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II. Physikalisches Institut, Technische Universität Berlin

Diffusion along Pipe Dislocations

By

J. MIMKES

Solutions of pipe diffusion In a simple approach isolated dislocations may be approximated by infinite pipes of radius a and diffusivity D' penetrating the crystal perpendicularly to the surface. The bulk diffusivities are $D_{\parallel}$ parallel and $D_{\perp}$ perpendicular to the pipes. The mean distance 2A between dislocations may be calculated from the dislocation density m, $A = (\pi m)^{-1/2}$. A solution may be calculated for $(D_{\parallel} t)^{1/2} < A$, the result for a constant initial source is given by

$$Q_c(\zeta) = \operatorname{erfc}(\zeta/2) + I(\zeta, k, \Delta, \varepsilon) \quad , \tag{1}$$

$$I = \int_1^{\Delta} \int_{\varepsilon}^{1} \sqrt{\frac{\varepsilon \varrho}{\pi \sigma^3}}\, \zeta \exp\left(-\frac{\zeta^2}{4\sigma} - \frac{\sigma - 1}{\Delta - 1}\left(\frac{k}{\varepsilon}\right)^2\right) x$$

$$x \operatorname{erfc}\left\{\sqrt{\frac{\Delta - 1}{\Delta - \sigma}}\left(\frac{\varrho - \varepsilon}{2k} + \frac{k}{\varepsilon}\,\frac{\sigma - 1}{\Delta - 1}\right)\right\} d\varrho\, d\sigma \quad ,$$

$$\zeta = \sqrt{\frac{z}{D_{\parallel} t}} \quad , \qquad k = \frac{\sqrt{D_{\perp} t}}{A} = \sqrt{m \pi D_{\perp} t} \quad , \tag{2}$$

$$\Delta = \frac{D'}{D_{\parallel}} \quad , \qquad \varepsilon = \frac{a}{A} = a\sqrt{\pi m} \quad .$$

The result is similar to Whipple's solution (1).

The solution for an instantaneous source may be calculated from the solution for a constant source (references (2, 3))

$$Q_i(\zeta) = -\frac{1}{\sqrt{D_{\parallel} t}}\,\frac{\partial}{\partial \zeta} Q_c(\zeta) \quad . \tag{3}$$

The corresponding time depending solutions have been given elsewhere (4).

Discussion A short review of pipe diffusion data from the literature, which may be evaluated according to solutions (1) and (3), will be given.

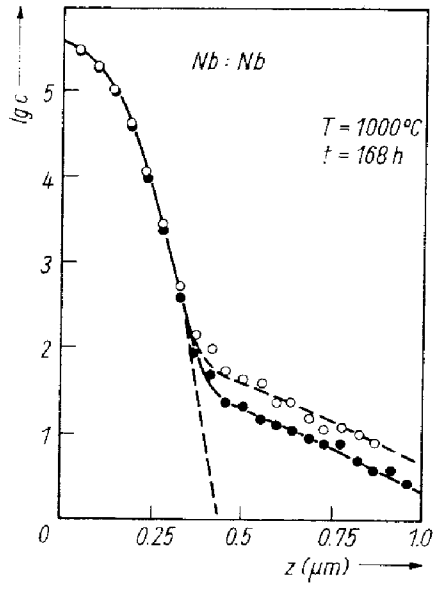

Fig. 1. Self-diffusion in Nb at 1000 °C after 168 h as a function of diffusion depth, reported by Reuther and Achter (6);
- ● single crystal, dislocation density $m = 4 \times 10^5$ cm^{-2},
- ○ polygonized crystal, dislocation density $m = 7.6 \times 10^5$ cm^{-2};

solid and dashed lines give the best fit according to equation (3)

Though many section experiments on pipe diffusion have been published recently (5), only few authors have provided all the information necessary for complete evaluation: Activity Q, diffusion depth z, diffusion time t, annealing temperature T, dislocation density m, and the initial condition.

Fig. 1 shows a Nb self-diffusion experiment by Reuther and Achter (6). A single crystalline (SC) sample of a total dislocation density $m = 4 \times 10^5$ cm^{-2} and a polygonized crystalline (PC) sample of $m = 7.6 \times 10^5$ cm^{-2} have been annealed simultaneously at 1000 °C for 168 h. As the dislocation density m is the only parameter that differs in both diffusion runs, ε according to equation (2) should vary by a factor $\varepsilon(\mathrm{PC})/\varepsilon(\mathrm{SC}) = [m(\mathrm{PC})/m(\mathrm{SC})]^{1/2} = 1.38$ causing the parallel shift of the tail in Fig. 1. (The parameter k in solutions (1) and (3) appears as a ratio k/ε only, which is independent of m.) These considerations are reflected by the best fit according to equation (3), which is represented by the solid and dashed lines in Fig. 1: $D = 6.3 \times 10^{-17}$ cm^{2}s^{-1}, $\Delta = 30$, $\varepsilon = 0.020$ for the SC sample and $D = 6.4 \times 10^{-17}$ cm^{2}s^{-1}, $\Delta = 30$, $\varepsilon = 0.028$ for the PC sample, with a ratio $\varepsilon(\mathrm{PC})/\varepsilon(\mathrm{SC}) = 1.4$. From these parameters a pipe radius $a = 2 \times 10^{-5}$ cm may be calculated for both samples.

