Self-diffusion in Au along isolated dislocations

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The complete solution of dislocation-pipe diffusion is applied to self-diffusion data of gold from the literature. The diffusivities reported herein are based on a fitted dislocation density of 10^9–10^{10} lines/cm^2. The resulting diffusivities are $D = 0.07 \exp[-(1.73\ \text{eV})/kT]$ for the bulk and $D_p = 2 \times 10^{-3} \exp[-(1.24\ \text{eV})/kT]$ for the dislocation pipes. The calculated radius of the pipes is $a = (1.5 \pm 1.0) \times 10^{-6}$ cm.

ANALYSIS

Several pipe-diffusion experiments[1–4] have been evaluated by means of the complete solution of the problem of diffusion along isolated dislocation pipes[5,6] for an instantaneous source

$$Q(\zeta, t) = \gamma(\pi D t)^{-1/2} \left\{ e^{-\zeta^2/4} + \int_1^{\Delta} \int_{\epsilon}^{1} \left(\frac{\epsilon\rho}{\sigma^3}\right)^{1/2} \left(\frac{\zeta^2}{2\sigma} - 1\right) \times \exp\left(-\frac{\zeta^2}{4\sigma} - \frac{\sigma - 1}{\Delta - 1}\frac{1}{\alpha^2}\right) \operatorname{erfc}\left[\left(\frac{\Delta - 1}{\Delta - \sigma}\right)^{1/2} \times \left(\alpha \frac{\rho - \epsilon}{2\epsilon} + \frac{1}{\alpha}\frac{\sigma - 1}{\Delta - 1}\right)\right] d\sigma\, d\rho \right\}, \tag{1}$$

$$\zeta = z/(Dt)^{1/2}, \quad \alpha = a/(Dt)^{1/2}, \quad A = (\pi m)^{-1/2}$$
$$\Delta = D_p/D, \qquad \epsilon = a/A = a(\pi m)^{1/2}, \tag{2}$$

where z is the penetration depth parallel to the dislocations, D and D_p are the diffusivities in the bulk and the pipes, respectively, a is the radius of the pipe, and m is the dislocation density. Since the results for the pipe-diffusion parameters so far[1–6] have indicated unexpected large values for a, more information may be expected from an analysis of the microsectioning data of Au self-diffusion by Gupta.[7] This analysis will be presented in this paper.

Since no experimental values of the dislocation density m are given in Gupta's paper, the data have been analyzed for $m = 10^9$, 3×10^9, and 10^{10} cm^{-2}. No fit has been obtained for the dislocation densities $m > 10^{10}$ cm^{-2} as calculated by the author[7] according to Hart's[8] analysis. The best fit for the pipe-diffusion parameters Δ and a is given in Fig. 1. The agreement of data points and theoretical curves is satisfactory within a narrow range of the dislocation density indicated in the figure. In Fig. 2 the resulting diffusivities are given as a function of temperature, the bulk diffusivity

$$D_{\text{app}} = 0.07 \exp[-(1.73\ \text{eV})/kT], \tag{3}$$

as given by the author,[7] and the pipe diffusivity

$$D_p = 2 \times 10^{-3} \exp[-(1.24\ \text{eV})/kT],$$

as obtained from Δ.

The effective dislocation-pipe radius a that will fit all five temperatures investigated may be found in Fig. 2 at $a = (1.5 \pm 1.0) \times 10^{-6}$ cm. The product of pipe diffusivity D_p^0 and the cross section of the pipe therefore is

$$\pi a^2 D_p^0 = 6 \times 10^{-15 \pm 1}\ \text{cm}^4\,\text{sec}^{-1}.$$

DISCUSSION

The activation energy $E_p = 1.24 \pm 0.1$ eV is in excellent agreement (within 0.04 eV) with the value calculated by Gupta who used Pavlov's[9] formula $E_p = 1.20 \pm 0.1$ eV, as well as Whipple's[10] formula for a homogeneous slab $E_p = 1.16 \pm 0.02$ eV. The preexponential term $\pi a^2 D_p^0 = 6 \times 10^{-15}$ cm^4 sec^{-1} is well within the range normally encountered in most fcc metals.[11] However, the calculated effective pipe radius $a = (1.5 \pm 1.0) \times 10^{-6}$ cm is much larger

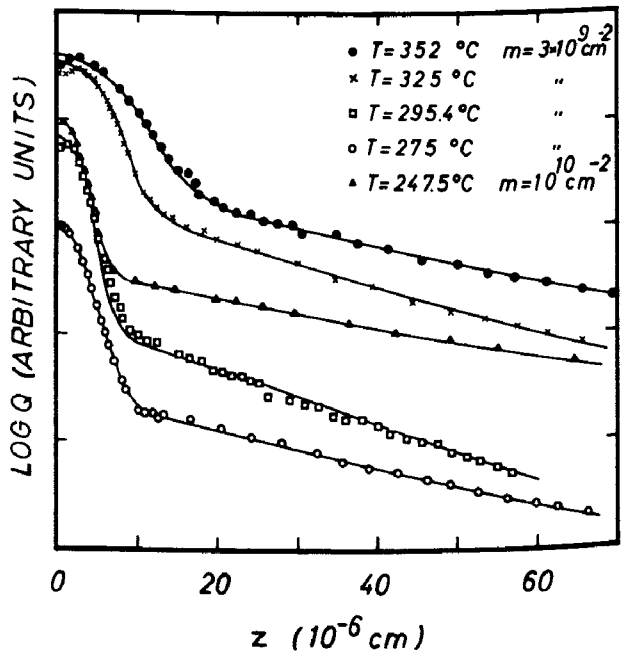

FIG. 1. Logarithm of Au activity Q vs penetration distance z. Data points from Ref. 7, solid lines according to Eq. (1) for dislocation densities m indicated in the figure.

