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DETERMINATION OF VACANCY MECHANISM FOR GRAIN BOUNDARY SELF-DIFFUSION BY COMPUTER SIMULATION

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1. Introduction

It is currently well established that the fast self-diffusion which occurs along grain boundaries (GBs) in metals must occur by a point defect exchange mechanism. For example, it is known that rapid GB diffusion can transport a net current of atoms along GBs during both sintering (1) and diffusional creep (2), and that the two species in a binary substitutional alloy diffuse at different rates in GBs (3). However, it has not been possible to establish firmly whether the defect mechanism involves the exchange of atoms with vacancy or interstitial point defects. It has been suspected that the vacancy exchange mechanism must apply (3,4), but it has been difficult to prove this hypothesis because of a lack of detailed information at the atomistic level.

In this note we report on the results of an effort to establish the GB self-diffusion mechanism in a bcc iron Σ=5 (36.9°) [001] (310) tilt boundary using the combined methods of computer molecular statics and molecular dynamics simulation. The methods are found to be complementary since the statics method efficiently provides information about the static defect energies and configurations, whereas the dynamics method allows one to observe the atomic motions associated with point defect jumps at temperatures equal to or greater than half the melting temperature. An account of the molecular dynamics results has been presented in Ref. 5 which gives evidence for fast vacancy migration in the present GB. In the present note we review the relevant dynamics work briefly and show how the results can be combined with the results of molecular statics calculations to provide quantitative microscopic evidence in favor of the vacancy mechanism.

The simulation model used in both the static and dynamic calculations consisted of 10 layers of [001] atomic planes with their normal along the tilt axis. Each plane contained 40 atom sites, and a portion of the model containing the boundary midplane and two periods of the symmetric GB is shown in Fig. 1. All atoms were assumed to interact via a central force pairwise potential of the empirical type with a force cutoff midway between second and third neighbors (6).

2. Molecular Statics Results

The molecular statics technique employed a modified method of steepest descent to minimize the potential energy of the atomic ensemble (7). All entropic effects arising from lattice vibrations and kinetic energy were therefore ignored so that the simulation effectively proceeded at zero absolute temperature.

The perfect GB structure in the absence of any point defects was first determined by relaxing the initial structure in which all atoms were located on the Σ=5 coincidence site lattice. This resulted in a minimum energy GB structure characterized by a rigid-body translation of one

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crystal with respect to the other along [$\bar{1}$30] causing an expansion of 0.18 a_o (a_o = lattice parameter).

A vacancy was then inserted at a site in the GB by removing the atom occupying that site, placing it on the surface of a reference crystal, and again relaxing the model. Configurations and energies of vacancies introduced at the sites A, B, C, and D (Fig. 1) by this procedure were determined. In each case the vacancy remained quite localized and recognizable as an empty site in the GB in agreement with expectations based on previous work (8,9). The formation energies, E_B^F, of these vacancies are listed in Table I along with their binding energies to the GB, E_B^B, determined from $E_B^B = E_B^F - E_L^F$, where $E_L^F = 1.35$ eV is the calculated formation energy in the lattice. We note that the binding energy can also be calculated by molecular dynamics techniques

TABLE I

Formation Energies, E_B^F, and Binding Energies, E_B^B, of Vacancies and Interstitials in Boundary Sites Shown in Fig. 1.

	Boundary Site	E_B^F (eV)	E_B^B (eV)
Vacancies	A	1.33	-0.02
	B	0.94	-0.41
	C	1.26	-0.09
	D	1.17	-0.18
Interstitials	I	1.06	-3.68
	A	2.55	-2.19
	B	2.55	-2.19
	C	3.30	-1.44
	D	2.32	-2.42

using a damping force. Such a calculation has been carried out at site B for the vacancy, and the result agrees with that calculated by the molecular statics method.

An interstitial was inserted by simply adding an extra atom in the boundary and again relaxing the structure. The largest "hole" in a hard sphere model of the perfect GB is located at the position I in Fig. 1, and an atom was therefore inserted at that point to simulate an interstitial. Considerable atomic relaxation occurred around this interstitial but it remained easily recognizable as an extra atom inserted at I. Interstitials were also introduced at the sites A, B, C, and D in Fig. 1. However, in these cases it was convenient to remove the atom originally at the site and then insert two atoms symmetrically disposed around the empty site. In the subsequent relaxation the two atoms were generally displaced, and the symmetric arrangement was destroyed. These interstitials were therefore somewhat more delocalized but remained as bona fide point defects in the GB structure. The calculated formation and binding energies for these interstitials are also listed in Table 1. (Here, the calculated formation energy in the lattice is $E_L^F = 4.74$ eV for a <110> split interstitial.)

