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Interaction of helium atoms with edge dislocations in α-Fe

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Abstract

Formation energies, binding energies, and migration energies of interstitial He atoms in and near the core of an a/2⟨1 1 1⟩{1 1 0} edge dislocation in α-Fe are determined in atomistic simulations using conjugate gradient relaxation and the Dimer method for determining saddle point energies. Results are compared as a function of the proximity of the He to the dislocation core and the excess interstitial volume in regions around the dislocation. Interstitial He atoms have negative binding energy on the compression side of the dislocation and strong positive binding energy on the tension side. Even at low temperatures, interstitial He atoms in the vicinity of the dislocation easily migrate to the dislocation core, where they form crowdion interstitials oriented along the close-packed slip direction, with binding energies in excess of 2 eV. Crowdion interstitial He atoms diffuse along the dislocation core, transverse to the crowdion direction, with a migration energy of 0.4–0.5 eV.

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1. Introduction

The production of helium (He) by transmutations resulting from bombardment by energetic neutrons is inescapable in fusion reactor materials because a significant fraction of fusion neutrons have energies well above the threshold for the (n, α) reactions that create He in most materials. The deleterious effects of radiation-induced He impurities on mechanical properties of metals and alloys are well known, for example the role of He in void swelling and high temperature embrittlement [1–4]. An important first step in mitigating the undesirable effects of He in designing fusion reactor materials is to understand quantitatively the fate of He atoms with respect to the microstructural features with which they can interact. Thus, we are using molecular statics, molecular dynamics and the dimer method of potential surface mapping [5] to study the fate of He atoms in the vicinity of dislocations in α-Fe, which is taken to be a first-order model for the ferritic steels that are promising materials for fusion reactors.

The classic atomistic studies of static He atoms in α-Fe by Wilson et al. [6–8] were performed 2–3 decades ago. More recently, molecular dynamics simulations and transition state determinations employing improved Fe–Fe interatomic potentials have been used to determine migration energies and mechanisms of He transport and interaction with lattice defects in α-Fe [9,10]. Using molecular

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dynamics Morishita et al. [9] determined that a single interstitial He atom in Fe has a migration energy of 0.08 eV, which was corroborated in the present work using the dimer method and the same interatomic potentials. These calculations indicate that an interstitial He atom easily migrates through a perfect α-Fe lattice at temperatures below 100 K. Also, atomistic calculations have been used to show that interstitial He is strongly trapped in a single vacancy in α-Fe as a substitutional atom with a binding energy of about 2.0 eV [10]. Furthermore, multiple He atoms can be strongly bound into vacancy clusters, which increases the lifetime of the vacancy clusters depending on the He-vacancy ratio [9]. Thus, under irradiation one expects strong interactions between He atoms and the vacancy component of displacement damage. Recently, we have begun using atomic-scale computer simulations to investigate quantitatively the detailed dynamics of He interactions with extended defects, such as dislocations and grain boundaries [11,12]. Atomistic simulations were used to explore the effect of grain boundary structure on the binding energy of He to four different symmetric tilt boundaries in α-Fe [11]. Both substitutional and interstitial He atoms are bound to all four boundaries, with binding energy that is related to the excess volume in the boundary. Long term molecular dynamics at elevated temperatures have been used to study the migration of interstitial He atoms within these grain boundaries [12]. The activation energies and diffusion mechanisms of interstitial He are strongly correlated to the binding properties of He atoms. In the present paper we report the results obtained from atomistic modeling of substitutional and interstitial He in and around core of the a/2[1 1 1] {1 1 0} edge dislocation in α-Fe. Such studies produce vital quantitative information for larger scale modeling of the microstructure evolution of materials under irradiation.

We report here results of calculating the formation energies of He atoms in interstitial positions near the dislocation, which are used to map the locations of the most stable configurations of the He atom-dislocation interaction. In addition, molecular dynamics simulations at 100 K have been performed to study the migration of interstitial He atoms within about 1 nm from the dislocation core. Also, the dimer method for finding transition state energies was used to determine the migration energies and migration mechanisms of He atoms trapped within the dislocation core. The correlation of this information with the spatial distribution of excess volume around the dislocation is demonstrated.

2. Procedure

The computational model consists of a cylindrical cell of Fe atoms, periodic along the cylinder axis, with a region of fixed boundary atoms surrounding a cylinder of moveable atoms 10 nm in diameter. The body-centered cubic structure is oriented such that the cylinder axis lies along the [−1 −1 2] direction as shown in Fig. 1. An a/2⟨1 1 1⟩{1 1 0} edge dislocation was created along the axis of the cell by displacing all the atoms (fixed and moveable) according to the anisotropic elastic displacement field of the dislocation, then relaxing the moveable atoms to allow the dislocation core field to develop. Then the He atoms or other defect complexes were placed within the cell and an additional relaxation was performed.

