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Exact Solution for a Model of Dislocation Pipe Diffusion*

J. Mimkes and M. Wuttig
Department of Metallurgical Engineering, University of Missouri – Rolla, Rolla, Missouri 65401
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The dislocations are treated as an ideal array of parallel pipes of radius a and diffusivity D_p embedded in the bulk material of the diffusivity D_b. The exact solution of this problem of diffusion along semi-infinite edge dislocations is presented for cubic, tetragonal, and hexagonal crystals. The solution makes it possible to evaluate the dislocation pipe radius a and the ratio of diffusivities Δ from one experiment. It is applied to experimental data for self-diffusion in tellurium available in the literature. The results of the calculations are a dislocation pipe radius $a=(1.5\pm0.5)\times10^{-4}$ cm and an activation energy for the pipe diffusion along edge dislocations in tellurium $E_p=0.80\pm0.05$ eV.

INTRODUCTION

Dislocation diffusion problems are usually solved by approximations[1-4] based on a model first reported by Fisher.[1] The more exact solution of grain boundary diffusion by Whipple[5] and Suzuoka[6] suggests a similar solution for the dislocation diffusion, and it is the purpose of this paper to present the exact solution of the problem of dislocation pipe diffusion for an instantaneous source. In order to reanalyze data by Ghoshtagore,[7,8] who investigated self-diffusion along dislocations in tellurium, the calculations are performed for cubic, tetragonal, and hexagonal crystals. The result is in general similar to Suzuoka's solution[6] of the grain boundary diffusion problem. The solution for a constant source may be obtained from the one presented in this paper by an integration.[6]

EXACT SOLUTION

The dislocation pipe is represented by a cylinder of radius a and isotropic diffusivity D' oriented perpendicular to the surface of the surrounding bulk. The diffusivities in the bulk are D parallel to the pipe and $D_\perp$ perpendicular to it. The differential equations for this diffusion problem with semi-infinitely long pipes and an instantaneous source of strength γ at the surface are

$$D_\perp\left(\frac{\partial^2 c}{\partial r^2}+\frac{1}{r}\frac{\partial c}{\partial r}\right)+D\frac{\partial^2 c}{\partial z^2}=\frac{\partial c}{\partial t}-\gamma\delta(z)\delta(t)\ ,\quad r>a \tag{1a}$$

$$D'\left(\frac{\partial^2 c'}{\partial r^2}+\frac{1}{r}\frac{\partial c'}{\partial r}\right)+D'\frac{\partial^2 c'}{\partial z^2}=\frac{\partial c'}{\partial t}-\gamma\delta(z)\delta(t),\quad r<a \tag{1b}$$

and the boundary conditions are given by

$$c'=c,\quad D_\perp\frac{\partial c}{\partial r}=D'\frac{\partial c'}{\partial r},\quad r=a\ . \tag{2}$$

The concentrations inside and outside the pipe are c and c', respectively, and $\delta(z)$ and $\delta(t)$ denote Dirac's δ function. The solution of Eqs. (1a), (1b), and (2) may be found using the Fourier-Laplace transformation

$$\bar{c}(r,\mu,\lambda)=\int_0^\infty\int_0^\infty c(r,z,t)\cos(\mu z)\exp(-\lambda t)\,dz\,dt\ . \tag{3}$$

With $\delta=D_\perp/D$ and $\Delta=D'/D$ the transformation of Eqs. (1a) and (1b) is

$$\frac{\partial^2\bar{c}}{\partial r^2}+\frac{1}{r}\frac{\partial\bar{c}}{\partial r}-\frac{k^2}{\delta}\bar{c}=-\frac{\gamma}{D\delta},\quad r>a \tag{4a}$$

$$\frac{\partial^2\bar{c}'}{\partial r^2}+\frac{1}{r}\frac{\partial\bar{c}'}{\partial r}-k'^2\bar{c}=-\frac{\gamma}{D'},\quad r<a \tag{4b}$$

$$k^2=\mu^2+\lambda/D,\quad k'^2=\mu^2+\lambda/D'\ . \tag{5}$$

Far away from the boundary $r=a$, the two solutions of Eqs. (4a) and (4b) will be independent of each other,

$$\frac{\partial c}{\partial r}=0\ \text{ for } r\to\infty,\quad \frac{\partial c'}{\partial r}=0\ \text{ for } r\to 0\ . \tag{6}$$

