Evidence for Vacancy Mechanism in Grain Boundary Diffusion in bcc Iron: A Molecular-Dynamics Study

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The dominance of vacancy migration in grain boundary self-diffusion has been established by molecular-dynamics simulation of a bcc iron $\Sigma = 5$ tilt boundary. The data yielded a reasonable value of the activation energy for migration and showed that the jump processes are highly structure dependent. The use of a temperature-dependent transition-probability matrix to describe the diffusion of the vacancies in the grain boundary is suggested. Formation of one type of boundary interstitial was observed, and the interstitial was found to be immobile during its lifetime.

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There has been considerable speculation[1,2] that the fast "short-circuit" self-diffusion which is commonly observed along grain boundaries (GB's) occurs by the exchange of atoms with vacancies which are present in the GB in thermal equilibrium. However, it is also conceivable that a defect exchange mechanism involving self-interstitials present in thermal equilibrium may be the dominant mechanism. Despite the long-standing interests in grain-boundary diffusion this question has not been settled because it has not been possible to observe directly the details of the various jump processes at the atomic level.

We present evidence which shows for the first time that a vacancy mechanism dominates in GB diffusion at intermediate temperatures. Our quantitative results are based on a computer molecular-dynamics study of a bcc iron $\Sigma = 5$ (36.9°) [001] (310) symmetrical-tilt boundary. By means of the simulation techniques[3-5] we have not only observed explicitly the thermal activation of vacancy migration but also deduced a realistic value of the activation energy for migration. Moreover, besides vacancies, the only other type of point defect observed was the spontaneous formation of Frenkel pairs. The interstitial atom in the pair configuration was found to be localized and annihilated within a few vibration periods.

The present study provides the quantitative information (not available by any other means) required to demonstrate that GB self-diffusion occurring at intermediate temperatures by a vacancy-exchange mechanism is highly structure dependent. The results further suggest that a complete description of the diffusion process can be formulated in terms of a transition-probability matrix which specifies the vacancy jump frequencies between various GB sites.

The model system chosen for study has been investigated recently by the method of molecular statics.[6] The system consisted of a stack of ten layers of atomic planes with their normal along the [001] tilt axis. Each plane contained 40 atomic sites. The equilibrium structure, as shown in Fig. 1(a), is characterized by a free volume in the boundary core corresponding to 82.4% of an atomic volume ($0.34a_0^3$, where a_0 is the lattice parameter) per period in each layer. All atoms were assumed to interact via an empirical central-force pairwise potential with a force cutoff midway between second and third neighbors.[7]

The grain boundary was simulated dynamically by applying standard molecular-dynamics tech-

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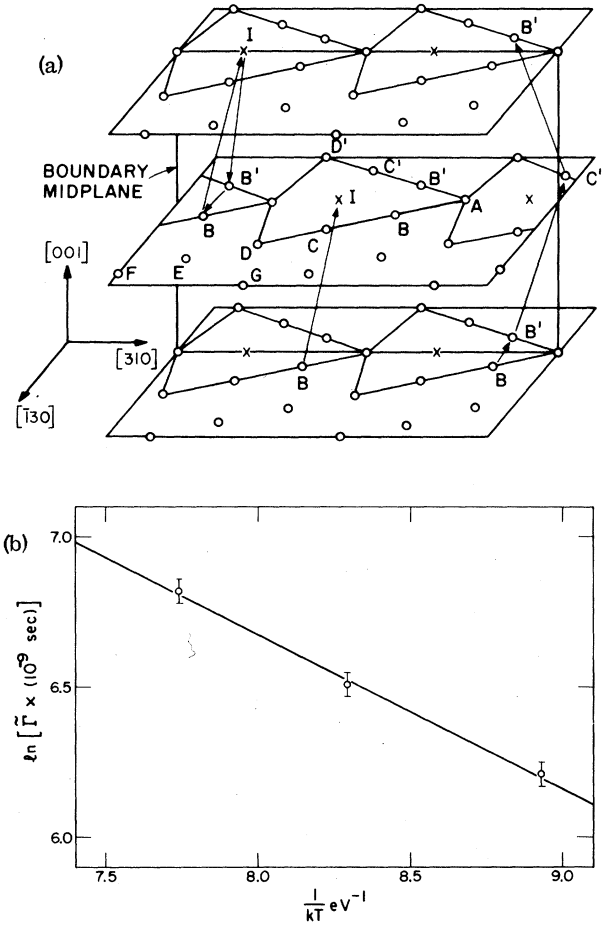

