocations after several of the annealing treatments. These experiments revealed that (1) a direct relationship exists between the magnitude of shrinkage after annealing treatments and the total neutron exposure, (2) during annealing dislocation loops decrease in diameter until they disappear, (3) the decrease in dislocation density is related to the volume shrinkage, (4) the changes in loop distribution could be predicted by a line-tension-climb equation, and (5) the activation energy for the annealing of irradiation-produced loops lies between 2.08 eV and 2.10 eV. The results indicated that the annealing process in neutron-irradiated copper is not the same as observed in quenched metals although a self-diffusion mechanism appears to be the controlling factor.

INTRODUCTION

IRRADIATION of copper with high-energy particles results in defects that produce an expansion in the lattice. Vook and Wert[1] bombarded copper foils with deuterons of an average energy of 8.5 MeV at 15°K and found that copper expanded; subsequent annealing to about 280°K resulted in a shrinkage curve which is the same form as the resistivity curve determined by other workers.[2,3] Although several experiments concerned with the dilatation of copper[4] were made, a detailed account of the effect of annealing after irradiation with neutrons at reactor temperature of approximately 50°C has not been reported. Experiments show, however, that the physical and mechanical properties of irradiated copper are affected by subsequent annealing[4,5] between 0 and 500°C. Moreover, Coltman, Klabunde, McDonald, and Redman[6] have shown that thermal neutrons as well as fast neutrons produce measurable damage at low temperatures; however, more investigation is necessary to ascertain the relationship between the effect of slow neutron bombardment at pile temperatures (50–70°C) and the recoverable damage.

Transmission electron microscopy investigations of neutron-irradiated copper revealed dark spots in copper which are believed to be prismatic dislocation loops.[7,8] These prismatic dislocation loops do not form in all cases, but their production is found to be dependent upon the material irradiated and the temperature of irradiation.[9,10] In copper the density and size distribution of these spots are related to the total radiation exposure and the neutron spectrum.[11] As the irradiation exposure is increased, the density increases to a saturation value and the loops grow in size; subsequent annealing of this material will lower the density of the loops.[7,11,12] Since the disappearance of these loops is equivalent to a decrease in dislocation density, the present experiments were designed to obtain data from which the change in volume of the copper could be correlated with the change in dislocation density during the annealing of irradiated copper. Conclusions can be made concerning (1) the amount of point defects remaining in the lattice after irradiation, (2) the volume occupied by the dislocation loops, and (3) the mode of diffusion during annealing treatments.

EXPERIMENTAL PROCEDURE

Single crystals, 3 mm in diameter by 140 mm long, of high-purity copper (99.9995%) were grown in graphite molds in a vacuum. These crystals were mechanically cut into two equal parts, 70 mm long, in order to make pairs of crystals of identical orientations suitable for the precise length change measurements.

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[1] R. Vook and C. Wert, Phys. Rev. **109**, 1529 (1958).

[2] R. O. Simmons and R. W. Balluffi, J. Appl. Phys. **30**, 1249 (1959).

[3] H. G. Cooper, J. S. Koehler, and J. W. Marx, Phys. Rev. **97**, 599 (1955).

[4] For a review, see D. S. Billington and J. H. Crawford, Jr., *Radiation Damage in Solids* (Princeton University Press, Princeton, New Jersey, 1961), Chap. 5, p. 100.

[5] T. H. Blewitt, R. R. Coltman, R. E. Jamison, and J. K. Redman, J. Nucl. Mater. **2**, 272 (1960).

[6] R. R. Coltman, C. E. Klabunde, D. L. McDonald, and J. K. Redman, J. Appl. Phys. **33**, 3509 (1962).

[7] J. Silcox and P. B. Hirsch, Phil. Mag. **4**, 1356 (1959).

[8] I. G. Greenfield and H. G. F. Wilsdorf, Naturwiss. **47**, 395 (1960).

[9] H. G. F. Wilsdorf and D. Kuhlmann-Wilsdorf, Phys. Rev. Letters **3**, 170 (1959).

[10] I. G. Greenfield and H. G. F. Wilsdorf, Conf. J. Phys. Soc. Japan **18**, Suppl. III, 20 (1963).

[11] M. J. Makin, A. D. Whapham, and F. J. Minter, Phil. Mag. **7**, 285 (1962).

[12] M. J. Makin and S. A. Manthorpe, Phil. Mag. **8**, 1725 (1963).

TABLE I. Neutron spectrum for irradiation treatments (temperature between 50–75°C).

Exposure	Specimens	Thermal flux	Epicadmium flux	Flux above 1 MeV	Effective time	Total thermal flux	Total epicadmium flux	Total flux 1 MeV
		(10^{13} *nv*)	(10^{11} *nv*)	(10^{11} *nv*)	(10^{6} sec)	(10^{19} *nvt*)	(10^{18} *nvt*)	(10^{17} *nvt*)
A	70, 81, 82	1.0	3.8	2.7	3.0	3.0	1.14	8.10
B	66	1.3	2.8	···	1.9	2.47	0.532	···

To reduce the possibility of spurious effects due to oxygen entering the lattice during the initial annealing treatments, the copper specimens were heated in an evacuated quartz tube in the presence of a zirconium getter. After annealing for 12 h one crystal from each orientation was sent to Brookhaven and irradiated in the BNL graphite reactor. Specimens 70, 81, and 82 were irradiated together in the same hole with a total integrated epicadmium flux of 1.14×10^{18} (*nvt*), exposure A, whereas specimen 66 was exposed to about one-half of this dose, exposure B. Table I contains the pertinent data concerning the neutron bombardment.

