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Self-Diffusion in Tellurium. II. Grain Boundary and Dislocation Effects

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Self-diffusion in tellurium has been determined directly and unambiguously using a Te^{127m} radiotracer in polycrystalline and dislocated single-crystal tellurium samples. The data along the grain boundaries between 280 and 390°C can be represented by $D_{\mathrm{GB}}=7.47\times10^{-4}\exp[(-0.87\pm0.08\text{ eV})/kT]$ cm^2/sec, whereas those along the edge (between 253 and 401°C) and screw (between 275 and 380°C) dislocations are described by $D_{\mathrm{ED}}=9.67\times10^{-6}\exp[(-0.65\pm0.02\text{ eV})/kT]$ cm^2/sec and $D_{\mathrm{SD}}=7.12\times10^{-3}\exp[(-0.98\pm0.10\text{eV})/kT]$ cm^2/sec, respectively. From these data, in conjunction with the available lattice-diffusivity data in single crystals, it is estimated that the activation energy of the motion of vacancies in tellurium is about 0.7 eV along [0001] and 1 eV along $\langle 10\bar{1}0\rangle$ or $\langle 11\bar{2}0\rangle$. The use of Fisher's analysis of Harrison's type-B diffusion kinetics, along with the directly measured data along dislocations and grain boundaries, substantiated the model of grain boundaries as a single-line array of dislocations. But the values of effective grain-boundary thickness and dislocation diameters obtained using the same analysis (1.5×10^{-5} cm) is about two orders of magnitude higher than usually assumed in grain-boundary diffusion studies.

I. INTRODUCTION

THE recognition of a free surface as a high-diffusivity path in solids probably started from the experiments of Volmer and Estermann.[1] However, Langmuir's[2] classical experiments on duffusion of Th on W established for the first time the lower activation energy and the higher diffusion rate at a fixed temperature on a free surface and along grain boundaries in solids compared to that in the bulk. But the identification of dislocations as high-diffusivity paths started only after Burgers[3] and Bragg[4] proposed that a grain boundary can be considered as a linear array of dislocation lines.

In the last two or three decades a wealth of information has been obtained on grain-boundary diffusion.[5] Read and Shockley[6] further analyzed the structure of grain boundaries which was utilized by Smoluchowski *et al.*[7,8] to formulate a theory of grain-boundary diffusion. However, experimentally most useful information came from the expressions for concentration profile for grain-boundary diffusion first obtained by Fisher.[9] Turnbull and Hoffman[10] used this analysis in silver with apparent success, even by violating the proposed boundary conditions. Fisher's analysis was further extended by Whipple[11] and Levine and MacCallum[12] and for a different method of treatment of data by LeClaire.[13] The essential difference in all these models is the value of the index m of the penetration distance as a linear function of the logarithm of concentration. This power m is 1 by Fisher's analysis, $\frac{4}{3}$ at large penetrations by Whipple's calculations, and 6/5 according to Levine and MacCallum. Considering the scatter of experimental data usually obtained, it is very difficult to distinguish the validity of any one of these models from another, as illustrated very recently by Rhodes.[14]

Analysis of diffusion along dislocations came, until very recently, from that of grain-boundary work in which the proposed correlations were assumed,[3,4,6–8] i.e., that tilt boundaries of between 9° and 15° mismatch are equivalent in local dislocation density to crystals having between 10^6 and 10^7 dislocations per cm^2. Hart's[15] initial analysis of diffusion along dislocations (as distinct from grain-boundary diffusion) was examined by Tomizuka[16] and modified by Mortlock.[17] However, Harrison's[18] comprehensive treatment of the kinetics of diffusion along dislocations correlated for the first time all the models of dislocation and grain-boundary diffusion (even including that of Lidiard and Tharmalingam[19]) in terms of the parameter D_Lt/L^2, where D_L is the bulk diffusivity, t is the time of anneal, and L is the average separation of adjacent dislocation cores (or grain size for polycrystalline materials), Thus, the previous analyses[9,11,12,15,18] which predicetd a linear relationship between $\ln C$ (concentration of diffusant) and x^m in the direction of diffusion ($m=1$, $\frac{4}{3}$ or 6/5) all come under Harrison's type-B diffusion kinetics (with $D_Lt/L^2 \geqslant 1 < 10^5$) where the influence of

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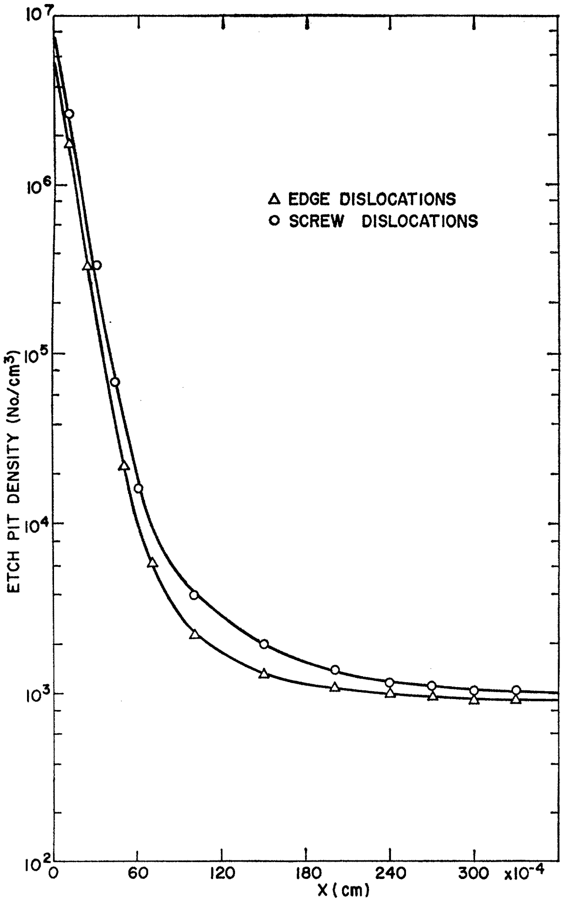