FIG. 1. (a) Schematic drawing of the GB model system. Only three of the ten atomic planes and half of the atoms in each plane (which contains four coincidence site lattice cells) are shown. The sequence on the right indicates a typical vacancy jump path. The arrow in the center shows an atom at B jumping into the interstitial site I. The sequence in the upper left shows the observed interchange of atoms at B and B' via a ring mechanism. The ratio of the scale used in the drawing is $[\bar{1}30]:[310]:[001]=1:1:5$. (b) Temperature dependence of observed effective vacancy jump frequence $\tilde{\Gamma}$ ($\sec^{-1}$) in a $\Sigma=5$ tilt boundary in bcc iron. Error bars denote the standard deviation assuming a Poisson distribution.

niques to the model using a periodic border condition in the [001] and [310] directions and fixed borders along the $[\bar{1}30]$ direction.[8,9] Each simulation run was carried out at constant volume; however, the system volume was adjusted at each temperature to ensure that the system pressure remained essentially atmospheric. A number of isothermal "diffusion runs" were then made in the range 900 to ~2100 K. The GB structure was found to be stable up to ~1650 K on the basis of

TABLE I. Distribution of observed vacancy jumps into the various sites [see Fig. 1(a)] of $\Sigma=5$ tilt boundary in bcc iron at three temperatures. (All the unlabeled sites in the model are considered to be L sites. The ratio of the number of each site in the model is $A:B:C:D:E:F:G:L=1:2:2:2:2:2:2:7$.)

Sites	A	B	C	D	E	F	G	L	All
1300 K	3	126	20	32	7	6	1	0	195
1400 K	5	153	34	46	6	9	5	6	264
1500 K	9	197	49	62	11	18	3	4	353

time-average atomic configurations and the local density distribution in the GB region. The vacancy free volume based on a hard-sphere model was found to be greater than 60% of an atomic volume during most of the time between jumps, and consequently, there was no difficulty in locating the vacancy. In the following only results at temperatures up to 1500 K will be reported.

During a typical "diffusion run" lasting ~2800 lattice vibration periods, the number of vacancy jumps observed amounts to 190 to 360 and depends on the temperature. To define a vacancy jump, each atomic site was assigned a spherical volume Ω equal to the atomic volume at the simulated temperature. An atom undergoing only thermal vibrations therefore would not move out of Ω. A volume Ω was also assigned to an empty site (i.e., a vacancy), and a successful vacancy jump occurred when an atom was found to move into the Ω assigned to a vacancy site; in case of a reverse jump, the jump is counted when the atom remains in the vacant site for at least two vibration periods.

The major characteristics of the vacancy jumps may be summarized by considering the sites labeled in Fig. 1(a) and the data given in Table I. Each run began with a vacancy at site B in the middle of the system. At the lower temperatures the ensuing jumps were confined mostly to the four sites labeled A, B, C, and D. (We note that sites B', C', and D' are equivalent sites because of the boundary symmetry.) However, as the temperature was increased jumps to sites further from the boundary midplane became more significant, indicating that they required more thermal activation. This reflects the transition in the grain-boundary–diffusion kinetics from the so-called "Harrison type C" regime to the "Harrison type B" regime.[10] A typical vacancy jump path is shown on the right-hand side of Fig. 1(a). It is clear from Table I that the vacancy

migration in the GB shows a strong structure dependence, particularly at the lower temperatures where GB and lattice diffusion rates are significantly different.

Another noteworthy feature of our data is that the vacancy trajectories took place predominantly along the tilt axis rather than perpendicular to it. This behavior can be understood qualitatively by considering the direction of maximum free volume. There was also significant correlation between successive jumps in contrast to simple random walk events,[3] but the overall distributions of jump directions relative to the preceding jump showed a strong bias in the forward direction, as well as reverse jumps which occurred mostly between sites B and B'.