The dilatometer[13] used in these experiments was designed to compare irreversible differential changes in length resulting from the rearrangement of point defects between an irradiated and a nonirradiated crystal of the same orientation. The dilatometer was similar in construction to the one used by J. Takamura in the study of changes in length of quenched metals after annealing at temperature near 20°C.[14] The present dilatometer can be operated in the temperature range from 75 to 400°C. The relative changes in length between the irradiated and nonirradiated crystals were magnified by an optical level system and a telescope; when necessary, the readings thus procured were recorded by a slow motion cine technique. In order to obtain precision measurements, the dilatometer was kept in a room in which the temperature did not vary more than 1.0°C over a 24-h period. It was necessary, however, to monitor the temperature of certain components of the dilatometer in order that accurate corrections could be applied to the dilatometer scale readings. An analysis of the calibration data has shown that the sensitivity was about 200 Å with the standard deviation of ±500 Å for the maximum variation of temperature of the components of the dilatometer. All annealing experiments were carried out in an atmosphere of high-purity argon that was passed over hot zirconium chips.

The size distribution and the density of dislocation loops were measured from micrographs in regions about 2000 Å thick. The thickness was measured, where possible, by calculating the perpendicular projection to the surface of the intersections of slip traces. Although dislocations producing these traces were active after long exposures to the electron beam, the dislocations were not always present in the regions where the density measurements were made. As a result some interpolation was necessary; however, the accuracy falls within ±500 Å of the thickness measurement.

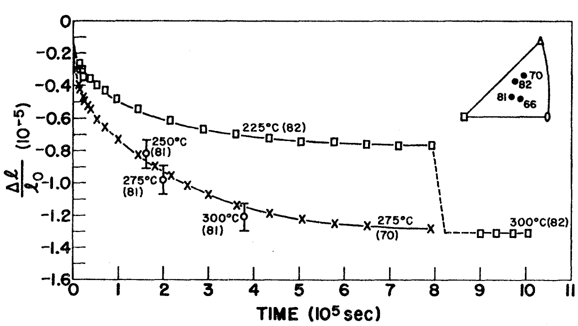


FIG. 1. Change in $\Delta l/l_0$ for isothermal annealing of irradiated copper crystals 70, 81, 82; irradiation exposure A.

RESULTS

Length Changes Due to Annealing

The effect of isothermal annealing on the change in length of single crystals of copper irradiated with neutron exposure A is shown in Fig. 1. In this graph of specific length change, $\Delta l/l_0$, is plotted against annealing times at the desired temperature. Consider first the results of annealing at 225°C (specimen 82) for 7.9×10^5 sec. The continuous record of the length changes has shown a high rate of shrinkage during the early part of the annealing treatment; however, after approximately 6×10^5 sec, the rate of shrinkage became negligible. Precise measurements of the irreversible difference in length were then made at room temperature after the irradiated specimen and the dummy specimen were cooled to room temperature; the measurements agreed with those taken at the annealing temperature. Then the specimen was heated to 300°C and again a rapid shrinkage took place during the initial heating; however, after about 0.5×10^5 sec, $\Delta l/l_0$ became constant. The total value for the specific change in length for 225°C was found to be -0.76×10^{-5} and for 300°C, -1.30×10^{-5}.

The isothermal annealing treatment carried out at 275°C (specimen 70) was also characterized by an initial rapid shrinkage rate that was greater than observed with the 225°C annealing treatment, and after about 7×10^5 sec, $\Delta l/l_0$ reached a constant value. The total specific length change was not significantly

[13] I. G. Greenfield and J. Takamura (to be published).
[14] J. Takamura, Acta Met. 9, 547 (1951).

different from the value of -1.30×10^{-5} found in the 300°C annealing treatment discussed above. The irradiated crystal treated at 275°C was not annealed at a higher temperature since it was necessary to preserve the prismatic-dislocation-loop distribution in the specimen for an electron microscope investigation that will be discussed later in this paper. Specimen 81 was annealed at 250, 275, and 300°C for lengths of time indicated in Fig. 1. The results of these dilatometric measurements agree with those described earlier. Annealing at higher temperatures, up to 350°C, did not produce significant additional shrinkage, and thus the maximum $\Delta l/l_0$ for this neutron exposure was -1.30×10^{-5}.

Thus, for the neutron dose A no detectable shrinkage occurred below 200°C; above 225°C considerable shrinkage initially took place, and, as the annealing time was increased, the shrinkage rate approached zero. Additional shrinkage occurred when the temperature was raised higher than this annealing temperature; however, after being annealed in the range of 275°C for more than 7×10^5 sec or 300°C for a shorter time, no additional changes in $\Delta l/l_0$ are detected. The maximum $\Delta l/l_0$ was about equal to -1.30×10^{-5} for this irradiation dose.