FIG. 1. Etch-pit density as a function of depth in samples polished with 100-g weight. Etchant, 1:1:3 = conc. $HCl:CrO_3:H_2O$ (by weight).

both bulk diffusion and grain-boundary or dislocation-pipe diffusion is reflected in the concentration profile. According to Harrison, a standard sectioning experiment will correctly determine D_L (for values of $D_Lt/L^2 \geqslant 10^5$) or D_P (with $D_Lt/L^2 \ll 1$, where D_P is the diffusion coefficient along dislocation cores) from the slopes of ln C-versus-x^2 plots under thin-film boundary conditions. So, by choosing appropriate values of D_Lt/L^2 one should be able to obtain separately D_L or D_P and the value of the product $D_B\delta$ (from type-B kinetics), where D_B is the grain-boundary diffusion coefficient, and δ is the effective dislocation pipe diameter or grain-boundary thickness. Now following the accepted assumption of $D_P = D_B$, one should be able to determine the value of δ unambiguously at least insofar as atom mobilities are concerned. The value of δ in any particular material should then be able to verify the correlation effects discussed by Lothe.[20] Very recently two different formulations[21,22] of Harrison's type-B diffusion kinetics (involving dislocations) came out from different considerations. Stark's[22] expressions involve too many parameters to be experimentally useful whereas Luther[21] predicted the same linear ln C-versus-X relationship as Fisher[9] and Smoluchowski.[7]

Very few independent determinations of diffusion coefficients along dislocations are available, particularly self-diffusion along edge or screw dislocations. Williams *et al.*[23] and Bendik *et al.*[24] obtained qualitative evidence of enhanced impurity diffusion along dislocations in silver and GaAs, respectively. Widmer's[25] findings of enhances self-diffusivity of Ge along dislocations was contradicted by Heldt and Hobstetter[26] for Sb and In diffusion along dislocations in Ge. A similar type of contradictory data were obtained by Panteleev *et al.* in silicon[27] and germanium.[28] The results have been more consistent with the theory in ionic materials[14,29–31] and metals.[32]

II. EXPERIMENTS AND RESULTS

A. The Use of Type-C Diffusion Kinetics

Harrison[18] defined type-C kinetics as the case where the dimensionless parameter $D_Lt/L^2 \ll 1$. This kinetics should only show the high-diffusivity paths (dislocations, for example) obeying Fick's law. Thus in a sectioning experiment ln C-versus-x^2 plot will be linear (in the thin-film boundary condition) whose slope will determine $D_{\rm ED}$, $D_{\rm SD}$ or $D_{\rm GB}$, where $D_{\rm ED}$ is the diffusivity along edge dislocations, $D_{\rm SD}$ is the diffusivity along screw dislocations and $D_{\rm GB}$ is the grain-boundary diffusion coefficient.

The essential experimental technique of using Te^{127m} radiotracer in conjunction with manual sectioning (for the determination of concentration profiles) has been described elsewhere.[33] For the determination of dislocation-pipe self-diffusivities, samples (about 2 mm thick) were finished on a polishing machine using 0.05-μ Linde semiconductor-grade alumina abrasive. Use of different weights on the sample during polishing (60–250 g) produced the desired dislocation densities[25]

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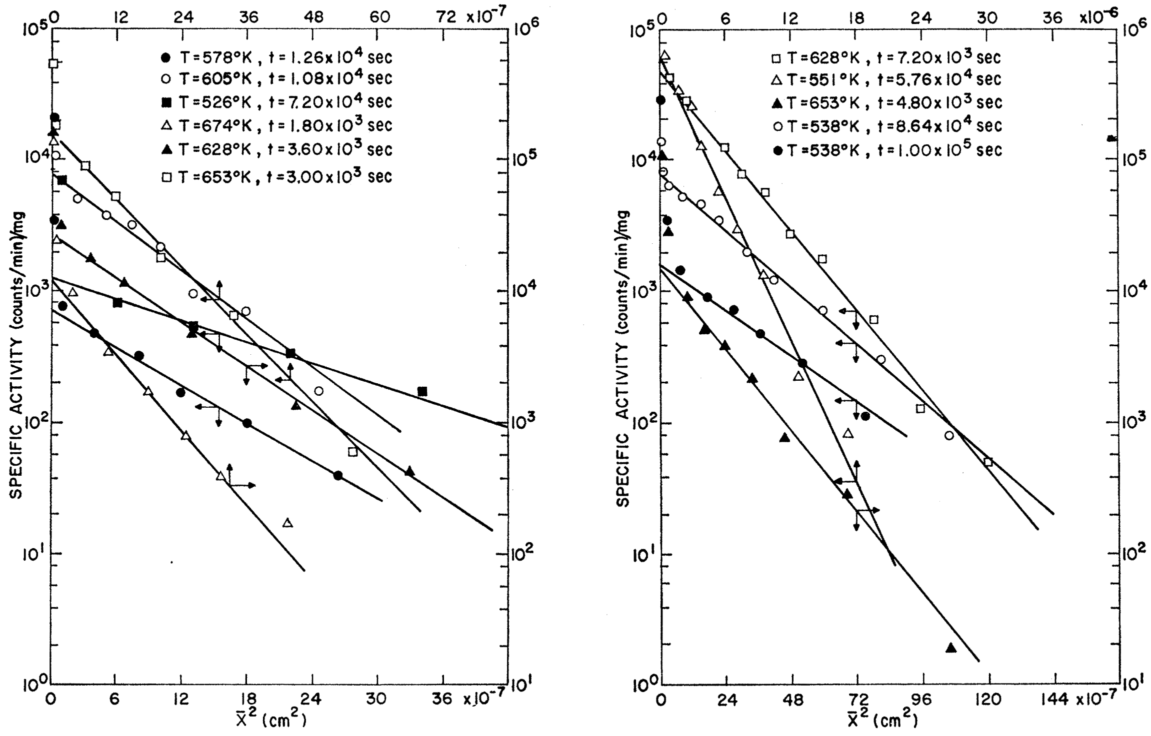