The solution of the differential equations (4a) and (4b) fulfilling the boundary conditions (2) and (6) are

$$\bar{c}(r,\mu,\lambda)=\gamma/Dk^2+A(\mu,\lambda)K_0(kr/\sqrt{\delta}),\quad r>a \tag{7a}$$

$$\bar{c}'(r,\mu,\lambda)=\gamma/D'k'^2+A'(\mu,\lambda)I_0(k'r),\quad r<a \tag{7b}$$

where K_0 and I_0 are Bessel functions of the second kind. A and A' are calculated from the boundary conditions (2),

$$A(\mu,\lambda)=-\gamma\frac{(\Delta-1)\mu^2}{D'k'^2k^2}\,\frac{1}{1+N}\,\frac{1}{K_0(ka/\sqrt{\delta})}, \tag{8a}$$

$$A'(\mu,\lambda)=\gamma\frac{(\Delta-1)\mu^2}{D'k'^2k^2}\,\frac{N}{1+N}\,\frac{1}{I_0(k'a)}\ , \tag{8b}$$

$$N=\frac{\delta k K_1(ka/\sqrt{\delta})I_0(k'a)}{\Delta k' K_0(ka/\sqrt{\delta})I_1(k'a)} . \qquad (9)$$

The exact solutions of the diffusion problem stated by the Eqs. (1a) and (1b) may be obtained through the Fourier-Laplace retransformation

$$c(r,z,t)=\frac{1}{2\pi^2 i}\int_{-\infty}^{+\infty}\int_{-i\infty}^{+i\infty}\bar{c}(r,\mu,\lambda)\cos\mu z\, e^{\lambda t}\,d\lambda\, d\mu . \qquad (10)$$

OUTSIDE SOLUTION

The solution for the outside region of the pipe is given by Eq. (7a). The integration of the solution retransformed according to Eq. (10) may be performed if a proper series expansion for the Bessel functions can be found. The replacement

$$xI_0(x)/I_1(x)=2 \qquad (11)$$

is equivalent to Whipple's[5] approach. Even though the approximation (11) seems to be very poor, it has been shown[9] that higher-order approximations do not contribute significantly in this case. Hence, Whipple's solution[5] for the outside is quite accurate. Similarly, the ratio of the Bessel functions of the second kind K_1 and K_0 is very well approximated by

$$xK_1(x)/K_0(x)=x+\tfrac{1}{2} , \qquad (12)$$

as can be verified numerically.[10, 11] Using (11) and (12) the function N in Eq. (9) may be simplified to

$$N=2\delta(ka+\tfrac{1}{2})/(\Delta k'^2 a^2) , \qquad (13)$$

and the ratio of Bessel functions K_0 used in Eq. (7a) yields for $a>0$, $r>a$,

$$\frac{K_0(kr/\sqrt{\delta})}{K_0(ka/\sqrt{\delta})}=\left(\frac{a}{r}\right)^{1/2} e^{-k(r-a)/\sqrt{\delta}} \times[1-\tfrac{1}{8}(1-r/a)^2+\cdots] . \qquad (14)$$

Equation (14) may be verified by calculating the Taylor series of $f(x)$ in Eq. (15) at $x=x_0$:

$$f(x)=\left(\frac{x}{x_0}\right)^{1/2}\frac{e^x K_0(x)}{e^{x_0}K_0(x_0)} =1+\left(x+\frac{1}{2}-\frac{xK_1}{K_0}\right)_{x_0}\left(\frac{x}{x_0}-1\right) +\left[x\left(x+\frac{1}{2}-\frac{xK_1}{K_0}\right)-\frac{1}{8}\right]_{x_0}\left(\frac{x}{x_0}-1\right)^2+\cdots . \qquad (15)$$