For the lower irradiation exposure B, on the other hand, the shrinkage behavior was somewhat different. Specimen 66 was annealed at temperatures and times listed in Table II. The annealing treatment was extended until it was certain the rate of change of $\Delta l/l_0$ reached zero; then the specimens were cooled to room temperature before the next isothermal treatment. The times listed in Table II are not necessarily the minimum time for $\Delta l/l_0$ to reach a constant value. Above 325°C additional shrinkage was not seen. If the specific shrinkages in Table II are compared with those shown in Fig. 1, it can be concluded that the cumulative $\Delta l/l_0$ for the crystals exposed to the smaller neutron dose approached a constant value at about 325°C, whereas for the greater dose the maximum $\Delta l/l_0$ is found at about 275°C. In addition, the maximum shrinkage for the lower dose is less than one-half that for the higher irradiation exposure. Thus, the range of temperature in which shrinkage of the specimen occurs and the total $\Delta l/l_0$ attainable depends upon the irradiation dose.

TABLE II. Annealing treatments for specimen 66; neutron exposure B.

Annealing temperature (°C)	Time at temperature (10^5 sec)	Cumulative $\Delta l/l_0$ (10^{-5})
75, 100, 150, 175, 200	...	...
250	2.52	0.24
275	1.80	0.34
300	3.42	0.75
325	2.16	0.82
350		0.82

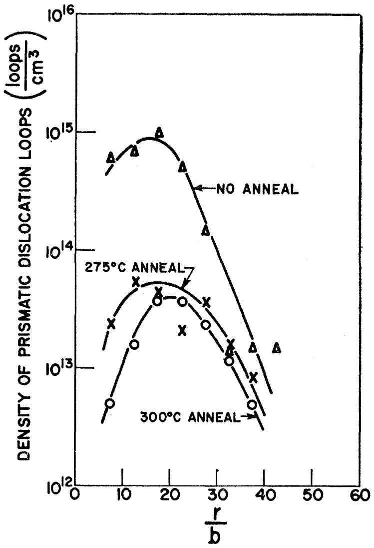


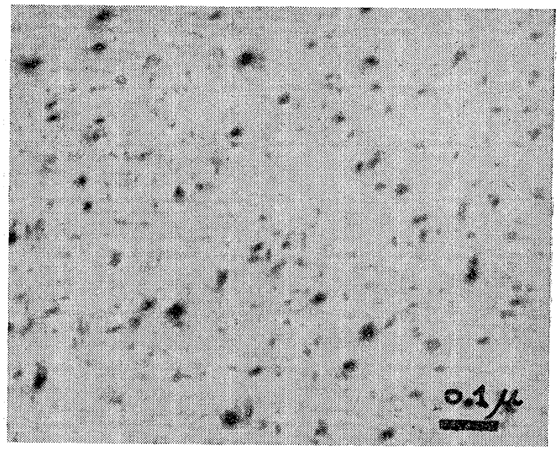
FIG. 2. Size distribution of prismatic dislocation loops in neutron irradiated copper after annealing.

Density and Distribution of Dislocation Loops after Annealing

The distributions of prismatic dislocation loops in neutron irradiated copper before and after annealing are shown in Fig. 2. The parameter r/b is the radius of the loop divided by the distance of closest approach between atoms. The upper curve represents the configuration observed in the copper crystals following irradiation treatment A (see Table I). Figures 3(a) and 3(b) are electron micrographs of specimens in the as-irradiated state and the annealed state. Small dark spots less than 25 Å in diameter were not seen in abundance as reported by Makin *et al.*[11] The geometry of the diffraction contrast in the small spots did not reveal, in general, the nature of the irradiation-produced defects, and consequently, it was not possible to infer whether these structures were tetrahedrons or small dislocation loops. Since the density and size distribution were measured in rather thick regions, the amount of inelastic scattering of the electrons has contributed to the limited image resolution.

The density of dislocation loops were decreased more than a factor of 10 after annealing crystal 70 at 275°C see Fig. 2. Moreover, the average size of loops has only increased slightly, indicating that loop growth plays a minor role during the annealing of neutron irradiated copper. After treating specimen 82 at 300°C, the loop distribution was not altered greatly although the average loop radius was slightly higher. Figure 3 illustrates the typical micrographs before and after annealing. It should be pointed out that loop size measurements are most accurate at the large-radii part of the distribution curve, and the density measurements are most accurate when the loop density is above 10^{13}/cc.

