Is Pipe Diffusion in Metals Vacancy Controlled? A Molecular-Dynamics Study of an Edge Dislocation in Copper

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(Received 9 May 1989)

The mobility of vacancies and interstitials trapped on a dissociated edge dislocation in copper is studied by molecular dynamics. Although fast diffusion is thought to occur exclusively in a pipe surrounding the dislocation core, in the present study a quasi-two-dimensional diffusion is observed for defects not only in the cores but also in the stacking-fault ribbon. Contrary to current assumptions, the activation energy for diffusion is found to be identical for both defects, which may therefore contribute comparably to mass transport along the dislocations.

PACS numbers: 61.70.Bv, 61.70.Ga, 61.70.Yq

One of the most intriguing features of extended defects in materials is the dramatic enhancement of mass transport in their vicinity with respect to the bulk. This is a general rule which holds for surfaces, grain boundaries, and dislocations in metals, for which the experiments lead to liquidlike values[1] of diffusivity, $D \simeq 10^{-5}$ $cm^2 s^{-1}$ near the melting point. Since the diffusion is intimately connected to the atomic structure, it may be used as a probe for structural studies. Indeed, for surfaces and grain boundaries, the existence of premelting effects associated with a local disorder has been invoked to explain the observed high diffusivities; this argument is supported by experimental and molecular-dynamics studies.[2,3]

For dislocations, however, direct experimental or simulation data are not available, or they are more difficult to obtain. The discussion of fast diffusion is mostly based on tracer diffusion experiments carried out on low-angle grain boundaries, and only sparse results have been obtained on isolated dislocations.[4] Current interpretations of these data assume that fast diffusion occurs in the inelastic region of the dislocation core, often assimilated to a cylindrical pipe of radius $r \simeq 5$ Å. The compilation of available data has led to the conclusion that pipe diffusion is due to a vacancy mechanism and that the observed enhancement with respect to bulk diffusion is due to the decrease of the vacancy formation energy in the dislocation core.[5]

Dislocations in metals are often dissociated, and some experiments have been interpreted assuming that the stacking-fault ribbon could contribute to fast diffusion.[6] However, Balluffi and Granato[5] criticized this interpretation by arguing that since nearest-neighbor relationships are conserved in the stacking-fault ribbon, neither a significant decrease of the defect formation energy nor fast diffusion is expected to occur in it.[5] More generally, the experimental data show that the diffusion in dissociated dislocations is slower than in perfect ones.[4]

The present work is devoted to a molecular-dynamics (MD) study of an easy-glide edge dislocation in copper with a special emphasis on pipe diffusion of vacancies and interstitials. Copper is a suitable choice to test the possible contribution of the stacking-fault ribbon to fast diffusion since the low value of the stacking-fault energy results in a large distance between the Schockley partials. Among available models for copper, we chose the resonant model pseudopotential derived by Dagens[7] which satisfactorily reproduces numerous physical properties of the real material such as elastic constants,[7(a)] phonon dispersion,[8] and temperature dependence of the atomic mean-square displacements.[9] Unfortunately a zero value is obtained for the energy γ of the infinite stacking fault when the interactions are summed up to convergence.[10] To bypass this limitation, we chose an empirical compromise[9] consisting of the choice of an appropriate cutoff radius r_c for the potential ($r_c \simeq 2.3a$; a is the lattice parameter) which leads to $\gamma = 73$ ergs/cm^2 (experimentally $\gamma = 55$ ergs/cm^2). The system contains $N = 7776$ dynamical particles, and periodic boundary conditions are applied in the z direction to build up a slab of pseudoinfinite length. A static crystal of $N_s = 4384$ particles, whose thickness is larger than the actual value of r_c, surrounds the system along the remaining two directions. Two Schockley partials are introduced in this perfect system, the dislocation lines being parallel to the z direction and located at a distance d from one another. The atomic displacements and the distance d are calculated using the standard results of the elastic theory of dislocations[11] as well as the previously reported value of the stacking-fault energy $\gamma = 73$ ergs/cm^2. Extra atoms in the overlapping regions of the crystal, resulting from the introduction of the Schockley partials, are eliminated during this stage. The system is then relaxed by a quasidynamic procedure,[12] and the

TABLE I. Calculated jump frequencies for pipe diffusion in copper.