2.1. Interatomic potentials

The interatomic potentials used for all the simulations were the set due to Ackland et al. [13], Wilson and Johnson [6], and Beck [14] for the Fe–Fe, Fe–He and He–He interactions, respectively. This set of potentials has been used in a number of recent stud-

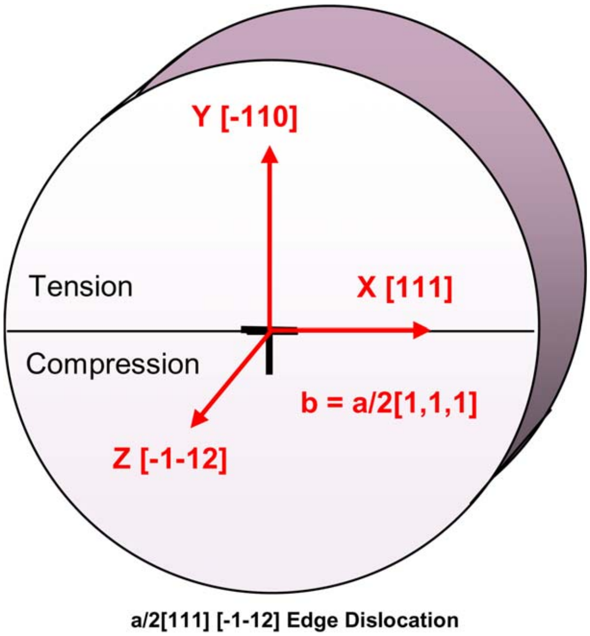

Fig. 1. Cylindrical cell for an a/2[1 1 1] [−1 −1 2] edge dislocation in α-Fe.

ies [9–12], and their implementation is described in detail elsewhere [10,11]. The Ackland potential [13] for Fe is based on the Finnis–Sinclair formalism, having a cut-off radius of 0.373 nm between the second and third nearest neighbors. The lattice parameter is 0.28665 nm, and the cohesive energy for bcc Fe is −4.42 eV/atom. The Wilson and Johnson Fe–He potential [6] was fit to ab initio calculations, and it has a cut-off distance of 0.38 nm. The He–He potential developed by Beck [14] was refit to decrease the cut-off distance to 0.54857 nm for increased computational efficiency. Using these potentials the following formation energies of defects in Fe have been calculated to be: octahedral interstitial He atom 5.25 eV, substitutional He atom 3.25 eV, a vacancy 1.70 eV, and a self-interstitial 4.88 eV. The tetrahedral interstitial He atom has a formation energy about 0.2 eV greater than the more stable octahedral configuration.

Very recently, density functional theory calculations of some properties of He atoms in Fe [15] have produced somewhat different results, due evidently to the tendency of He to quench the magnetic moment of Fe at small separations. These interactions are not accounted for in the pair potentials used in the present calculations. One result of this is that the density functional calculations predict that the tetrahedral He interstitial configuration is more stable, having a formation energy about 0.2 eV *less* than the octahedral He position. This qualitative difference in stability is due to the smaller interatomic distances in the tetrahedral configuration and the short-range effects on magnetic moments, However, for configurations such as He in dislocations and grain boundaries, where some atomic separations are larger and He atoms are trapped in regions containing significant excess volume, there may be much less difference between the results using pair potentials and the density functional calculations (at least qualitatively). Another consideration is that, using pair potentials, we find that the most stable configuration for the interstitial He atom within dislocations and grain boundaries is the crowdion. Because of the small separation of He and Fe atoms along the close-packed direction in crowdions, He crowdions might be found to be even more stable when using density functional theory calculations. Unfortunately, the density functional calculations do not lend themselves easily to investigating such extensive, nonsymmetrical defect configurations as dislocations and grain boundaries.

Binding energy calculations were performed for He atoms placed at substitutional and interstitial positions in the dislocation-distorted lattice on both the tension and compression sides of the dislocation slip plane. Conjugate gradient relaxations were performed to determine the relaxed configurations of the He and surrounding Fe atoms, as well as the energy of the relaxed configuration. The binding energy of the He atom to the dislocation is defined as the difference of the formation energy of a He atom in a perfect Fe lattice and the formation energy of the He atom in the 'dislocated' lattice.