(a) (b)

FIG. 2. Concentration profiles of Te^{127m} in pure single-crystal tellurium for diffusion along edge dislocations. $\rho = 1.75\times10^6$ cm/cm^3.

which were subsequently stabilized by annealing in a pure-argon atmosphere (static). This operation at the desired diffusion-annealing temperature for a duration about the same as that for the diffusion run reduced the dislocation densities by a factor of 1.5–2.0 and no further change in the dislocation density was observed during the subsequent diffusion anneal. The dislocation densities were determined by etch-pit counting[34] in either ⟨10$\bar{1}$0⟩ or [0001] oriented samples. A typical distribution of dislocations as a function of distance from the surface is shown in Fig. 1. As is evident, any desired density of dislocations can be used by chemically polishing the sample.[33] The reported dislocation density is the average of that at the surface and that at a distance 3 $(D_Lt)^{1/2}$ from the surface. The sensitivity of the counting equipment allowed sectioning up to a distance of 3 $(D_Lt)^{1/2}$ from the surface (on an average). The materials used for both edge- and screw-dislocation-diffusivity determinations were 99.9999% pure single crystal (from R. C. Keezer of this laboratory) and was characterized by a room-temperature resistivity of 0.65 Ω-cm and majority-carrier density of 2×10^{14} at 77°K. The parameter D_Lt/L^2 was maintained between 10^{-2} and 10^{-4} for both the edge and screw-dislocation type-*C* kinetics study. The concentration profiles obtained under such conditions are shown in Figs. 2(a), 2(b), and 3. As expected the profiles show a sharp drop near the surface (due to lattice diffusion) and become linear at deep penetrations. The lesser number of data points along screw dislocations is due to easy accidental bending of the samples at ⟨10$\bar{1}$0⟩ orientation (after diffusion anneal and during handling prior to sectioning). The difference in the units of the coordinates between Figs. 2 and 3 was to take into account the fact that the edge dislocations were coincident in direction with that of diffusion whereas the screw dislocations were oriented at 60° to the diffusion direction. Consequently the penetration along the screw-dislocation cores was obtained by multiplying the section thickness (along ⟨10$\bar{1}$0⟩) by a constant factor of 1.1547 and the specific activity of all sections was expressed in counts per minute per micron of penetration along the screw-dislocation cores. Only one of the two possible screw-dislocation systems (along [11$\bar{2}$0] or [2$\bar{1}\bar{1}$0][34]) was observed (from the orientation of etch pits) in any sample. The diffusion coefficients calculated from these profiles using Fick's second law solution under thin-film boundary condition,

$$C(x,t) = [\alpha/(\pi D_P t)^{1/2}] \exp(-x^2/4D_P t) \qquad (1)$$

(where D_P = dislocation-pipe diffusivity) are shown in Fig. 4. As expected, no dependence of dislocation den-

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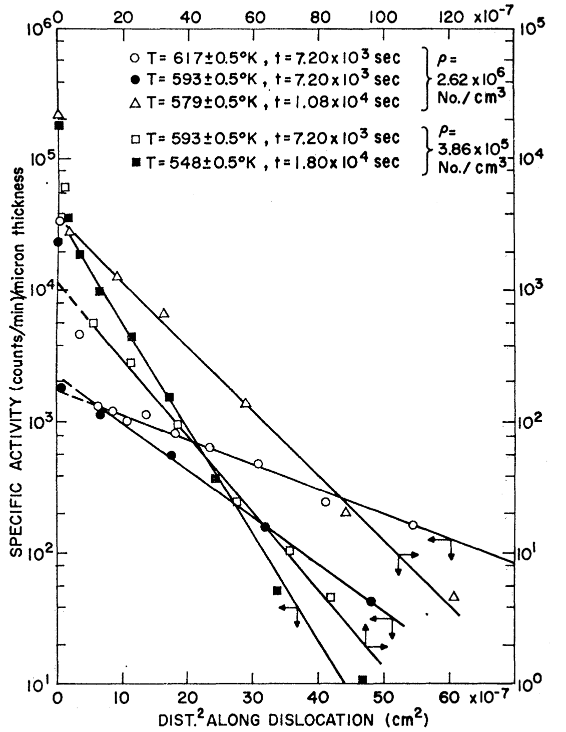

FIG. 3. Concentration profiles of Te^{127m} in pure single-crystal tellurium for diffusion along screw dislocations (along ⟨10$\bar{1}$0⟩).

sity was observed. Along edge dislocations the diffusivity (between 253 and 401°C) can be described by the equation

$$D_{\mathrm{ED}}=9.67\times10^{-6}\times\exp[(-0.65\pm0.02\ \mathrm{eV})/kT]\ \mathrm{cm^2/sec.}, \tag{2}$$

whereas the same along screw dislocations (between 275 and 380°C) can be described by the equation

$$D_{\mathrm{SD}}=7.12\times10^{-3}\times\exp[(-0.98\pm0.10\ \mathrm{eV})/kT]\ \mathrm{cm^2/sec}. \tag{3}$$

Type-C kinetics was also used for diffusion along the grain boundaries. Polycrystalline tellurium (99.9999%) obtained from the Atomergic Chemetals Company of New York City was melted in a sealed 8-mm-diam quartz capsule (G.E. "copper-free") at 10^{-6} Torr and immediately quenched in liquid nitrogen. This method produced about a 75-μ average grain size (by linear analysis) with more than 90% of the grains preferentially oriented (within a few degrees tilt or twist) along the c axis (axis of the capsule). The orientation of the adjacent grains was determined (within a few degrees) from the orientation of dislocation etch-pit patterns as has been done in NaCl.[35] These frozen-in grain boundaries (showing cloverleaf pattern from the center out) were stabilized by annealing at 100°C for a few hours before breaking the capsule and making samples. Attempts to make polycrystalline samples by slowly quenching at room temperature (from the melt) or by crystallizing just below the melting point produced too large grains (2–3 mm across) to be of any use. However in all attempts to crystallize tellurium from the melt, oblong grains were obtained (dimension along the boule axis or c axis about 8–10 times higher than that perpendicular to it). Moreover, the polycrystalline samples had to be carefully selected to be practically free from microcracks (due to the quenching technique used).