Fig. 2 shows the diffusion of Nb into Ta at 1250 °C after 2 h annealing time by Pawel and Lundy (7). The best fit has been obtained for $D = 1.5 \times 10^{-15}$ cm^{2}s^{-1}, $D' = 2.4 \times 10^{-13}$ cm^{2}s^{-1}, and $\varepsilon = 0.02$. With the observed dislocation density $m = 10^5$ cm^{-2} the dislocation radius $a = 3.5 \times 10^{-5}$ cm may be calculated. Additional diffusion runs at 1350 °C by the same authors (7) indicate an activation energy $E_b = 4.2$ eV for the bulk and $E_p = 1.7$ eV for pipe diffusion of Nb into Ta.

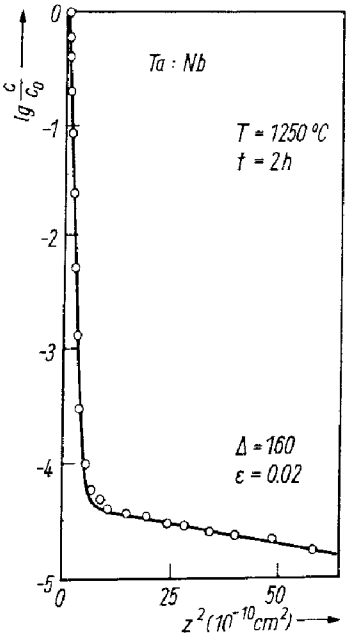

Fig. 2. Nb diffusion in Ta at 1250 °C after 2h as a function of square of diffusion depth reported by Pawel and Lundy (7). Solid line corresponds to the best fit according to equation (3)

Self-diffusion of Se has been investigated by Brätter and Gobrecht (8). Fig. 3 shows the result of the best fit according to equation (1). The calculated diffusivities have been plotted versus the reciprocal temperature. Open circles for bulk diffusivities represent calculations by the authors (8), solid circles are the results from equation (1). The activation energies calculated by the best fit are $E_b^{\parallel} = (1.4 \pm 0.1)$eV for bulk diffusion parallel to the c-axis, $E_b^{\perp} = (1.0 \pm 0.5)$eV for bulk diffusion perpendicular to the c-axis, $E_p^{\parallel} = (0.85 \pm 0.2)$eV for pipe diffusion parallel to the c-axis.

No reasonable activation energy has been obtained for pipe diffusion perpendicular to the c-axis due to large variations of dislocation densities (or ε) at different temperatures, whereas $\varepsilon = 0.02 \pm 0.01$ was found constant at all temperatures for pipe diffusion parallel to the c-axis. At a dislocation density of about $m = 10^5$ cm^{-2} this leads to a mean dislocation radius $a = 3 \times 10^{-5}$ cm.

From all calculations so far un unexpectedly high value for the mean dislocation radius has been obtained, a 10^{-5} cm. A similar result has been reported for Te (9). This large value may be due to sub-grain-boundaries, which

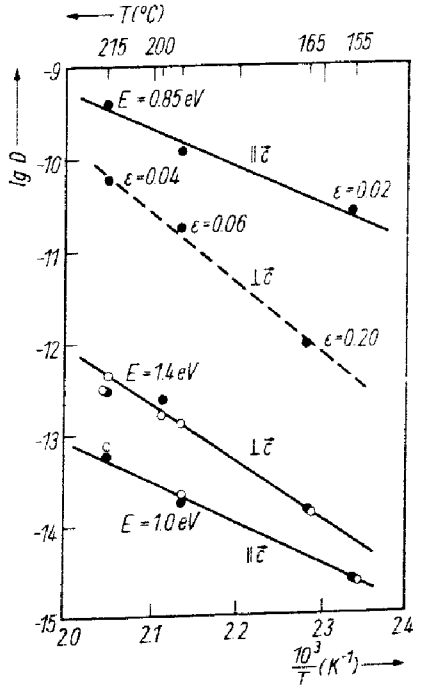

Fig. 3. Bulk and pipe diffusivities of Se self-diffusion as a function of reciprocal temperature;
o bulk diffusivities given by Brätter and Gobrecht (8),
• bulk and pipe diffusivities calculated according to equation (1)

are present even though isolated dislocations may prevail. This has indeed been observed for Ta and Nb (6, 7).

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