3. Molecular Dynamics Results

The molecular dynamics of the GB model were investigated by adding thermal kinetic energy to the previously described static model. Standard molecular dynamics techniques (10,11) were used to simulate the behavior of the GB point defects as well as the atomic motions in the system. A number of isothermal "diffusion runs" was made in which a single vacancy was introduced in the GB and observed to migrate as a function of time. The results are described in Ref. 5 and are briefly reviewed and discussed further below.

(i) The vacancy migrated in the core of the GB by executing jumps between a variety of

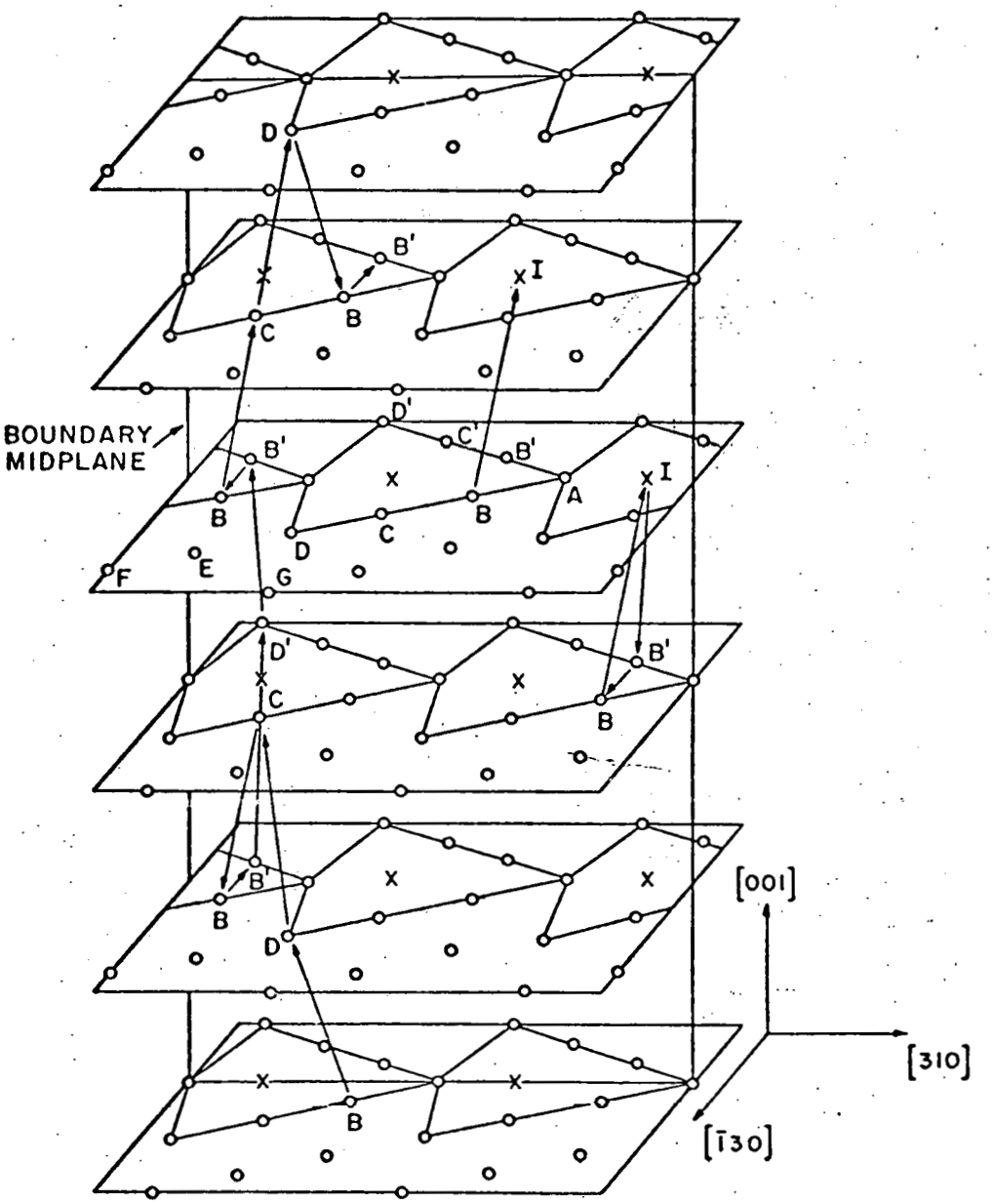

FIG. 1

Six of the 10 atomic planes used to model the bcc iron [001] (310) tilt boundary ($\Sigma = 5$, $\theta = 36.87°$) for computer simulation. Only half of the atoms in each plane (which contains four coincidence site lattice cells) are shown. A vacancy created at site B preferentially jumps among the boundary sites A, B, C, D rather than into the sites E, F, G which are further away from the boundary midplane. The sequence on the left indicates a typical vacancy jump path. The arrow in the center shows an atom at B jumping into the interstitial site I, thus creating a boundary interstitial and a boundary vacancy. The sequence on the right shows the observed interchange of atoms at B and B' via a ring mechanism involving the interstitial site at I. The ratio of the scale used in the drawing is $[\bar{1}30]:[310]:[001] = 1:1:5$.