Samples were finished from these polycrystalline ingots[33] using practically no weight. Still, about 50–100 μ from the sample surface had to be chemically polished to attain about 10^3 cm/cm³ average dislocation density in the grains. The dislocations were mostly localized in the grains with the highest degree of misfit with respect to the c axis. The subsequent steps of the sectioning experiment were identical with that of the single crystals. The concentration profiles for type-C diffusion along grain boundaries are shown in Fig. 5. These data were treated as in edge dislocations since no particular degree of misorientation of grains could be used. The same data in a 2000 ppm absolute (ppma) In-doped

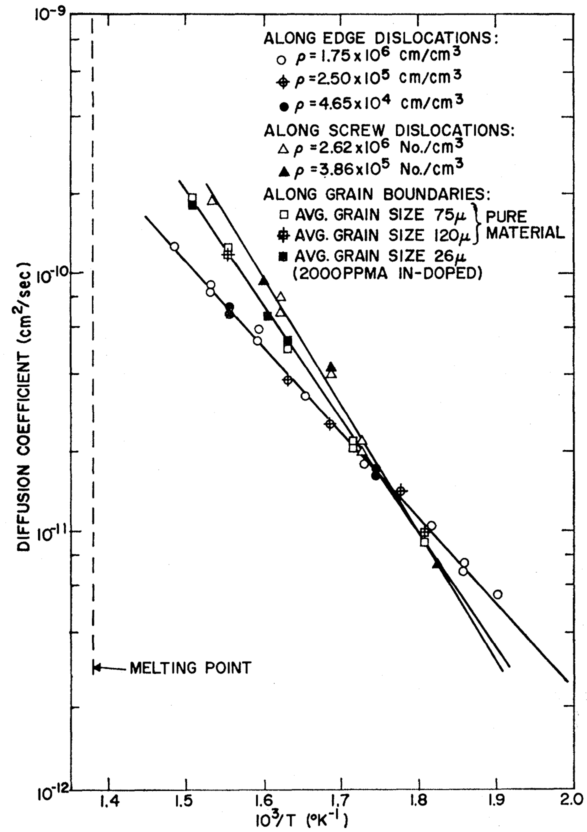

FIG. 4. Self-diffusion coefficients of Te^{127m} in tellurium along high-diffusivity paths as a function of temperature (under type-C kinetics).

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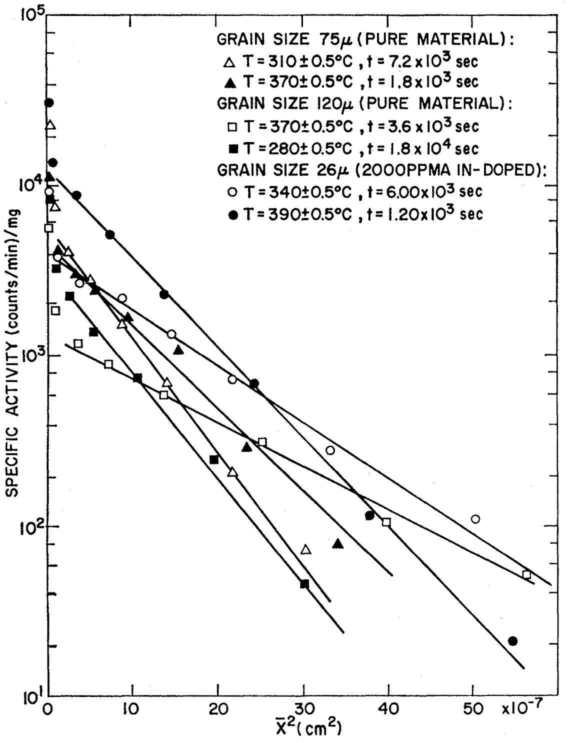

FIG. 5. Concentration profiles of Te^{127m} in polycrystalline tellurium under type-C-diffusion kinetics.

polycrystalline sample (average grain size 26-μ) are also shown in Fig. 5. Equilibrium polyhedral-shaped grain boundaries (still mostly aligned along the c axis) were, however, observed in these doped samples. Grain-boundary-diffusion coefficients calculated from the slopes of Fig. 5 using Eq. (1) are shown in Fig. 4. The parameter D_Lt/L^2 was maintained between 10^{-2} and 10^{-5} in the case of grain boundaries. These grain-boundary diffusivity data (between 280 and 390°C) can be described by the equation

$$D_{\mathrm{GB}}=7.47\times10^{-4}\times\exp[(-0.87\pm0.08\ \mathrm{eV})/kT]\ \mathrm{cm}^2/\mathrm{sec}. \quad (4)$$

It is noteworthy that within the range of error no difference in D_{GB} was observed between the pure and 2000 ppma In-doped polycrystalline samples even though electron microbeam-probe analysis indicated about 2 times higher concentration of In near the grain boundaries than in the matrix.