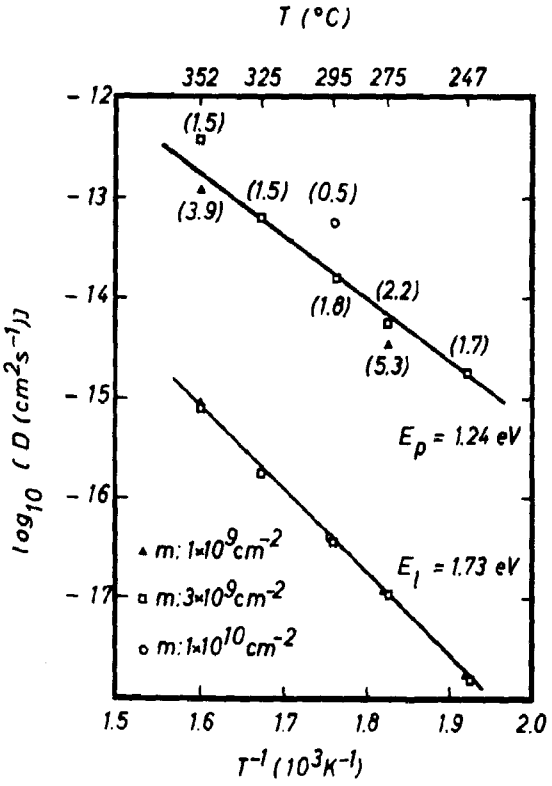

FIG. 2. Logarithm of diffusivities for bulk and pipe diffusion as a function of reciprocal temperature at various dislocation densities m. Numbers at pipe-diffusion data correspond to pipe radii a (in 10^{-6} cm) calculated according to Eq. (1).

than generally accepted and shall be discussed in more detail.

In earlier calculations of pipe radii[1-6] the large values of a may have been due to the inaccuracy of the etching method. If only a fraction of the real dislocation density m had been observed, the pipe radius a would increase considerably, according to Eq. (2)

$$a = \epsilon/(\pi m)^{1/2} .$$

But this is not a possible explanation for the diffusion data in Au. In order to achieve a more generally accepted dislocation radius $a = 1.5\times10^{-8}$ cm, a density $m = 3\times10^{13}$ cm^{-2} has to be assumed. This is a physically unrealistic figure and contrary to investigation of epitaxial Au films,[12] where dislocation densities 10^{10}–10^{11} cm^{-2} have been observed, as well as to the calculations above, where no fit has been obtained for dislocation densities $m > 10^{10}$ cm^{-2}. This leaves $a = 5\times10^{-7}$ cm as the lowest possible radius resulting from Eq. (1) with $m = 10^{10}$ cm^{-2} at $T = 295.4$ °C (see Fig. 2).

Dislocations at high densities tend to form networks, and it is to be discussed, whether solution (1) for isolated dislocations may still be applied. The distance of the branching points will be of the order of the mean distance of dislocations $2A$ if all dislocations form a perfect grid, but it will be larger by at least one order of magnitude in real crystals, if the dislocations are not all lined up along glide planes. This will limit Eq. (1) to a penetration depth $z < 10\times2A$. However, this condition is satisfied as $z = 7\times10^{-5}$ cm in Fig. 1, and $2A = 2(\pi m)^{-1/2} = 2\times10^{-5}$ cm. This conclusion is also supported by the fact that the lines in Fig. 1 are smooth and do not change abruptly. Thus effects due to dislocation networks may be excluded.

Enhanced diffusion along dislocations is generally[11] assumed to occur by a vacancy mechanism. For a constant vacancy concentration in the vicinity of the dislocation the activation enthalpy will be $h_p = h_m + h_b$. The enthalpy of migration in gold is $h_m = 0.89$ eV.[13] The binding enthalpy h_b for a vacancy near a dislocation with a Burgers vector $\vec{b}$ may be calculated from the theory of elasticity

$$h_b = h_b^0 |\vec{b}|/r .$$

For copper $h_b^0 = 0.05$ eV has been calculated[14] leaving $h_p = 0.89 \pm 0.05$ eV at the core $r = |\vec{b}|$. For grain-boundary diffusion in gold an activation enthalpy $h_{gb} = 0.88 \pm 0.02$ eV has been reported recently by Gupta,[15] supporting the validity of the vacancy mechanism.

However, the model of a constant vacancy concentration does not seem to apply for diffusion along dislocations in thin films of gold, as neither the activation enthalpy nor the dislocation radius are predicted correctly. Electron-microscopic studies[12] in gold have indicated that dislocations in thin epitaxial films are dissociated, the distance of the partials being $d \geq 3\times10^{-7}$ cm. This agrees quite well with the calculated dislocation radius $a \geq 5\times10^{-7}$ cm, leading to the mechanism of rapid diffusion along the stacking faults between partial dislocations. This mechanism had earlier been suggested for self-diffusion in Ni[16] and Ni-Co,[17] where similar large pipe radii were obtained. While it thus seems possible to reconcile the large values of the dislocation-pipe radii, the discrepancy between activation enthalpy of pipe diffusion in gold, and the value obtained from a constant-vacancy model prevails. This discrepancy seems to be independent of the analytical model used to extract the enthalpies from the diffusion data and deserves further attention.

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