Molecular-Dynamics Study of Self-Interstitial Diffusion in bcc-Iron

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Self-interstitial diffusion in α-iron is investigated using an embedded-atom-method potential and molecular-dynamics simulations. Curved Arrhenius plot is obtained for the temperature dependence of diffusion coefficients, which is well explained by the superposition of two transition processes among the two allotropic states of self-interstitial defects, the reformation of (110) dumbbell into another (110) configuration and one-dimensional solitonic propagation of a crowdion on (111) axis. [doi:10.2320/matertrans.47.1906]

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1. Introduction

It will be of much interest from both engineering and physical viewpoints, to know what kind of defects play major roles in phenomena related to radiation damage in materials. In particular, radiation-induced interstitial atoms, which have been reported to move very fast, 1-4 will greatly affect the mechanical properties of materials by changing the growth and annihilation rates of radiation-induced defect clusters. Unfortunately only a few indirect methods such as measuring stress and magnetic relaxation as well as monitoring changes in residual resistivity and hardness have been available to estimate the behavior of defects that play roles at annealing stages after irradiation, and it is impossible to directly observe such small defects as self-interstitial atoms (SIAs) and vacancies in irradiated materials. Most promising methods overcoming this difficulty are theoretical calculations and atomistic simulations using proper interatomic potentials. Using molecular-dynamics simulations, the present work aims at both measuring the diffusion coefficient of SIA in α-Fe and elucidating its essential mechanism.

2. Modeling and Calculational Procedures

It has been known that in BCC metals two types of split interstitial atoms so-called (110) dumbbell and (111) dumbbell (or crowdion) have stable configuration compared to being a single interstitial atom located at an octahedral or tetrahedral lattice site. Most calculations 3-8 give higher heat of formation to the (111) dumbbell than to the (110) dumbbell at ground state, and naturally we consider that the (111) dumbbell is at an excited state from the (110) dumbbell (see Fig. 1). An experimental result 9 on the magnetic anisotropy of point defects in α-Fe at 70 K also supports this. We applied an embedded-atom-method (EAM) interatomic potential proposed by Haftel et al. 10 for the construction of non-magnetic α-Fe crystals. The potential reproduces many crystal properties such as lattice constant, cohesive energy, elastic constants and vacancy formation energy of the real iron, and has been ascertainment to give higher formation energy to the (111) dumbbell configuration by 0.218 eV 11 than that of the (110) dumbbell. α-Fe crystals with three dimensional periodic boundaries were constructed by the EAM potential. With use of both the velocity and volume rescaling methods 12,13 pressure and deviations from aimed annealing temperature (T_a) of the system were controlled to be less than 10^3 Pa and 0.5% of T_a throughout the simulation runs. The time step (Δt) for solving the Newton’s equation of motion 14 was set to be 1% of the period (τ = 0.974 × 10^-13 s) for the lattice vibration of α-Fe crystal.

3. Results and Discussion

We suppose for simplicity that the overall diffusion coefficient is simply expressed as,
\[
D(T) = p_{(110)}(T)D_{(110)}(T) + p_{(111)}(T)D_{(111)}(T),
\]
\[
p_{(110)} + p_{(111)} = 1,
\]
where p_{(110)}(T) is the probability that an interstitial dumbbell is at (110) configuration, and vice versa for p_{(111)}(T). Since the elemental processes for the diffusion of SIAs are thought to be caused by transitions between the (110) and the (111) dumbbell configurations, there are four candidate transitions, a) (110) → (110), b) (110) → (111), c) (111) → (110), and d) (111) → (111), responsible to the overall diffusion of the present system. Among the four candidate transitions, the energy required for the transition from (110) to (111) is incorporated into the function p_{(110)}(T) and the energy required for the reverse transition is also incorporated into the
function \( p_{111}(T) \). Then transitions between same types of dumbbell configurations, that means only a simple sequential reproduction of a specific dumbbell configuration, should be taken into consideration in both the terms \( D_{111}(T) \) and \( D_{110}(T) \). Migration paths for atoms during the transition between two (110) configurations are shown in Fig. 2(a), and the activation energy \( Q_{110} \) required for this reconstruction is calculated to be 0.2205 eV (Fig. 2(b)). The transition between two (111) configurations means that the (111) dumbbell structure simply propagates on a same (111) atom row, and the energy \( Q_{111} \) required for this propagation is calculated to be 0.006 eV, which value is obtained as follows.