The effective activation energy for GB vacancy jumping, $\tilde{E}_B^M$, was determined by plotting the total vacancy jump frequency (summed over all types of jumps) $\tilde{\Gamma}$ in the form of an Arrhenius plot in Fig. 1(b). A reasonably straight line obeying the relation $\tilde{\Gamma} = \tilde{\Gamma}_0 \exp(-\tilde{E}_B^M/kT)$ was obtained with $\tilde{E}_B^M = 0.51$ eV and $\tilde{\Gamma}_0 = 4.85 \times 10^{13}$ sec^{-1}. The preexponential factor $\tilde{\Gamma}_0$ is seen to be of about the expected magnitude, since, if we write it in the form $\tilde{\Gamma}_0 = \tilde{z}\tilde{\nu}_0$, where $\tilde{z}$ is the effective coordination number and $\tilde{\nu}_0$ is the effective "attempt frequency," we obtain $\tilde{\nu}_0 = 6.06 \times 10^{12}$ sec^{-1} with $\tilde{z} = 8$. This frequency is of similar magnitude as the Debye frequency, 7.1×10^{12} sec^{-1}, corresponding to the Debye temperature of 464 K for bcc iron.

In addition to vacancies, the other major type of defect revealed by the simulation was the formation of interstitials at the I locations where there was considerable free volume [cf. Fig. 1(a)]. Atoms in B sites were frequently observed to jump into I sites, the process occurring more frequently as the temperature was increased. This process, illustrated in the center of Fig. 1(a), may be regarded as the spontaneous formation of a vacancy-interstitial pair, i.e., a Frenkel pair. The atomic motion in the pair configuration was observed to occur predominantly by interstitial exchange within a few vibration periods with either the vacancy in the pair or a neighboring vacancy, a process which effectively annihilates the interstitial. A small fraction of the atomic motion occurs by the vacancy diffusing away, thus leaving behind an interstitial trapped at the I site. Therefore, these results indicate that an interstitial in the GB is incapable of promoting self-diffusion.

The dynamical simulations also revealed the interchange of atoms at B and B' illustrated in the sequence on the left-hand side of Fig. 1(a). In this process an atom in site B jumped into site I in the adjacent boundary plane, followed by an atom in site B' jumping into the newly created vacancy in the site B. The sequence was then completed by the interstitial in the site I jumping into the vacancy sitting in site B'. This process also occurred more frequently as the temperature increased; it does not contribute to self-diffusion because the two atoms involved remain trapped in the same pair configuration, thus producing no net matter transport relative to other atoms.

At temperatures close to the melting point, a number of infrequent events, which were not observed at lower temperatures, were detected. Included were the double jump, which had been observed in previous molecular-dynamics studies of vacancy migration in single lattice systems,[4] and jumps over distances greater than the nearest-neighbor separation either across the boundary midplane in the same atomic plane of the stack [e.g., jumps between C and C' in Fig. 1(a)] or through the boundary midplane between two second-neighbor atomic planes of the stack.

Since the different boundary sites for vacancy migration are not equivalent, a set of transition probabilities P_{ij} between sites i and j can be introduced to describe the diffusion of vacancies in the GB. Each GB structure would then be characterized by such a temperature-dependent matrix which is essentially the information needed to calculate the correlation factor effect.[11]

For purposes of illustration, the matrix P obtained from the 1300-K data is shown in Table II. Here, the matrix has been drastically simplified by including sites B', C', and D' in B, C, and D, so that, for example, jumps between B sites on

TABLE II. Elements of transition probability matrix P_{ij} for vacancy jump from site i to site j in a $\Sigma = 5$ tilt boundary in bcc iron deduced from molecular-dynamics simulation data.