TABLE II

Number of Vacancy Jumps into Various Boundary Sites (Fig. 1) during Vacancy Diffusion Run Involving 195 Jumps at 1300 K.

Site	A	B	C	D	E	F	G
Number of Jumps	3	126	20	32	7	6	1

sites. Essentially all jumps occurred between sites of the types labeled A, B, C, and D in Fig.1. (Note that the A', B', C', and D' sites are equivalent sites because of the boundary symmetry.) The jumping was therefore confined almost entirely to the core of the GB. A typical trajectory is shown on the left of Fig. 1. The number of times a vacancy jumped into a given type of site during a run at 1300 K involving 195 jumps is shown in Table II. Comparison of Table II with Table I shows a clear correlation between the vacancy binding energy at different sites and the frequency with which a site received jumps; i.e., the larger the binding energy the more frequently it received jumps. The sites E, F, and G are at distances from the GB midplane where the binding energy was relatively small, and they therefore received very few jumps.

(ii) The vacancy migration took place predominantly along the tilt axis rather than perpendicular to it (Fig. 1).

(iii) The effective vacancy jump frequency (due to all jumps) obeyed the Arrhenius expression:

$$\tilde{\Gamma} = \tilde{\Gamma}_o \exp(-\tilde{E}_B^M/kT) \quad , \tag{1}$$

with $\tilde{\Gamma}_o = 4.85 \times 10^{13}$ sec^{-1}, and $\tilde{E}_B^M = 0.51$ eV. Here, $\tilde{E}_B^M$ is the effective migration energy, and the pre-exponential factor can be written as $\tilde{\Gamma}_o = \tilde{z}\tilde{\nu}_o$, where $\tilde{z}$ = effective coordination number, and $\tilde{\nu}_o$ is an effective "attempt frequency". If $\tilde{z} = 8$, $\tilde{\nu}_o = 6.06 \times 10^{12}$ sec^{-1}, which is of the same magnitude as the Debye frequency (i.e., 7.1×10^{12} sec^{-1}) as might be expected (12) if effects due to the entropy of migration are not large.

(iv) Atoms on B sites occasionally jumped into interstitial I sites by a process illustrated in the center of Fig. 1, which is essentially the thermally activated formation of a Frenkel pair. Inspection of Table I shows that this type of Frenkel pair must have a considerably lower formation energy than any other possible Frenkel pair, and this is evidently the reason for its occurrence. The vacancy formed in this way often diffused away leaving the interstitial behind at I. Furthermore, the interstitial at I remained completely immobile and could only be eliminated by mutual annihilation with a neighboring vacancy. The immobility of the interstitial at I is readily understood on the basis of the results in Table I where it is seen that the formation energies of the interstitial at the other interstitial sites are larger by at least 1.26 eV. The activation energy for the interstitial to migrate must therefore be larger than 1.26 eV, and this process was therefore not observed. These results indicate therefore that any interstitial in the GB will be strongly trapped at I sites and will therefore be rendered immobile and incapable of promoting self-diffusion.

(v) The interchange of atoms at B and B' by the process illustrated on the right side of Fig. 1 was observed occasionally. 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 process was then completed by the interstitial in the site I jumping into the vacancy sitting in site B'. This sequence was found to occur more frequently as the temperature increased. The process does not contribute to diffusion because the two atoms involved remain trapped in the same pair configuration, thus producing no net matter transport relative to the other atoms.

4. Discussion

The previous results, taken all together, provide strong evidence for a vacancy exchange mechanism for self-diffusion in the present GB. We now show that we can derive an approximate

expression for the GB self-diffusion coefficient on the basis of a vacancy exchange model using the vacancy parameters that we have obtained. Furthermore, the expression predicts diffusivities which are in reasonable agreement with experimentally determined values. For a mechanism involving the exchange of atoms with vacancies in the GB core we may write (12) the self-diffusivity as:

$$D_B \simeq f \cdot g \cdot \tilde{\alpha}^2 \cdot \tilde{N}_v \cdot \tilde{\Gamma} \quad , \tag{2}$$

where f = correlation factor, g = geometrical factor, $\tilde{\alpha}^2$ = effective squared jump distance, and $\tilde{N}_v$ = effective equilibrium vacancy concentration. Therefore, by writing $\tilde{N}_v = \tilde{A} \exp(-\tilde{E}_B^F/kT)$, where $\tilde{A}$ = effective pre-exponential factor, and $\tilde{E}_B^F$ = effective formation energy, we have:

$$D_B \simeq \tilde{D}_{B_o} \exp(-\tilde{Q}_B/kT) \quad , \tag{3}$$

where

$$\tilde{Q}_B = \tilde{E}_B^F + \tilde{E}_B^M \quad , \tag{4}$$

and

$$\tilde{D}_{B_o} = f \cdot g \cdot \tilde{\alpha}^2 \cdot \tilde{A} \cdot \tilde{\Gamma}_o \quad . \tag{5}$$