The most significant result due to annealing is the



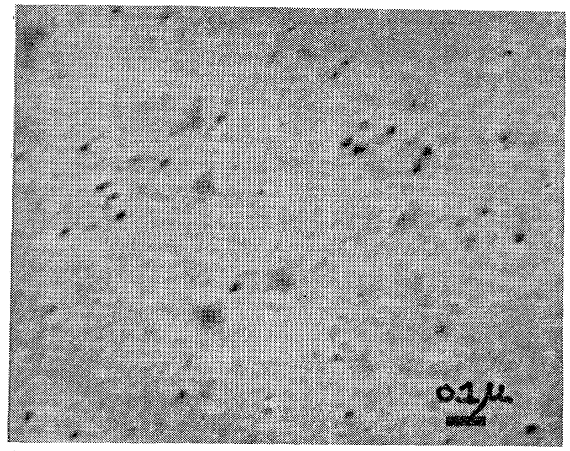


FIG. 3. Electron micrographs of irradiated copper (exposure A) (a) before annealing and (b) after annealing at 275°C for 7×10^5 sec.

great decrease in density of dislocation loops with only a slight increase in average radii of the loops.

ANALYSIS OF RESULTS

Dependence of Prismatic Loop Size on Annealing Conditions

Silcox and Whelan[15] have demonstrated that the shrinkage of prismatic dislocation loops formed by quenching in aluminum can be described by an equation originally derived by Friedel.[16] It was shown that the rate of change of the radius of a prismatic-dislocation loop is related to three temperature-dependent conditions: (1) diffusivity of the point defects, (2) the line tension of the dislocation loop and (3) the supersaturation of point defects in the vicinity of the loop.

The rate of change of the radius is then

$$dr/dt=-Z\nu_a b\exp(-E/kT)\times[\exp(F_cb^2/kT)-\exp(F_sb^2/kT)]C_c,\quad (1)$$

where Z is the atomic coordination number, ν_a is the atomic frequency, b is the Burgers vector, E is the activation energy for vacancy diffusion, $F_c=Gb\ln(r/b)/[4(1-\sigma)r/b]$, G is the shear modulus, σ is Poisson's ratio, and $F_s=(kT/b^2)\ln(c/c_0)$. The factor $\exp(F_cb^2/kT)$ is dependent upon the line tension of the loop, and the factor $\exp(F_sb^2/kT)$ is the supersaturation term which indicates whether the loop will accept or emit vacancies. The term C_c is considered to be the concentration of jogs and in a prismatic dislocation loop can be considered as equal to $\frac{1}{2}$. Friedel[17] has pointed out that this analysis depends upon the assumption that the growth process is controlled by climb and not by the migration of point defects to sinks. It has been shown that when loops are considered in thin foils, Eq. (1) can be simplified by considering the surface as a sink for the vacancies. Then c/c_0 is approximately equal to unity (i.e., nearly an equilibrium concentration of vacancies), and Eq. (1) can be written as

$$dr/dt=-\tfrac{1}{2}Zb\nu_a\exp(-E/kT)[\exp(F_cb^2/kT)-1].\quad (2)$$

Since prismatic dislocation loops are produced in copper by neutron bombardment, it may be assumed (1) that shrinkage of these irradiation-produced loops is controlled by the same forces as the quenched-in loops, and (2) sinks and sources of point defects are available during annealing, and (3) the average distance between sinks and sources of point defects is about the same as the average distance between loops. In contrast to the annealing behavior of isolated loops which have been studied,[15] this investigation is concerned with a multitude of small loops in bulk material, however, if the assumption is made that the vacancies move to sinks faster than they are produced by the loops and clusters, then Eq. (2) can be used.

For aluminum and copper which contain loops of sizes larger than 50 atomic diameters in radius, this equation may be simplified since the reciprocal of the bracketed term is merely a linear function of r/b.

For loops of smaller radii, this relationship is not linear; and, to determine the time required for a prismatic dislocation loop to shrink to a given size, it is necessary to consider the bracketed term in Eq. (2) for various values of r/b (radius/Burgers vector). If Eq. (2) is rearranged into the following form and integrated between the limits indicated,

$$\int_{t_0}^{t}dt=-\frac{2}{Z}\nu_a\exp\left(\frac{E}{kT}\right)\times\int_{r_0/b}^{r/b}\left[\exp\left(\frac{F_cb^2}{kT}\right)-1\right]^{-1}d\left(\frac{r}{b}\right),\quad (3)$$

[15] J. Silcox and M. J. Whelan, Phil. Mag. **5**, 1 (1960).
[16] J. Friedel, *Les Dislocations* (Gauthier-Villars, Paris, 1956).
[17] J. Friedel's discussion at the end of Ref. 13.

then the time necessary for a prismatic dislocation loop climbing from radius r_0 to radius r can be determined.

Equation (3) can be integrated numerically after the values of the constants are substituted. It has been found that the appropriate value for the activation energy E falls between 2.08 and 2.10 eV (the evidence for these values will be discussed later) and the relationships between r/b and time for various size loops are shown in Figs. 4 and 5. In Fig. 4 the solid lines represent the theoretical shrinkage of dislocation loops at 275° with a self-diffusion activation energy of 2.08 eV. The initial values for r/b are found at the ordinate when the annealing time is zero and the values of r/b decrease in a homologous manner during the annealing treatment.