	A	B	C	D	E	F	G
A	0	0.005	0.010	0	0	0	0
B	0	0.485	0.052	0.108	0	0	0
C	0.015	0.072	0	0.010	0.005	0	0
D	0	0.082	0.031	0	0.026	0.026	0
E	0	0	0.010	0.021	0	0	0.005
F	0	0	0	0.026	0.005	0	0
G	0	0	0	0	0	0.005	0

second-neighbor layers and between B and B' are included in the element P_{BB}. Also, the elements are normalized so that $\sum_{i,j} P_{ij} = 1$. One should notice that the asymmetry in P_{ij} does not violate microscopic reversibility; rather the inequality $P_{CB} > P_{BC}$ reflects the difference between "downhill" and "uphill" jumps between sites with different potential energies. It is also worthwhile to point out that although the relative magnitudes of the P_{ij} may be estimated approximately from static calculations of vacancy binding energies, molecular-dynamics simulation appears to be the only practical means of determining the absolute values of the P_{ij} and their temperature dependence for different sites.

In conclusion, we believe the present results provide the first detailed, microscopic evidence of the migration of vacancies in GB's. Some of the characteristics observed in our results are believed to be general features of the structure-dependent nature of grain-boundary diffusion. In Ref. 12 these molecular-dynamics data are combined with molecular-statics calculations to demonstrate further the vacancy-exchange mechanism for GB self-diffusion. Further simulations can be expected to yield additional information regarding the characteristics of different GB structures, and the dependence on interatomic potential functions of the diffusion dynamics and structural stability at various temperatures.

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[1]N. L. Peterson, in *Grain Boundary Structure and Kinetics* (American Society for Metals, Metals Park, Ohio, 1980), p. 209.

[2]R. W. Balluffi and J. W. Cahn, Acta Metall. 29, 493 (1981).

[3]C. H. Bennett, in *Diffusion in Solids*, edited by J. J. Burton and A. S. Nowick (Academic, New York, 1975), p. 73.

[4]A. DaFano and G. Jacucci, Phys. Rev. Lett. 39, 950 (1977).

[5]An attempt to calculate the vacancy migration energy in a 6° tilt boundary in α-iron with use of a quasidynamic method of simulation has been made by R. E. Dahl, J. R. Beeler, and R. D. Bourquin, in *Interatomic Potentials and Simulation of Lattice Defects*, edited by P. C. Gehlen, J. R. Beeler, and R. I. Jaffee (Plenum, New York, 1972), p. 673.

[6]A. Brokman, P. D. Bristowe, and R. W. Balluffi, to be published.

[7]R. A. Johnson, Phys. Rev. A 134, 1329 (1964).

[8]*Interatomic Potentials and Simulation of Lattice Defects*, edited by P. C. Gehlen, J. R. Beeler, and R. I. Jaffee (Plenum, New York, 1972).

[9]G. H. Bishop, R. J. Harrison, T. Kwok, and S. Yip, in *Progress in Materials Science*, Chalmers Anniversary Volume, edited by B. Chalmers, H. W. Christian, and T. B. Massalski (Pergamon, Oxford, 1981), p. 49.

[10]L. G. Harrison, Trans. Faraday Soc. 57, 1191 (1961).

[11]J. Bardeen and C. Herring, in *Imperfections in Nearly Perfect Crystals*, edited by W. Shockley *et al.* (Wiley, New York, 1952), p. 261; J. R. Manning, *Diffusion Kinetics for Atoms in Crystals* (Van Nostrand, Princeton, 1968).

[12]R. W. Balluffi, Thomas Kwok, P. D. Bristowe, A. Brokman, P. S. Ho, and Sidney Yip, to be published.

Laser-Induced Melt Dynamics of Si and Silica

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Microscopic observations of blackbody emission from high-power cw-laser-irradiated silicon films on silica reveal: (I) Radiation of 1.06 μm produces a thermal runaway phenomenon in polycrystalline Si that terminates with the melt. (II) The laser-induced melt is inhomogeneous at the melting temperature. Lamellae of solid Si, which has a high emissivity, coexist with the low-emissivity melt. These lamellae transmit near-band-gap radiation, which is blocked by the molten phase, and they appear and disappear dynamically.

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Laser crystallization of semiconductors on insulating substrates might emerge as an important technology in general and specifically for large-area Si electronics. It is important and interesting to understand the underlying mechanism for optically induced crystallization.

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