Applying Eq. (12) to this Taylor series yields Eq. (14). The outside solution, Eq. (7a), integrated according to (10) can now be simplified by inserting the approximations, Eqs. (11)–(14),

$$c(r,z,t)=\frac{1}{2\pi^2 i}\int_{-\infty}^{+\infty}\cos\mu z\, e^{\lambda t}\,d\lambda\,d\mu \times\left[\frac{\gamma}{Dk^2}-\frac{\gamma}{D'k^2k'^2}\,\frac{1}{1+2\delta(ka+\frac{1}{2})/\Delta k'^2a^2} \times\left(\frac{a}{r}\right)^{1/2}\exp\left(-\frac{k(r-a)}{\sqrt{\delta}}\right)\right] . \qquad (16)$$

Equation (16) is very similar to the retransformation calculated by Whipple,[5] and it may be integrated with the same techniques by substituting $\mu^2\to\mu^2/Dt$, $\lambda\to\lambda/t$, $\nu^2=\lambda-\mu^2$ and replacing any denominator by an integration, as in Eq. (17),

$$(1+N)^{-1}=\int_0^\infty \exp[-(1+N)\sigma]\,d\sigma . \qquad (17)$$

Upon introducing the reduced coordinates $\zeta=z/\sqrt{(Dt)}$, $\rho=r/\sqrt{(Dt)}$, $\alpha=a/\sqrt{(Dt)}$, and $\beta=(\Delta-1)\alpha$ the outside solution of the pipe diffusion problem for an instantaneous source is then given by

$$c(\rho,\zeta,t)=\gamma(\pi Dt)^{-1/2}\left\{e^{-\zeta^2/4}+\left(\frac{\alpha}{\rho}\right)^{1/2}\int_1^\Delta\left(\frac{\zeta^2}{4\sigma}-\frac{1}{2}\right)\exp\left(\frac{-\zeta^2}{4\sigma}-\frac{\sigma-1}{\alpha\beta}\right) \times\operatorname{erfc}\left[\frac{1}{2}\left(\frac{\Delta-1}{(\Delta-\sigma)\delta}\right)^{1/2}\left(\rho-\alpha+2\delta\frac{\sigma-1}{\beta}\right)\right]\frac{d\sigma}{\sigma^{3/2}}\right\} \qquad (18)$$

with $\rho>\alpha>0$. Equation (18) is equivalent to Suzuoka's solution of the grain boundary diffusion problem.

INSIDE SOLUTION

The solution for the inside region, $r<a$, is given by Eq. (7b). As in a previous paper[9] the retransformation of Eq. (7b) will not be performed by an integration according to Eq. (10), but rather with the use of the boundary conditions (2). For this purpose the even function $I_0(k'r)$ is developed into a Taylor series at $r^2=a^2$,

$$I_0(k'r)=\sum_{n=0}^{\infty}\left[\left(\frac{1}{r}\frac{\partial}{\partial r}\right)^n I_0(k'r)\right]_a \frac{(r^2-a^2)^n}{n!}\,. \quad (19)$$

Ordering Eq. (19) by powers of differentiation, $I_0^{(n)}(k'r)$, and using Eq. (8b) for $A'(\mu,\lambda)$ the first two terms of the inside solution equation (7b) may be written as

$$\bar{c}'(r)=\bar{c}'(a)-p(r^2-a^2)\times\tfrac{1}{2}a\left(\frac{\partial\bar{c}'}{\partial r}\right)_a, \quad (20)$$

where $p(r^2-a^2)$ is the polynomial

$$p(r^2-a^2)=\sum_{n=1}^{\infty}(1/n)[1-(r/a)^2]^n\,. \quad (21)$$

Applying the boundary conditions (2) to Eq. (20) yields

$$\bar{c}'(r)=\bar{c}(a)-a\delta p(r^2-a^2)\left(\frac{\partial\bar{c}}{\partial r}\right)_a\Big/2\Delta\,. \quad (22)$$

The solution for the inside equation (22) is now expressed in terms of the outside solution, which has already been calculated. Higher-order approximations involve higher-order derivatives of $c(r)$ at $r=a$ and do not contribute significantly.[9]