B. The Use of Type-B Diffusion Kinetics

According to Harrison[18] type-B or mixed kinetics should be observed in diffusion experiments where D_Lt/L^2 is maintained between 1 and 10^5. Among the several analyses available for type-B diffusion kinetics[9,11,12] only Fisher's analysis was used because of its simplicity (even though it violated the experimental boundary conditions). Type-B kinetics was applied independently to edge and screw dislocations in single crystals and grain boundaries in practically bulk-dislocation-free polycrystalline samples (by chemical polishing). The value of the parameter D_Lt/L^2 was maintained around 10. The concentration profiles of Te^{127m} in tellurium under type-B kinetics are shown in Figs. 6 and 7. According to Fisher[9] the slope of these log c-versus-x profiles is given by

$$\frac{d\log c}{dx}=-[(2D_L/D_P\delta)^{1/2}\log e]/(\pi D_Lt)^{1/4}. \quad (5)$$

$D_P\delta$ calculated using Eq. (5) are shown in Fig. 8. The concentration profiles given in Figs. 6 and 7 are better described by the Fisher equation in the case of grain boundaries than in the case of dislocations. The grain sizes in the polycrystalline samples changed from 75 to 145-μ in the undoped samples and 26 to 64-μ in the 2000 ppma In-doped polycrystalline samples. The reported grain sizes are arithmetic averages of those before and after the diffusion anneal. Since the dislocation-density distributions shown in Fig. 1 were unsuitable for the study of type-B kinetics, the samples were successively polished and annealed for 24 h (at about 420°C) several times before attaining the reported density. Moreover, electrochemical polishing,

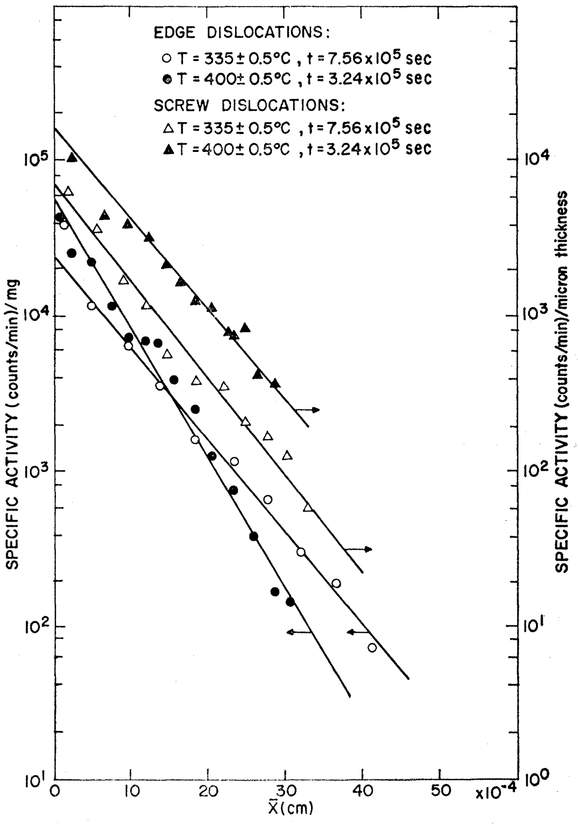

FIG. 6. Concentration profiles of Te^{127m} in pure single-crystal tellurium for type-B-diffusion kinetics along screw and edge dislocations. $\rho=7.0\times10^6/\mathrm{cm}^2$.

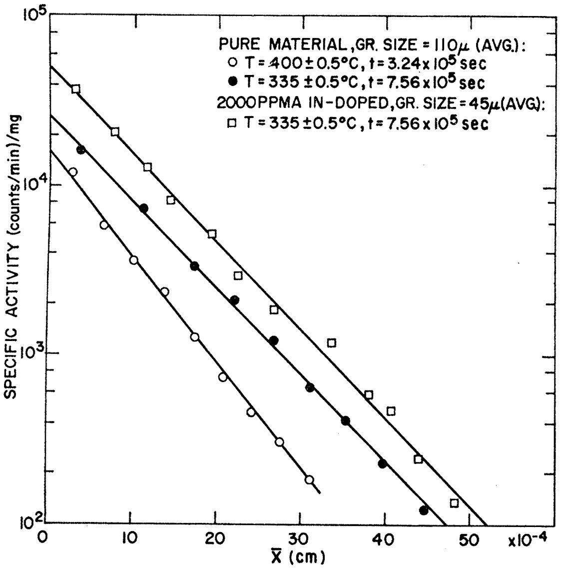

FIG. 7. Concentration profiles of Te^{127m} in polycrystalline tellurium for type-B-diffusion kinetics (pure and In doped).

etching, and etch-pit counting revealed practically no change in the dislocation density for a depth of about 200 μ from the surface. The values of the product $D_P\delta$ shown in Fig. 8 can be described by the following least-squares fit equations (between 335 and 400°C): (i) For edge dislocations $[\rho=7.0(\pm0.3)\times10^6\ \mathrm{cm/cm^3}]$,

$$D_P\delta=4.38\times10^{-10}\times\exp[(-0.67\pm0.05\ \mathrm{eV})/kT]\ \mathrm{cm^3/sec}. \quad (6)$$

(ii) For screw dislocations $[\rho=7.0(\pm0.3)\times10^6\ \mathrm{cm/cm^3}]$,

$$D_P\delta=9.45\times10^{-8}\times\exp[(-0.94\pm0.10\ \mathrm{eV})/kT]\ \mathrm{cm^3/sec}. \quad (7)$$

and (iii) For the polycrystalline samples (avg. gr. size $\simeq 110\ \mu$),

$$D_P\delta=1.11\times10^{-8}\times\exp[(-0.83\pm0.07\ \mathrm{eV})/kT]\ \mathrm{cm^3/sec}. \quad (8)$$

Within the range of experimental error no difference in the value of $D_P\delta$ was observed between the 2000 ppma In-doped and pure polycrystalline tellurium samples (Fig. 8).