From this graph the change in loop sizes can be estimated for the irradiated copper single crystal 70 after annealing at 275°C for 7.9×10^5 sec. For example the loops represented by $r/b=60$ shrink to $r/b=58$; the loops of initial size $r/b=30$ shrink to $r/b=19$; and loops of initial sizes below about $r/b=26$ completely disappear after this annealing treatment.

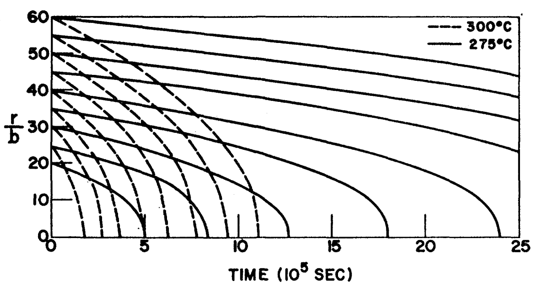


FIG. 4. Shrinkage of loops of size r/b when $E=2.08$ eV at 275 and 300°C.

A similar analysis can be made from the data in Fig. 5 where $E=2.10$ eV. With this information and the original size distribution after irradiation, a new size distribution can be estimated after an annealing treatment; these results are shown in Fig. 6. The shaded area represents the expected values for the density distribution when activation energy between 2.08 and 2.10 eV is used.

For r/b greater than 25, the experimental curve falls in the shaded region of the estimated curves, however, for low values of r/b the estimated curve rises above the experimental curve and ends in a region where $r/b\simeq15$. The differences between the experimental and estimated values of size distribution in the region where $r/b<25$ can be ascribed to the experimental difficulty in positively identifying all the small loops. Thus, the measured density values would tend to be below the theoretically estimated values which were derived from the distributions of larger loops. In addition, the theoretical description of the shrinkage of loops predicts that all loops with initial sizes $r/b<26$ will disappear during the annealing treatment; consequently, the estimated curve results in a sharp cutoff. It is more probable, however, that the curve does not abruptly end, and that a maximum would occur as the measured evidence indicates. Thus, a compromise between the measured data and the calculated data is reasonable. If the same analysis is made for specimen 82 (first annealed at 225°C and then annealed at 300°C), a new distribution can be estimated which is shown in Fig. 7. As in the previous case, the new distribution has the proper form and is a reasonable fit with the actual distribution. These estimated curves of size distribution after annealing are affected greatly by the value of the activation energy E, and the best fit has been found to be between 2.08 and 2.10 eV. Other investigators have found activation energies of this magnitude for annealing irradiated copper in this

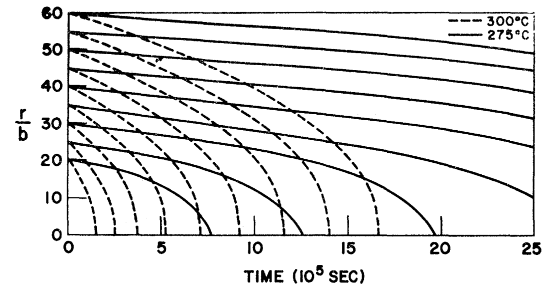


FIG. 5. Shrinkage of loops of size r/b when $E=2.10$ eV at 275 and 300°C.

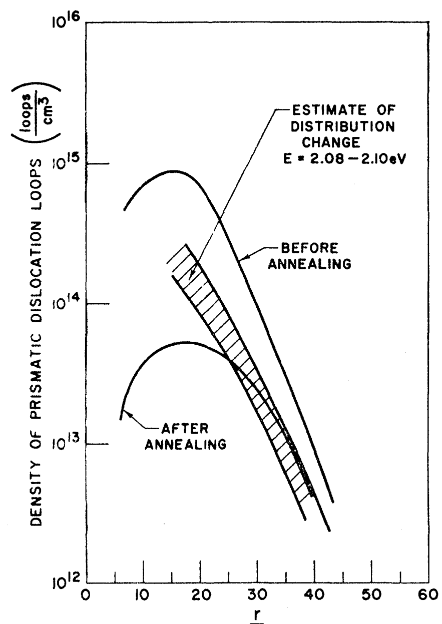


FIG. 6. Estimate of distribution change for annealing treatment at 275°C for 7.9×10^5 sec when $2.08\text{ eV}\leqq E\leqq2.10$ eV.

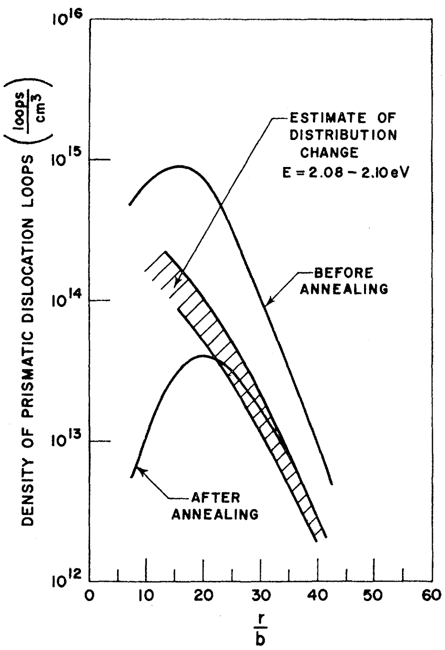


FIG. 7. Estimate of distribution change for the combination of annealing treatments (1) at 225°C for 7.9×10^5 sec and (2) at 300°C for 2.1×10^5 sec when 2.08 eV$\leqq E\leqq$2.10.

temperature range.[18,19] Makin[12] has concluded from recent experiments that the annealing of small spots is associated with an activation energy of 2.0 eV and the annealing of the large spots is associated with an activation energy of 1.0–1.5 eV. His determination was not based on the line-tension-climb relationship described by Eq. (1).