SECTION INTEGRAL

For the evaluation of sectioning experiments the solutions, Eq. (18) for the outside and (22) for the inside region of the pipe, have to be integrated with respect to r over the complete section. The total amount $Q(z,t)$ of diffused material in a section at a distance z from the surface of the crystal after a diffusion anneal of time t is

$$Q(z,t)=2\pi\int_0^a c'(r,z,t)r\,dr+2\pi\int_a^A c(r,z,t)r\,dr\,, \quad (23)$$

where A is the radius of the mean bulk area surrounding each single dislocation pipe. The radius A may be calculated from the dislocation density d,

$$A=(\pi d)^{-1/2}\,. \quad (24)$$

The r integration of the polynomial Eq. (21) yields

$$\int_0^a p(r^2-a^2)r\,dr=\tfrac{1}{2}a^2\,. \quad (25)$$

Applying Eq. (25) and the reduced coordinates of Eq. (18) the complete-section integral (23) reads ($\epsilon=a/A$)

$$Q(\zeta,t)=\gamma\pi A^2(\pi Dt)^{-1/2}[Q_1(\zeta)+Q_2(\zeta)+Q_3(\zeta)]\,, \quad (26)$$

with the three functions

$$Q_1(\zeta)=\exp(-\tfrac{1}{4}\zeta^2)\,,$$

$$Q_2(\zeta)=2\epsilon^{1/2}\int_1^{\Delta}\int_{\epsilon}^{1}\left(\frac{\zeta^2}{4\sigma}-\frac{1}{2}\right)\exp\left(-\frac{\zeta^2}{4\sigma}-\frac{(\sigma-1)\delta}{\alpha\beta}\right)r^{1/2}\times\operatorname{erfc}\left[\frac{1}{2}\left(\frac{\Delta-1}{(\Delta-\sigma)\delta}\right)^{1/2}\left(\frac{\alpha}{\epsilon}(r-\epsilon)+2\delta\frac{\sigma-1}{\beta}\right)\right]\frac{dr\,d\sigma}{\sigma^{3/2}}\,,$$

$$Q_3(\zeta)=\epsilon^2\left(1+\frac{\delta}{4\Delta}\right)\int_1^{\Delta}\left(\frac{\zeta^2}{4\sigma}-\frac{1}{2}\right)\exp\left(-\frac{\zeta^2}{4\sigma}-\frac{(\sigma-1)\delta}{\alpha\beta}\right)\operatorname{erfc}\left\{\left[\frac{(\Delta-1)\delta}{\Delta-\sigma}\right]^{1/2}\frac{\sigma-1}{\beta}\right\}\frac{d\sigma}{\sigma^{3/2}}+\frac{\epsilon^2\alpha}{2\pi^{1/2}\Delta}\int_1^{\Delta}\left[\frac{(\Delta-1)\delta}{\Delta-\sigma}\right]^{1/2}\left(\frac{\zeta^2}{4\sigma}-\frac{1}{2}\right)\exp\left(-\frac{\zeta^2}{4\sigma}-\frac{(\sigma-1)\delta}{\alpha\beta}-\frac{(\sigma-1)^2\delta}{(\Delta-\sigma)\alpha\beta}\right)\frac{d\sigma}{\sigma^{3/2}}\,. \quad (27)$$

Equations (26) and (27) give the section integral for the solution of the dislocation pipe diffusion problems for hexagonal, tetragonal, and cubic ($\delta=1$) crystals with an instantaneous source at the surface. $Q_1(\zeta)$ is the bulk contribution far away from the dislocation. $Q_2(\zeta)$ represents the bulk next to the pipes where the material has diffused into the bulk predominantly from the dislocation pipe. The two parts of $Q_3(\zeta)$ represent the contribution from the inside of the dislocation pipe. The first part of $Q_3(\zeta)$ is larger than the second by an order of magnitude, as can be shown numerically. The second part of $Q_3(\zeta)$ may thus be dropped in all calculations and has been presented for completeness only.

The section integral $Q(\zeta,t)$ in Eq. (26) contains all dominant parts of the series approximation for the solution of dislocation pipe diffusion. The exact solution may be obtained by taking into account all terms of the series approximations that have been used. However, as numerical calculations have shown that higher-order approximations are smaller by orders of magnitude, Eqs. (26) and (27) may be considered the exact solution.