C. Alternative Analysis of Type-B Kinetics

Since Harrison's criteria for the transition of type-C to type-B kinetics has been found unduely restrictive (with type-B kinetics observed for the value of D_Lt/L^2 as low as 10^{-2}), several detailed studies of concentration profiles were made. Figure 9 shows that plots of $\ln C$ versus x^2 can be used to determine independently both D_L and D_P correctly using a graphical method[36] as long as the abscissa scale can represent adequate amount of data necessary for two linear parts of the profile (the one near the surface for D_L and the other at deep penetrations for D_P). The second linear part of the profile at deep penetrations was extrapolated to the surface and graphically subtracted from the experimental profile near the surface. This operation produced a satisfactory linear profile at low penetrations for the determination of lattice diffusivity. Figure 9 also shows the same concentration profile plot with $\ln C$ versus x which is adequately linear and whose slope should provide the value of the product $D_P\delta$. The values of D_P, D_L, and $D_P\delta$ thus determined fit the data in Figs. 8 and 11. Figure 10 shows the effect of longer and longer lattice penetration on the composite profile. As is evident, the misfit region between the two linear profiles gets wider with greater lattice penetration superimposed on larger dislocation penetration. Data from two different samples were normalized in Fig. 10 to dramatize the effect.

III. DISCUSSION

The activation energy of pipe self-diffusivity along any particular type of high-diffusivity path (edge dislocations, screw dislocations, or grain boundaries) is found to be (within experimental error) identical under both type-B and C kinetics. Thus, type-B or mixed kinetics also represents the faster kinetics energetically.

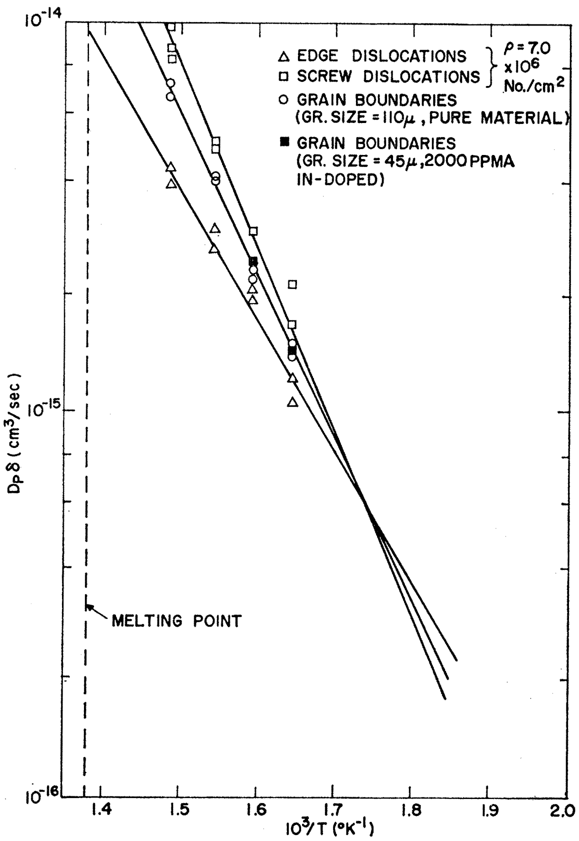

FIG. 8. Plot of $D_P\delta$ versus $1/T$ using Fisher's analysis.

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[36] T. S. Lundy and J. I. Federer, Trans. AIME 224, 1285 (1962); J. Askill, Appl. Phys. Letters 9, 82 (1966).

Also, as is shown in Sec. II C, the controversial subject of mathematical analysis of type-B kinetics can be avoided using a simple graphical method of analysis (if only D_P and/or D_L are desired) at low penetrations. This subject, however, needs further exploration to set quantitative restrictions as to time, temperature, and dislocation density (or grain size) for the concentration to be amenable to this kind of analysis.

No experiment was possible for the unambiguous determination of D_P (type-C kinetics) in doped samples with high grown-in dislocation density. Consequently, any effect of high-impurity concentration along dislocation cores on the measured diffusivity and the activation energy of the process can only be conjectured. However, from the limited data on the negative effect of 2000 ppma In doping in polycrystalline samples on the measured D_P and $D_P\delta$ indicate that the electrically active impurities do not further self-diffusivity or change activation energy of self-diffusion along high-diffusivity paths. This, of course, assumes that indium is identical to aluminum[33] in its effect of changing the point-defect concentration in tellurium lattice. This leads us to conclude that the dislocations and grain boundaries are always saturated with vacancies and the impurity attracted vacancies,[37] if any, are left unused for the diffusion process. Thus the activation energy for self-diffusion along high-diffusivity paths could not be higher than that required for vacancy motion (in vacancy mechanism). From the available data on ionic materials[30] it seems possible that this activation energy is actually somewhat lower than that required for vacancy motion even though any reason for this observation is not obvious. Consequently, from the available data on lattice self-diffusion in tellurium[33] it is concluded that the activation energy for the motion of vacancies is about 0.7 eV along the c axis and about 1 eV perpendicular to it. This difference in the energy of mobility of vacancies is exhibited in the anisotropy of lattice diffusion[33] as well as in the difference of activation energy of diffusion along screw and edge dislocations (whose crystallographic directions are also perpendicular to each other) by both type-C and type-B kinetics.

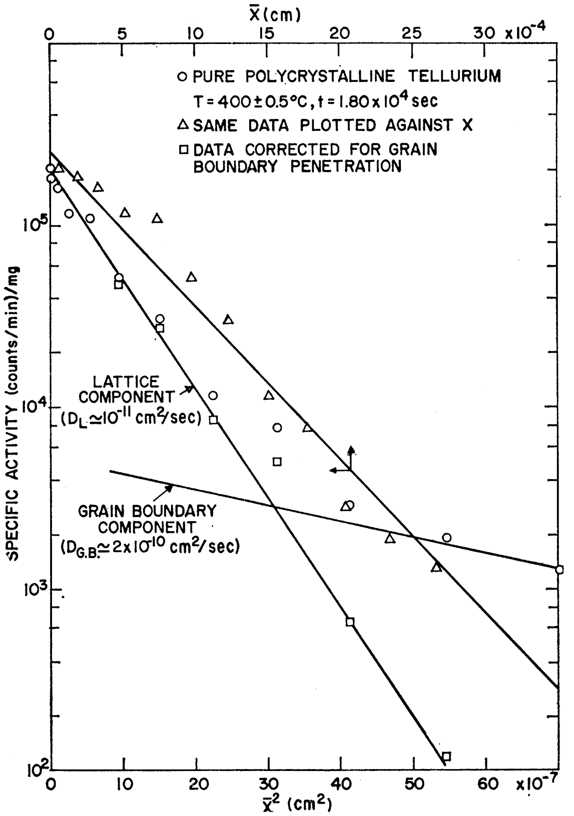

FIG. 9. Concentration-profile analysis for Te^{127m} diffusion into pure polycrystalline tellurium.