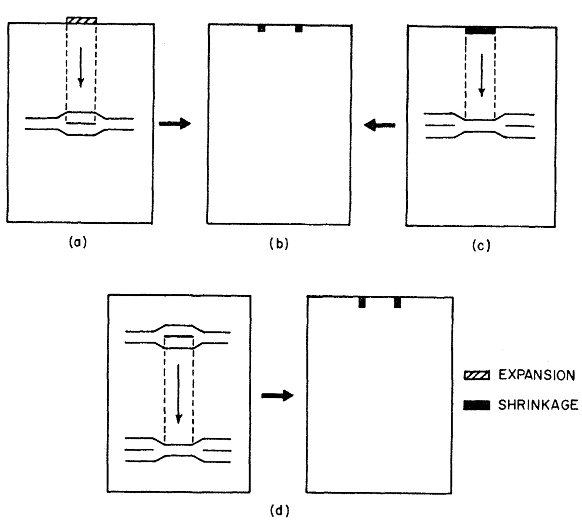


FIG. 8. (a) Increase of volume as a result of plate of atoms moving to surface; (b) shrinkage after relaxation in the vicinity of loop; (c) decrease in volume as a result of plate of atoms moving into loop; (d) transfer of plate of atoms from extrinsic loop and the over-all shrinkage after relaxation.

[18] A. W. McReynolds, W. Augustyniak, M. Mckeown, and D. B. Rosenblatt, Phys. Rev. **98**, 418 (1955).

[19] R. R. Eggleston, Acta Met. **1**, 679 (1953).

Relationship Between Volume Shrinkage and Dislocation Loops

The specific volume change $\Delta V/V_0$ for isotropic shrinkage is three times the specific length change. Comparisons between the length changes after annealing for the crystals of the orientations shown in Fig. 1 give evidence that $\Delta l/l_0$ is isotropic; hence, the specific volume changes are readily computed.

The relationships between volume change and the removal of dislocation loops from a crystal is illustrated by the schematic diagram in Figs. 8 and 9. In Fig. 8(a) the "plate of atoms" is transported from the dislocation loop to the surface, thus, increasing the volume of the crystal by the extra plate of atoms; a void equal to the volume of the atoms transported plus the volume of dislocation of length $2\pi r$ remain in the lattice. After a readjustment of the lattice planes, the differential volume change corresponds to the strain field associated with $2\pi r$ length of dislocation; and, consequently, a small shrinkage occurs [dark areas in Fig. 8(b)]. A similar argument is applicable for a vacancy loop and is diagrammed in Fig. 8(c). Moreover, when both vacancy and interstitial loops co-exist, the "extra plate of atoms" can replace the "plate of vacancies" if the loops are the same size or can replace portions of the vacancy loops if the loops are of different sizes; the decrease in volume is again proportional to the decrease in dislocation length [see Fig. 8(d)]. The same relationship results if loops moved out of the material by slip along the glide cylinder. The volume change due to the annihilation of an interstitial loop by vacancies which are in super-

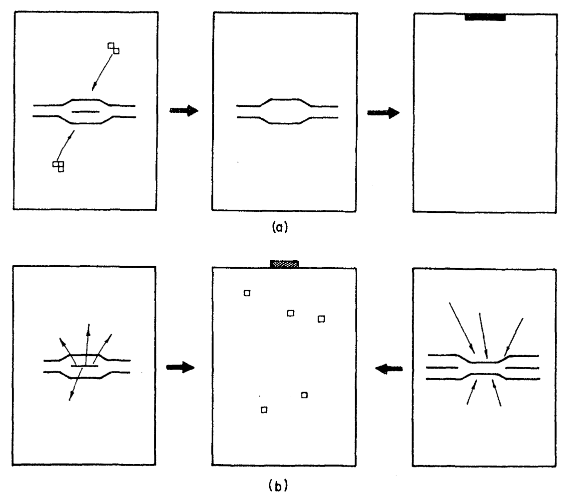


FIG. 9. (a) Change in volume due to the annihilation of interstitial loops by vacancies in the lattice; (b) dissolution of vacancy or interstitial loops.

TABLE III. Specific volume changes based on the reduction of dislocation.