DISCUSSION

The exact solution for dislocation diffusion (26) and (27) contains two parameters, which have to be fitted to experimental data, the ratio of diffusivities Δ and the radius of the dislocation pipes a. At different temperatures only Δ is expected to vary with the energy $\Delta E = E_b - E_p$, where E_b and E_p are the activation energies for the diffusion process in the bulk and the pipe, respectively. Thus, the exact solution will reproduce dislocation diffusion data at any temperature once the two constant parameters a and E_p are properly chosen. This will be shown using the experimental data of Ghoshtagore,[7,8] who investigated self-diffusion along dislocations in tellurium.

Ghoshtagore evaluated his data using Fisher's[1] approximation for the contribution $Q_2(\zeta)$ next to the pipes; he further used

$$Q_3(\zeta) \sim \exp(-\zeta^2/4\Delta) \tag{28}$$

for the contribution from the inside of the pipes. According to these approximations he calculated the values of the two parameters $a = 1.5 \times 10^{-5}$ cm and $E_p = 0.65 \pm 0.05$ eV. However, the use of the above two approximations results in a systematic deviation for the activation energy E_p, as has been pointed out by LeClaire.[12] The deviation is due to the fact that the approximations are only valid for low temperatures, where the diffusion parameter β is large. At higher temperatures the value of β is not large enough to ensure the validity of the approximations. This is shown in the following

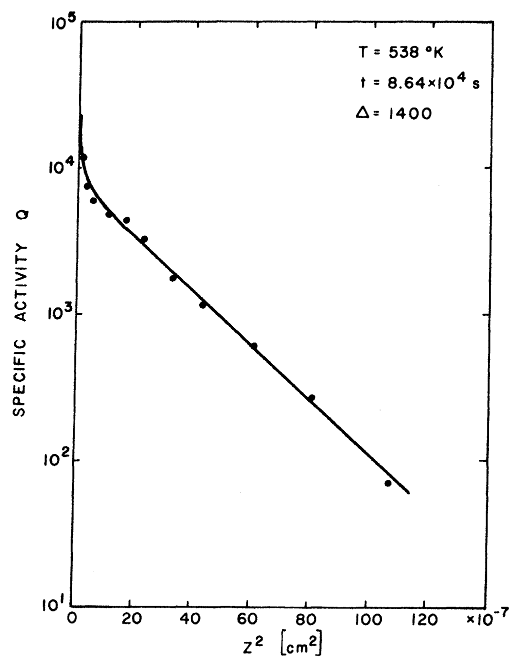

FIG. 1. Low-temperature penetration plot of tellurium containing edge dislocations. The plotted points are Ghoshtagore's data (Ref. 8), and the line is calculated on the basis of Eq. (26).

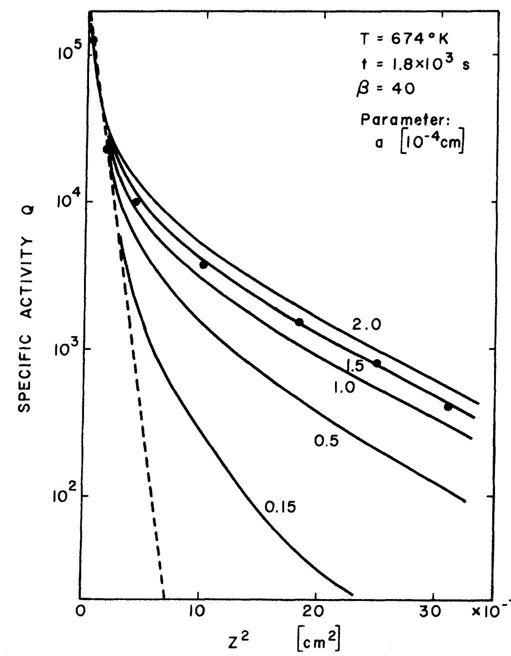

FIG. 2. High-temperature penetration plot of tellurium containing edge dislocations. The plotted points are Ghoshtagore's data (Ref. 8), and the solid lines have been calculated on the basis of Eq. (26). The broken line reflects the pure bulk contribution.

figures.