A (111) dumbbell is initially introduced into a crystal sized \( 18 \times 22 \times 26 \) in units of lattice parameter, and then after sufficiently long equilibration time of \( 3 \times 10^4 \Delta t \) at \( 10^{-3} \) K one of dumbbell atoms is knocked-on at a velocity of \( v_h \) with a kinetic energy of \( E_k = m v_h^2 / 2 \), \( m \) is the mass of an iron atom) toward a direction of the dumbbell axis. In case when \( E_k \) is low enough, only small oscillation of the atoms is observed, whereas, in case when \( E_k \) exceeds a critical value \( E_h \) the (111) dumbbell is observed to change slightly into a type of crowdion and then steadily propagate on the (111) atom row. In Fig. 3 the initial propagation velocity \( v_0 \), defined as the tangent of the propagation distance versus elapsed time immediately after the knock-on, is plotted against the knock-on velocity \( v_h \). The critical values for the occurrence of the steady propagation are \( v_h^c = 7.5 \times 10^3 \) cm/s and \( E_h^c = 6.0 \times 10^{-3} \) eV, which value is regarded as the activation energy \( Q_{111} \) for the \( (111) \to (111) \) transition. It is remarkable that the value of \( Q_{111} \) is extremely low compared to that of \( Q_{110} \) and other relevant energies such as vacancy formation energy and cohesive energy of \( \alpha \)-Fe. This result suggests that so far as the propagation energy on the (111) atom row is higher than a critical value the energy is localized to only a small region around the (110) dumbbell or crowdion, indicating that the crowdion in \( \alpha \)-iron behaves as a soliton, which is defined as a localized wave that propagates along one space direction only, with undeformed shape.\(^{(15)}\)

Diffusion coefficients of an SIA in \( \alpha \)-Fe crystals were obtained as follows. Crystals with an initially introduced SIA, sized \( 22^3 \) (21296 atoms therein) in units of lattice parameter, were annealed for about 10 ns at fixed temperatures from 250 K to 1300 K. The interatomic potential used in the present calculation was developed to reproduce only the properties of non-magnetic bcc iron, and this relatively wide temperature range, which exceeds that for real iron crystal with bcc structure, is needed to make precise fitting of observed diffusion coefficients to eq. (1). The trajectories of the SIA positions were recorded and time evolution of the mean square displacements for all atoms in the crystals were calculated. As an example one of the trajectories of the SIA position is shown in Fig. 4, where the position is projected onto a (100) plane. Detailed investigation into the trajectory revealed that every trajectory is, despite of annealing temperatures, composed of two characteristic parts, long ranged straight migrations along (111) direction and occasional stops where the SIA having (110) configuration changed its migration direction. The x-component of the trajectory at 300 K is shown in Fig. 5, where migration at (111) dumbbell is observed to contribute greatly to the overall diffusion of SIA at low temperatures.

The Arrhenius plotting of self-diffusion coefficients

![Fig. 3 Initial propagation velocity \( v_0 \) of a crowdion versus knocked-on velocity \( v_h \).](image-url)
obtained from the time derivatives of the mean square displacements gives not a linear but a curved line with upward convexity (filled circles in Fig. 6). As has been mentioned, this convexity is clearly explained by assuming that the diffusion of SIA’s in α/Fe is considered to be superposition of two coexisting mechanisms, transitions among the two allotropic defect’s states of SIA. Actual values for the probability function in eq. (1) has been obtained for the present system and is given in a form of the Fermi-Dirac type distribution function,

\[
p_{(111)} = \frac{1}{1 + \exp(\Delta G/k_B T)},
\]

where transition energy \( \Delta G \) is given as a function of annealing temperature,

\[
\Delta G = a_0 + a_1 T + a_2 T^2 + a_3 T^3.
\]

Applying the above probability functions and calculated values for \( Q \)’s, the simulated values of overall diffusion coefficients obtained by the present molecular-dynamics simulations (shown as the filled circles in Fig. 6) are fitted to eq. (1). Result is shown as the solid line in Fig. 6 together with analytic contributions from the \( (111) \) to \( (111) \) and \( (110) \) to \( (011) \) transitions.

The present result ascertains that both the energy barriers for the reformation of \( (110) \) dumbbell configuration into another \( (110) \) one and one-dimensional solitonic propagation of \( (111) \) crowdion are responsible to the overall diffusion of SIA in α-Fe. Although the interatomic potential used in the present simulations cannot reproduce the magnetic structures of iron, it will be of interest whether the magnetic transition can affect the mechanism of self-interstitial diffusion in α-Fe.
4. Conclusion

(1) Diffusion mechanism of self-interstitial atoms (SIA) in α-Fe is investigated using molecular-dynamics simulations. An EAM potential is applied for the construction of iron crystals.

(2) Both the transition energies for reconstructions from (110) to (101) and (111) to (111) dumbbell configurations are obtained by molecular-static calculations.

(3) Curved Arrhenius plot for the temperature dependence of self-interstitial diffusion coefficients obtained by the molecular-dynamics simulations are well expressed by superposition of the above two transition processes. It is ascertained that the transition accompanied by the reformation of (111) dumbbell configuration plays an essential role in long ranged self-interstitial diffusion, which is attributed to the solitonic nature of (111) crowdion as an allotropic configuration of the (111) dumbbell.

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REFERENCES