(1) Annealing temperature °C	(2) Prismatic dislocation density (loops/cm³) 10^{15}	(3) $2\pi\bar{r}$ (10^{-6} cm)	Densities After Annealing (4) Dislocation density (10^8/cm²)	(5) Total cumulative volume change $\Delta V/V_0$ (10^{-5})	(6) Dislocation density (10^8/cm²)	(7) $\Delta V/V_0$ (1)[a]	(8) $\Delta V/V_0$ (2)[b]
Room	2.90	2.59	75.1	...	...	...	...
275	0.226	3.26	7.37	−3.84	66.8	−0.62	−3.15
300	0.144	3.43	4.94	−3.93	70.2	−0.65	−3.28

[a] The value of $\Delta V/V_0$ (1) is based on the volume associated with the dislocation-density change after annealing.
[b] The value of $\Delta V/V_0$ (2) is based on the summation of the specific volume change in column 7 and the specific volume change associated with the reduction of the supersaturation of point defects.

saturation in the lattice is illustrated in Fig. 9(a). The over-all shrinkage is larger than shown in Fig. 8 and depends upon the area enclosed in the loop, the lattice relaxation around the vacancies or clusters of vacancies, and the volume associated with the dislocation loop. A similar analysis for vacancy loops and a supersaturation of interstitial atoms also indicates volume shrinkage. Another possible interaction between loops and point defects is shown in Fig. 9(b). In this case the loops dissolve into point defects which remain in the crystal, and thus, a volume expansion should be found. Experimentally only shrinkage was measured, and the latter process will not be considered.

The dislocation density, $\rho_\perp$, is equal to the total dislocation-loop density, ρ_0, times the circumference of an average loop, $2\pi r$. If the change in $\rho_\perp$ is compared with the specific volume change after an isothermal annealing treatment, then the volume for a unit length of dislocation can be evaluated. These data are compiled in Table III. Stehle and Seeger[20] have calculated the change in volume associated with a dislocation by applying a nonlinear model to describe the dilation. Their results indicate that the dilation is greatest in the region from one Burgers vector to the center of the core, and the volume associated with a dislocation of length b is about twice the atomic volume. These calculations were applied to straight dislocations. For dislocation loops, however, the volume per unit length of dislocation loop would be somewhat dependent upon the diameter of the loop. If the loops are considered to be prismatic, and if it is assumed that the volume per unit length is the same as in a straight edge dislocation, the specific volume change associated with the loop density change can be calculated for the various annealing treatments. The results are given in Table III. For the annealing treatments at 275 and 300°C the calculated shrinkage is about one-sixth the measure value [see columns (5) and (7)].

If the decrease in density of the loops is a result of the combination of point defects from defect clusters with the loops as shown in Fig. 9(a), then the specific volume change will be the sum of the volume of the dislocation and the volume previously occupied by the clusters. Assuming that a cluster having n point defects has a volume of $n\times$atomic volume (relaxation not considered), the $\Delta V/V_0$ derived from the experimental data of dislocation density is in good agreement with the experimentally measured values [see columns (5) and (8) in Table III].

The present and other annealing experiments[7,11,12] have demonstrated that the dislocation loops in neutron-irradiated copper will decrease in diameter during annealing until they disappear. A similar loop behavior is noted in quenched metals in regions near sinks such as grain boundaries and dislocations that are able to climb.[15] In contrast, when sinks are not available there is a tendency for loops to grow as evidenced in quenched Al–0.5 at.% Mg.[21] Since the loops decrease in size during annealing in irradiated copper, it is assumed that loops are emitting or accepting defects in such a way as to cause loops to shrink. It is expected that the rate-controlling process is diffusion; and, thus, the average distance a vacancy may move during the annealing treatments can be computed. For the 275°C anneal, the vacancy can travel about 1000 Å in 7.9×10^5 sec; this diffusion distance is too small for vacancies to migrate to the surface in bulk material. However, the dislocation loops are on the average 700 Å apart and can serve as sinks for point defects. A direct determination of the intrinsic or extrinsic nature of the dislocation loops in neutron-irradiated copper has not appeared in the literature although loops produced by α-particle[22] bombardment have been found to be interstitial. A recent electron diffraction experiment concerning loops that appear in molybdenum after neutron irradiation at elevated temperatures has shown conclusively that these loops are interstitial.[23] Makin *et al.*, on the bases of annealing experiments in which large and small spots are seen, have concluded that the large spots are interstitial loops and the small are vacancy clusters.[11,12] The nature of the dislocation loops cannot be determined from the present experiment, but the

[20] H. Stehle and A. Seeger, Z. Physik **146**, 217 (1956).

[21] J. Takamura, K. Okazaki, and I. G. Greenfield, Conf. J. Phys. Soc. Japan **18**, Suppl. III, 78 (1963).
[22] R. S. Barns and D. J. Mazey, Phil. Mag. **5**, 1247 (1960).
[23] J. D. Meakin and I. G. Greenfield (to be published).

evidence indicates that both loops and submicroscopic defect clusters exist in these neutron irradiated specimens.

SUMMARY

Copper crystals irradiated with neutrons between 50 and 70°C show the following characteristics when isothermally annealed between 75 and 350°C:

(1) A decrease in volume is detected and is proportional to the neutron exposure. The maximum specific volume changes for 1.14×10^{18} (*nvt* total epicadmium flux) and 0.532×10^{18} (*nvt* total epicadmium flux) are -3.93×10^{-5} and -2.46×10^{-5}, respectively.