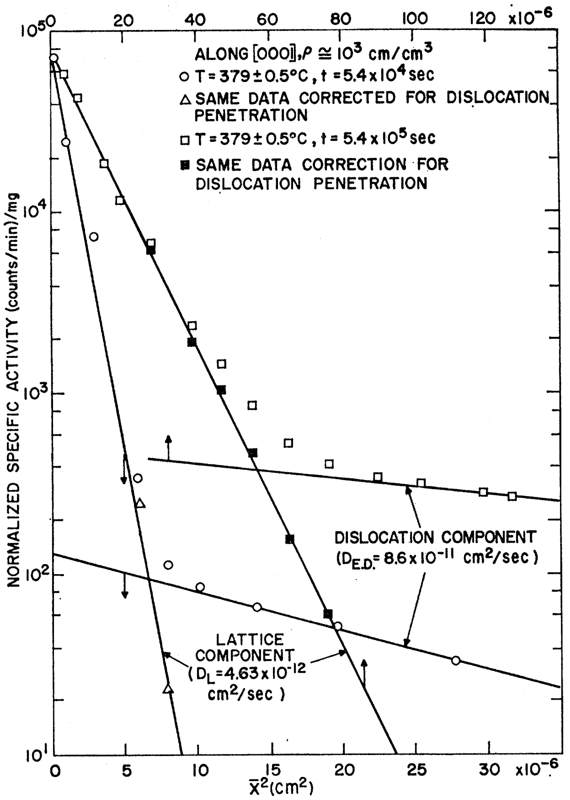

FIG. 10. Change in the form of Te^{127m} concentration profiles as a function of lattice penetration $[2(D_Lt)^{1/2}]$.

Since at present there is no understanding of the factors constituting D_0 along high-diffusivity paths, the pre-exponential factors in Eqs. (2), (3), and (4) can hardly be examined. But from the order-of-magnitude values of D_P compared to D_L (Fig. 11) it is evident that the high-diffusivity paths in tellurium are prominent at temperatures as high as 400°C (52°C below the m.p.) contrary to the existing general ideas. Again these high-diffusivity paths may have influenced the self-

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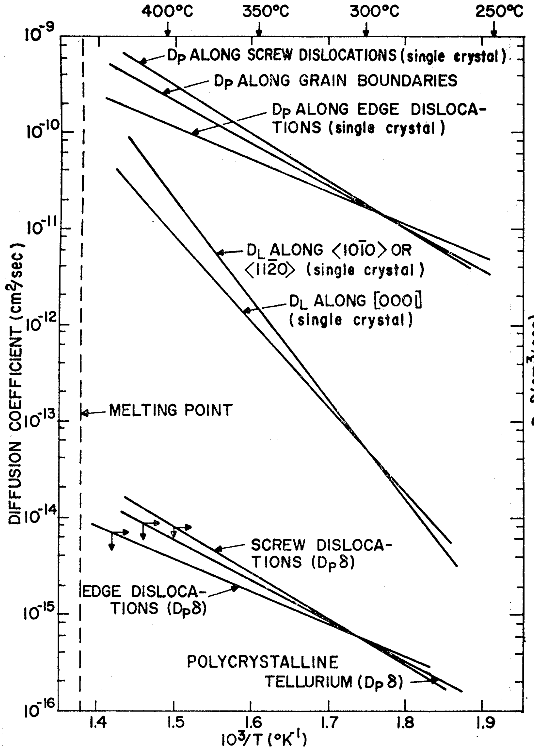

FIG. 11. Compiled diffusion-coefficient data in tellurium (along high- and low-diffusivity paths) as a function of temperature.

diffusivity data of Kazhlaeva *et al.*[38] in polycrystalline material in producing higher apparent lattice self-diffusion coefficients and lower activation energy of self-diffusion. Since these authors have not published any concentration profile this effect can not be analyzed.

Analysis of pre-exponential factors in Eqs. (6), (7), and (8) provides some interesting information. Dividing these factors by the pre-exponential factors of Eqs. (2), (3), and (4), respectively, we get

$$\delta = 4.53\times10^{-5} \text{ cm for edge dislocations} \quad (\rho = 7.0\times10^{6} \text{ cm/cm}^{3}), \qquad (9)$$

$$\delta = 1.33\times10^{-5} \text{ cm for screw dislocations} \quad (\rho = 7.0\times10^{6} \text{ cm/cm}^{3}),$$

and

$$\delta = 1.49\times10^{-5} \text{ cm for grain boundaries (gr. size} \simeq 110\,\mu).$$

The parameter δ has been defined[9] as the width of the grain-boundary disordered region, but its meaning (as obtained by Fisher's analysis) is unclear for dislocations.

Now if ρ = edge-dislocation density/cm² δ_B = grain-boundary thickness (cm), r_1 = radius of an average grain (cm) in the polycrystalline sample, r_2 = dislocation core radius (cm), and $n = 1/\pi r_1^2$ = No. of grains (av.) per cm², then the total grain-boundary area (to first approximation) $= (2\delta_B/r_1)$ cm² per cm² and total dislocation area $= \pi r_2^2 \rho$ cm² per cm² (assuming cylindrical grains and dislocation pipes).