Temperature (K)	Number of jumps	Jump frequency (10^{11} Hz)
	Vacancy	
1197	56	2.2 ± 0.3
1310	64	4.3 ± 0.5
1352	66	5.9 ± 0.7
1423	78	7.2 ± 0.8
	Interstitial	
737	40	5.3 ± 0.8
1035	60	8.1 ± 1.05
1344	102	13.6 ± 1.35

final dissociation distance is compared to the initial one. If they are different, the procedure is reinitialized using the relaxed value of the dissociation distance. This procedure is repeated until initial and final values of d are identical within a $\langle 110 \rangle$ interplanar spacing distance. The resulting configuration is then used as the initial condition for standard MD at constant volume. The equations of motion are integrated by using a time step $\delta t = 2.5 \times 10^{-15}$ s. At each temperature the experimental density values have been used and the potential parameters were modified according to the prescriptions given by Dagens.[9,13] Because of their high formation energies, defects are not spontaneously created near the partials, as is observed in grain boundary or surface MD simulations.[3] Therefore, to investigate pipe diffusion, a vacancy or an interstitial is introduced into the system by removing or adding an atom in the core region of one of the partials.

Trajectories of 3×10^4–10^5 time steps produced a statistically meaningful number of defect jumps (Table I) at temperatures $T > 0.55 T_m^{\exp}$ ($T_m^{\exp} = 1356$ K). Figures 1(a) and 1(b) display the atomic trajectories we obtained for the interstitial during a simulation of 75 ps at 1035 K. They are projected respectively onto a $(1\bar{1}2)$ plane and on the stacking-fault plane. The curve displayed in Fig. 1(c) helps in localizing the partials; it is derived from an analysis of the local deformation[8] around the fault ribbon in terms of Burgers-vector density ρ. It can be seen that the interstitial migrates without marked preference near the dislocation cores as well as in the stacking-fault region. A similar behavior, not shown here, is observed for the vacancy.[14] A more detailed analysis reveals that, as expected, the trajectories of the defects are confined in the region in compression for the vacancy and in the region under tension for the interstitial. The qualitative features of diffusion illustrated by Fig. 1 are in contradiction with the above reported arguments of Balluffi and Granato[5] against the possibility of fast diffusion over the region of the stacking fault. This behavior can be understood by referring to the Burgers-vector distribution associated with the

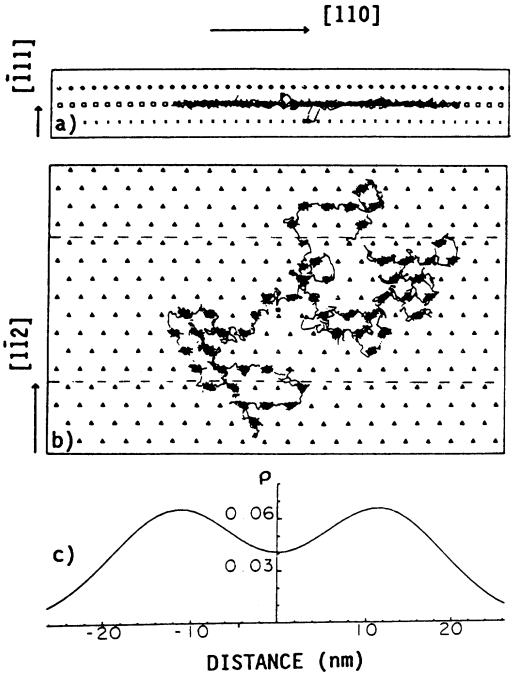

FIG. 1. Trajectories of the atoms displaced by the migration of an interstitial at 1035 K. The symbols (squares, diamonds, crosses, and triangles) correspond to the average positions of the nonjumping atoms. (a) Projection onto a $(1\bar{1}2)$ plane perpendicular to the dislocations. (b) Projection onto the $(\bar{1}11)$ stacking-fault plane. The dashed lines indicate the limits of the MD box along the $[1\bar{1}2]$ direction parallel to the dislocation lines. Beyond these limits, the periodic images are used to disentangle the defect trajectory. In the [110] and $[1\bar{1}2]$ directions only a small part of the MD system is displayed in (a) and (b). (c) Burgers-vector density distribution ρ at the fault ribbon plane; the curve is obtained by superimposing two Gaussian distributions fitted to the MD results. The maxima are identified with the average positions of the Shockley partials.

partials shown in Fig. 1(c). This profile indicates that the partials' cores relax largely by invading the fault ribbon region whose structure is now different from that of an infinite stacking fault. This invalidates the argument used by Balluffi and Granato against the interpretation of experimental data by Wuttig and Birnbaum[6] which suggested that the stacking fault may contribute to pipe diffusion in Ni. Moreover, rather than being a cylinder around each partial, the pipe is now a slab including the cores of the partials and the fault ribbon. Large pipe radii may result from such effects.

By counting the jump events for a vacancy and an interstitial at each temperature, the associated migration energies were found to be equal to $E_m^v = 0.77$ eV and $E_m^i = 0.13$ eV, respectively (Table II). These values are practically identical to those obtained from bulk diffusion data provided by experiments or by computations using the same potential (Table II). It has been ar-

TABLE II. Calculated and experimental data for pipe and bulk diffusion in copper. Experimental values are given in parenthesis. The superscripts p and bulk refer respectively to pipe and bulk diffusion.