(2) Measurable shrinkage of the single crystals takes place between 225 and 325°C, and the temperature where the maximum shrinkage rate occurs appears to be higher for the lower neutron dose.

(3) The change in size distribution of prismatic dislocation loops can be predicted by Eq. (1).

(4) The activation energy for the annealing process corresponds to the activation energy for self-diffusion.

(5) Dislocation loops and submicroscopic point-defect clusters are present in neutron irradiated copper.

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Thermal Conductivity of Silicon and Germanium from 3°K to the Melting Point*

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The thermal conductivity K of single crystals of silicon has been measured from 3 to 1580°K and of single crystals of germanium from 3 to 1190°K. These measurements have been made using a steady-state, radial heat flow apparatus for $T>300$°K and a steady-state, longitudinal flow apparatus for $T<300$°K to give absolute K values. This radial flow technique eliminates thermal radiation losses at high temperatures. The accuracy of both the low-temperature apparatus and the high-temperature apparatus is approximately $\pm5\%$. Some special experimental techniques in using the high-temperature apparatus are briefly considered. At all temperatures the major contribution to K in Si and Ge is produced by phonons. The phonon thermal conductivity has been calculated from a combination of the relaxation times for boundary, isotope, three-phonon, and four-phonon scattering, and was found to agree with the experimental measurements. Above 700°K for Ge and 1000°K for Si an electronic contribution to K occurs, which agrees quite well with the theoretical estimates. At the respective melting points of Si and Ge, electrons and holes are responsible for 40% of the total K and phonons are responsible for 60%. The measured electronic K yields values for the thermal band gap at the melting point of 0.6 ± 0.1 eV for Si and 0.26 ± 0.08 eV for Ge.

INTRODUCTION

In a semiconductor, various carriers can contribute to the thermal conductivity. These are phonons, photons, electron-hole pairs, and the separate electron and holes. The problem of sorting out the contributions from these processes has been handicapped by the lack of accurate high-temperature measurements. In this paper, we report on measurements of the thermal conductivity K of single crystals of germanium and silicon between 300 and 1580°K taken with an improved cylindrical heat flow apparatus. The measurements of K of silicon below 300°K have been taken with an existing longitudinal heat flow apparatus.[1] Germanium and silicon were measured because they are easily obtained with high purity and known electrical characteristics. As a consequence of this investigation, they could serve as standard materials for K measurements.

The purpose of this investigation was to measure and analyze the K of these materials up to the melting point and, in particular, to unravel the magnitude of the contributions from the various carriers of heat. It was found that the phonon or lattice thermal conductivity is dominant and decreases faster than $1/T$ at high temperatures. The bipolar thermal conductivity, i.e., from electron-hole pairs, is significant at high temperatures and agrees with a simple theory. The polar thermal conductivity, i.e., from the separate electrons and holes, is small, and the photon thermal conductivity is not detectable.

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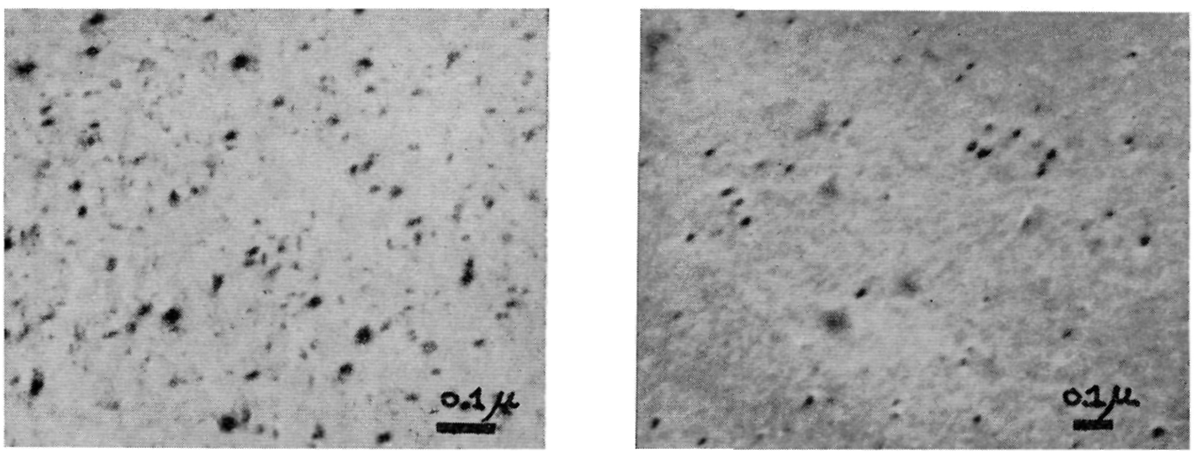
[1] G. A. Slack, Phys. Rev. 122, 1451 (1961).



(a) (b)

FIG. 3. Electron micrographs of irradiated copper (exposure A) (a) before annealing and (b) after annealing at 275°C for 7×10^5 sec.