Consider first the quantity $\tilde{Q}_B$. Since the equilibrium vacancy population in the various GB sites in the core should obey a Boltzmann distribution we can take the concentration at each site as proportional to $\exp(-\tilde{E}_B^F/kT)$. If we assume that the constant of proportionality is the same for all sites we can estimate the total effective vacancy concentration in the core (to within the constant of proportionality) by using the data in Table I. The effective vacancy formation energy can then be found from the temperature dependence of the total concentration. The result of this procedure is $\tilde{E}_B^F \simeq 1.0$ eV. Since the effective migration energy [see Eq. (1)] is $\tilde{E}_B^M \simeq 0.51$ eV, we obtain $\tilde{Q}_B \simeq 1.51$ eV.

Consider next the magnitude of the effective pre-exponential factor, $\tilde{D}_{B_o}$. The geometrical factor should be of order $g \simeq 1/3$. Since there is a variety of vacancy jumps which occur in three dimensions in the boundary (i.e., it does not consist of a single row of jump sites), we expect the correlation factor f to be of order 0.5 (4). Also, reasonable values of $\tilde{A}$ and $\tilde{\alpha}^2$ are $\tilde{A} = \exp(2)$ (see Ref. 12), and $\tilde{\alpha}^2 = [0.85\, a_o]^2$. Using these values and $\tilde{\Gamma}_o = 4.85 \times 10^{13}$ sec^{-1}, we find $\tilde{D}_{B_o} \simeq 3.66 \times 10^{-2}$ cm^2 sec^{-1}, and obtain finally:

$$D_B \simeq 3.66 \times 10^{-2} \exp(-1.51/kT) \quad . \tag{6}$$

The value of $\tilde{Q}_B = 1.51$ eV is significantly lower than the measured value of 2.5 eV for lattice self-diffusion in bcc iron (13), and the pre-exponential factor, 3.66×10^{-2} cm^2 sec^{-1}, is in the range generally expected for this quantity. The calculated result therefore predicts rapid GB self-diffusion as required. Our conclusion about the relative magnitude of $\tilde{Q}_B$ agrees with one reached earlier by Brokman (14) on a more qualitative basis.

Further examination shows that Eq. (6) predicts values of D_B which are consistent with those reported in the literature. Martin and Perraillon (15) have recently plotted all available GB self-diffusion data on an Arrhenius plot using a reciprocal temperature scale normalized by the factor $1/T_m$ where T_m = melting temperature [see Fig. 18(b) of Ref. 15]. The D_B values given by Eq. (6) fall within the range of values appearing on the plot but they are generally lower than the average values by about an order of magnitude. In view of all the uncertainties which are involved in the calculations we may therefore regard the values of D_B predicted by Eq. (6) as quite satisfactory. In this respect it is interesting to note that the present GB is a

relatively special boundary with a high coincidence site density misorientation and a short wave length periodicity (16). There is some evidence (4) that the GB self-diffusivity along such boundaries is generally slower than along more general boundaries. Since the data plotted in Fig. 18(b) of Ref. 16 are representative of general boundaries, we may speculate that at least part of the above difference may be explained on this basis. We also note that the molecular dynamics simulation showed that the vacancy GB migration was more rapid along the tilt axis than perpendicular to it (5). According to the vacancy exchange mechanism the GB self-diffusion rates should exhibit the same behavior, and this is confirmed experimentally (4).

In contrast to the behavior of vacancies in the GB core, interstitials appear to be relatively immobile and would therefore not be expected to contribute significantly to GB self-diffusion rates. The dynamics simulation (5) already demonstrated the immobility of the interstitial at the site I (Fig. 1). Also, the results in Table I indicate that $\tilde{E}_B^M \simeq 1.26$ eV and $\tilde{E}_B^F \simeq 1.06$, and, therefore, $\tilde{Q}_B \simeq 2.32$ eV. This result suggests that GB self-diffusion by an interstitial mechanism is probably slower than even lattice self-diffusion.

Finally, we mention that it would be interesting at this point to carry out further calculations of the present type for boundaries of different kinds. As has already been mentioned, the present $\Sigma=5$ tilt boundary is a rather special boundary in which the vacancies remain quite recognizable as empty sites. We have already shown (8,9) that in other GBs the relaxation around vacancies may be greater causing them to dissociate or "split". The GB migration of such relaxed vacancies may be even easier than that of the present vacancies leading to even faster relative GB self-diffusion rates. Further calculations investigating this possibility are planned.

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