Now, since Eqs. (6), (7), and (8) intersect at 300±10°C as has been found for the anisotropy of D_L[33] [as also Eqs. (2), (3), and (4)], then

$$2\delta_B/r_1 = \pi r_2^2 \rho . \qquad (10)$$

Putting $\rho = 7.0\times10^{6}/\text{cm}^2$, $r_1 = 5.5\times10^{-3}$ cm, and $\delta_B = 1.49\times10^{-5}$ cm, we get r_2 (edge dislocation) $= 1.57\times10^{-5}$ cm.

So, if the grain boundary can be described by an array of dislocations the calculated dislocation radius comes out to be almost the same as the grain-boundary thickness. Thus, the values of δ obtained by Fisher's analysis of type-B kinetics [Eq. (9)] represent the edge-dislocation core diameter (approximately) in tellurium. Again it appears from Eq. (9) that the effective diameter of an edge dislocation is about three times that of a screw dislocation (at the same dislocation density). Considering the fact that these values were obtained only from the considerations of atom mobility in tellurium this difference may be due to the correlation effects in a linear chain as discussed by Rickert.[39]

Another striking result obtained in this analysis is the order-of-magnitude values of grain-boundary thickness or dislocation-core diameters. This average value of about 0.15 μ is about 1.5×10^2 to 3×10^2 times larger than the values usually assumed for grain-boundary diffusion analysis (5–10 Å). This means that in tellurium the disordered region in a grain boundary or at a dislocation extends about 300 lattice parameters in contrast to the value of 4 Å obtained from electrical measurements in tellurium by Blakemore *et al.*[34] At the other extreme, microhardness measurements around grain boundaries in sulfur-segregated iron indicate about a 100-μ wide hardened region around the boundary.[40] Whether this high value of δ is a peculiarity of tellurium only or the analyses of type-B kinetics available do not describe $D_P\delta$ remains to be examined by a similar type of measurement in other materials. Again, this r is about the same order of magnitude as a dislocation including jogs as calculated by Lothe.[20]

The value of the activation energy for self-diffusion along grain boundaries has been found to be intermediate between those along the two types of dislocations. A model of the grain boundary (with no tilt or twist angle) as an array of edge dislocations inclined by a few degrees to the direction of diffusion lets us visualize this observation.

IV. CONCLUSION

Direct determination of diffusivity along high-diffusivity paths (dislocations and grain boundaries) is possible using Harrison's type-C diffusion kinetics.

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However, Harrison's criterion of transition from type-B to type-C kinetics is found to be too restrictive by about 10^2. Analysis of self-diffusion data (under type-B conditions) using Fisher's formula provided similar activation energies as those obtained from type-C kinetics. Moreover, the two kinetics together provided a method of determining the effective disordered region around a grain-boundary or dislocation pipe. The experimental values of this parameter, obtained for the first time in any system, is about 1.5×10^{-5} cm. This is about two orders of magnitude higher than usually assumed in grain-boundary diffusion studies (about three lattice parameters).

2000-ppma indium impurity (which is expected to affect point-defect concentration as aluminum) has been found ineffective in enhancing self-diffusivity along the grain-boundary high-diffusivity path. Thus, it is concluded that the high-diffusivity paths are always saturated with vacancies and the activation energy of self-diffusion along these paths could be less than but not greater than the activation energy of motion of vacancies in tellurium lattice (in corresponding crystallographic directions). From these observed data and from the behavior observed in ionic materials,[30] it can be estimated that the activation energy of motion of vacancies in tellurium is about 0.7 eV along $[0001]$ and about 1 eV along $\langle 10\bar{1}0\rangle$ or $\langle 11\bar{2}0\rangle$.

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Resistance and Magnetoresistance of Thin Indium Wires*

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The resistances of indium wires of diameter ranging between 0.642 and 0.0156 mm were measured at regular temperature intervals between 1.2 and 4.2°K and in transverse magnetic fields up to 18 kG. The bulk resistivity at 4.2°K, $\rho_b(4.2)=(0.93\pm0.03)\times10^{-9}$ Ω cm, and bulk mean free path, $l_b(4.2)=(1.61\pm0.08)\times10^{-2}$ cm, deduced from our data agree with other recent measurements, as does the average Fermi momentum, $p_F=(1.0\pm0.15)\times10^{-19}$ g cm/sec, determined from observations of the MacDonald-Sarginson effect. Size-dependent deviations from Kohler's rule suggest that a new magnetoresistive mechanism may be effective in wires of very small diameter ($d<0.08$ mm). Comparison of the product $\rho_b l_b$ at 4.2 and 0°K shows evidence of the size- and temperature-dependent resistivity contribution observed previously in indium and a number of other metals.

I. INTRODUCTION

TRANSPORT measurements on thin metallic wires and films are of considerable interest because the results provide a variety of information on both bulk and surface properties. The character of surface scattering (diffuse or specular), the bulk mean free path, and the average Fermi momentum of conduction electrons can be extracted from resistance and magnetoresistance data[1,2]; measurements of thermoelectric power as a function of sample size yield information on the dependence of the electronic mean free path on energy and also shed some light on phonon mean free paths and phonon-surface scattering.[3]

We report here resistance and transverse magnetoresistance results for very thin indium wires. Although several previous studies on size effects in indium wires[4,5] and foils[6,7] have already appeared in the literature, our measurements exhibit new effects that manifest themselves only in very thin wires ($d<0.08$ mm) and were not observed in earlier work[4,5] wherein only wires of larger diameter were employed.

An exact treatment of scattering of electrons at external surfaces requires a careful analysis of the character of the surface and should include effects of localized surface states.[8] In the theoretical discussion of transport[1,2] in thin samples, this difficulty is generally circumvented by assuming that a fraction p of the electrons suffer specular reflection upon striking the

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