	Vacancy		Interstitial
E_m^p (eV)	0.77		0.13
$\tilde{E}_f^p$ (eV)	1.15		1.82
E_D^p (eV)	1.92	(1.53) [c]	1.95
E_m^{bulk} (eV) [a]	0.82 (0.76) [b]		0.11 (0.12) [e]
E_f^{bulk} (eV) [a]	1.42 (1.31) [b]		2.61 (2.2) [f]
E_D^{bulk} (eV) [a]	2.24	(2.19) [d]	2.72
E_D^p/E_D^{bulk}	0.85	(0.8) [c]	0.7

[a]Reference 7(b). [d]Reference 18.
[b]Reference 15. [e]Reference 16.
[c]Reference 5. [f]Reference 17.

gued[19] that the large binding energies expected for interstitials with dislocations may reduce their mobility with respect to the bulk. The comparison of activation energies for interstitial migration in the bulk and along the dislocation does not allow for this assertion. To decide on the relative importance of the contributions to mass transport of both vacancies and interstitials, one needs to evaluate their formation energy E_f. These values have been obtained at $T=0$ K using the quasidynamic energy-minimization technique and the procedure suggested by Lam, Dagens, and Doan [Ref. 7(b)]: The internal energy of the systems with and without the point defect are compared and corrected to account for the change in the virial induced by the lattice relaxation at constant total volume. Several lattice positions have been explored and the values obtained[14] have been used to deduce an effective formation energy using the procedure suggested by Balluffi *et al.*[20] These effective values are reported in Table II. The activation energies E_D^v and E_D^i for pipe diffusion associated with the vacancy and the interstitial are practically identical. Thus if one neglects the possible differences due to the entropy terms, as is currently done in the reference papers, one may conclude that vacancies and interstitials contribute comparably to pipe diffusion. This result contradicts the current opinion according to which pipe diffusion is principally controlled by vacancies. It is also worth noticing that the ratio of activation energies for diffusion in the pipe and in the bulk amounts to $E_D^p/E_D^{\text{bulk}} \simeq 0.7$–$0.85$. This ratio is in agreement with the compilation of experimental data.[5] Moreover, the computed activation energy for pipe diffusion agrees quite well with its estimation based on extrapolated heterodiffusion data in copper (Table II).

In its equilibrium position in the dislocation core, the interstitial is found to be dissociated along a ⟨110⟩ direction, whereas the split direction is parallel to ⟨100⟩ in the bulk. This result seems to be independent of the nature of the potential since it has already been obtained in previous studies based on empirical pair potentials.[21]

The enhanced pipe diffusion with respect to the bulk is mainly due to the important decrease of the formation energy of defects near the dislocation core and in the stacking-fault ribbon. This result supports the suggestion made by Baker, Wuttig, and Birnbaum,[22] who argued that a high vacancy concentration in the stacking-fault ribbon, due to a "Suzuki segregation" effect,[23] contributes to a decrease of the vacancy formation energy. A number of previous static or quasidynamic computations has been devoted to a comparative study of bulk and pipe diffusion. Many of them, however, used empirical potential functions (e.g., Refs. 21 and 24) which are known to be inadequate for metals.[25] Therefore we restrict the present discussion to the work of Fidel'man and Zhuravlev[26] whose calculations on fcc and bcc metals use the Animalu[27] pseudopotential. These authors come to a conclusion similar to the one quoted above: Fast pipe diffusion is mainly due to the defect-formation-energy decrease in the pipe. However, the formation energy for vacancies in the pipe and in the bulk are significantly smaller than those reported here (Table II). In this framework the following remarks are of interest: (i) The Animalu resonant potential for Cu is based on a local form of the transition-metal model potential, whereas nonlocal effects are known to play a major role in noble metals. This is reflected by the large discrepancies (30%–50%) observed between computed and experimental phonon frequencies at the zone-boundary points.[8] The pseudopotential we used in the present study has been derived with special reference to nonlocal effects and therefore displays an excellent agreement with the phonon experimental data.[8] (ii) When using pseudopotentials, the agreement between experimental and computed vacancy formation energies must be carefully considered in general, since such models do not account for the electron density variation near defects with respect to the bulk. The Dagens pseudopotential satisfactorily reproduces the experimental bulk diffusion data.[7(b)] In this framework the present study, in addition to its generic purpose, mimics real copper rather well.

Our study showed that the atomic structure of the partials' cores changes gradually with increasing temperature;[9] however, no significant influence of this disorder has been noted on the migration rates of the defects. Detailed MD results concerning the temperature dependence of the core structure have been obtained and will be published elsewhere.[9]

This work has benefited from the financial support of the stimulation action of the European Community through Contract No. ST2J-0094.

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