Figure 1 gives the specific activity $Q(\zeta, t)$ as a function of the square of the penetration depth z^2 at the lower temperature $T = 538$ °K. The solid circles represent the data by Ghoshtagore, the solid line gives the best fit calculated from the exact solution and $\Delta = 1400$. The slope of the theoretical line is determined by Δ and is independent of the dislocation pipe radius a.

The value of Δ may also be calculated by approximation (28). With[7]

$$D = 130 \exp[(-1.75 \pm 0.05)\ \text{eV}/kT], \tag{29}$$

the slope in Fig. 1 yields $\Delta = 1300$. As expected, the accuracy of Eq. (28) is satisfactory at the lower temperature.

Figure 2 shows the specific activity $Q(\zeta, t)$ as a function of z^2 at the higher temperature 674 °K. The solid circles are taken from Ref. 8; the lines represent calculations according to the exact solution (26) for various values of the dislocation pipe radius a. A best fit is obtained for the values of the parameters $\beta = 40$, and $a = (1.5 \pm 0.5) \times 10^{-4}$ cm resulting in $\Delta = 38 \pm 13$. As the data deviate from a simple penetration plot it is obvious that the approximation (28) does not apply at this high temperature. This approximation, using the slope at large values of z^2 in Fig. 2, would yield a much lower value for Δ, Δ = 12. A similar difference between the values of Δ obtained through Eqs. (27) and (28), respectively, is calculated at all temperatures, as may be seen from Fig. 3. In this figure the ratio of diffusivities Δ is plotted versus the inverse of temperature. The solid circles represent the best fit of Δ according to the exact solution (26) with a dislocation pipe radius $a = 1.5 \times 10^{-4}$ cm. The straight line through the circles corresponds to an energy $\Delta E = 0.95$ eV leading to an activation energy $E_p = 0.80 \pm 0.05$ eV for the diffusion along the dislocation pipes if $E_b = 1.75 \pm 0.05$ eV[7] is chosen. The solid squares in Fig. 3 represent the values of Δ calculated according to approximation (28). As expected, the difference between the two Δ's becomes larger with rising temperature, leading to a 20% lower activation energy $E_p = 0.65 \pm 0.05$ as given by Ghoshtagore.[8]

The surprising result of this analysis is the rather large value of the radius of the dislocation pipes. It must be recalled that this number has only limited accuracy mainly due to the approximation of the radial variation of the diffusion constant by a step function. Nevertheless, its order of magnitude should be correct. Certainly, the observed diffusion enhancement in tellurium cannot be restricted to the dislocation core as is the case for metals.[12] A two-defect model whereby the concentrations of the two defect species strongly depend on the long-range stresses of the dislocations might be considered. On the other hand, dislocation precipitates could also be the cause for the unexpected large value of the pipe radius.

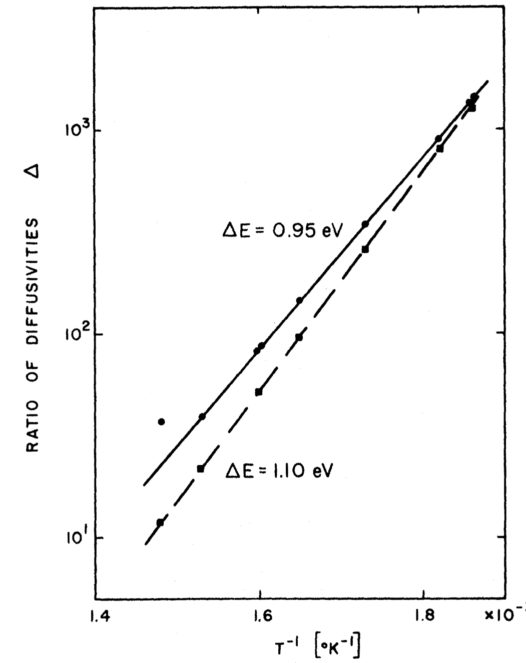

FIG. 3. Arrhenius plot of the diffusion enhancement in tellurium containing dislocations: The solid line and solid circles are data calculated on the basis of Ghoshtagore's experimental results (Ref. 8) and Eq. (26). The dashed line and solid squares are data given by Ghoshtagore (Ref. 8) based on approximation (28).

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