Molecular dynamics (MD) simulations were also performed using the same computational cell, where all the atoms were given kinetic energy and equilibrated at a lattice temperature of 100 K. Simulations were run in the 100 K lattice for individual interstitial He atoms starting from several different positions about the dislocation for simulated times as long as 8.4 ps.

Atomic volumes at atom sites at various distances from the dislocation were determined by the Voronoi volume method [16]. The Voronoi volume about an atom is defined as the volume that contains all points closer to the atom than to any other atom. It can be obtained by determining the volume of the polyhedron formed by the planes that are perpendicular bisectors of the lines connecting the central atom to all other atoms (typically 2–3 neighbor shells). Also the volumes associated with interstitial sites in the vicinity of the dislocation were determined using a variation of the Voronoi technique, where the volume is centered at the center of an interstitial site. The centers of interstitial sites were determined from the positions of surrounding atoms, then the interstitial volume for that position was determined using the Voronoi construction. To determine excess volumes, the atomic and interstitial volumes in the dislocated crystal were compared to the atomic and interstitial volumes, respectively, in the perfect crystal.

The dimer method [5] was used to determine saddle point energies for possible transitions of interstitial He atoms to other locations, starting from initial positions near the dislocation. The dimer results give the migration energies and saddle point atom configurations for He interstitials as they migrate from one equilibrium position to another. In a single run the dimer method attempts multiple trials, so it can find saddle points for more than one transition from a given starting configuration, not just the transition of lowest energy. Thus, it is useful for locating unexpected and competing transitions, which can be especially important in exploring a complicated potential energy landscape such as near a dislocation or grain boundary.

3. Results

3.1. Substitutional He

The binding energy of a substitutional He atom to the dislocation was determined as a function of the distance of the He atom from the slip plane along a line running through the center of the dislocation from the compression to the tension side (along [−1 1 0] in Fig. 1). In Fig. 2 the binding energies and excess atomic volumes in the same positions are plotted as a function of their distance from the slip plane. As expected, the binding energy is negative on the compression side of the dislocation (negative distance from the glide plane) and positive on the tension side. There is a strong correlation between the excess atomic volume at the substitutional site and the binding energy of the He atom. The maximum binding energy is about 0.5 eV at the first atom plane of the tension side.

3.2. Interstitial He

In these simulations, using the interatomic potentials described above, a He atom in an octahedral interstitial position is somewhat more stable than in the tetrahedral interstitial position, both in the perfect Fe lattice (formation energies differ by 0.17 eV) and in the model containing the edge dislocation, except near the dislocation. Within about 2 Burgers vectors (about 0.5 nm) of the dislocation core, interstitial He atoms initially placed in octahedral or tetrahedral locations spontaneously relax into crowdion interstitial sites. The He atoms take positions in close-packed atom rows along the direction of the Burgers vector, [1 1 1], also resulting in significant displacements of their neighboring Fe atoms within the close-packed row; see Fig. 3. The binding energies of interstitial He atoms to the dislocation are shown in Fig. 4(b), plotted as a function of their initial unrelaxed positions as shown in Fig. 4(a). He atoms initially within the dislocation core region relax to crowdion interstitial positions and have binding energies in excess of about 1–2 eV, depending on their location, with a maximum binding energy of 2.3 eV for (crowdion) interstitial He atoms in the core of the dislocation. He atoms placed farther away from the dislocation core on the tension side relax to positions near their original octahedral interstitial sites, and they have signifi-

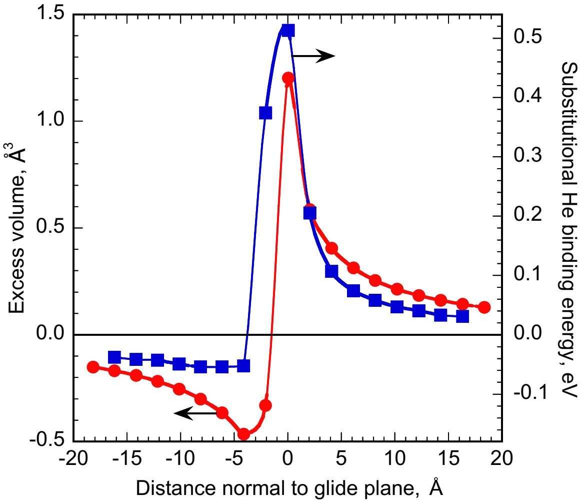

Fig. 2. Binding energies (right axis) of substitutional He atoms to the a/2[1 1 1] [−1 −1 2] edge dislocation in Fe as a function of their distance from the glide plane along a line through the center of the dislocation normal to the glide plane. Excess atomic volumes (left axis) along the same line through the dislocation are plotted for comparison.

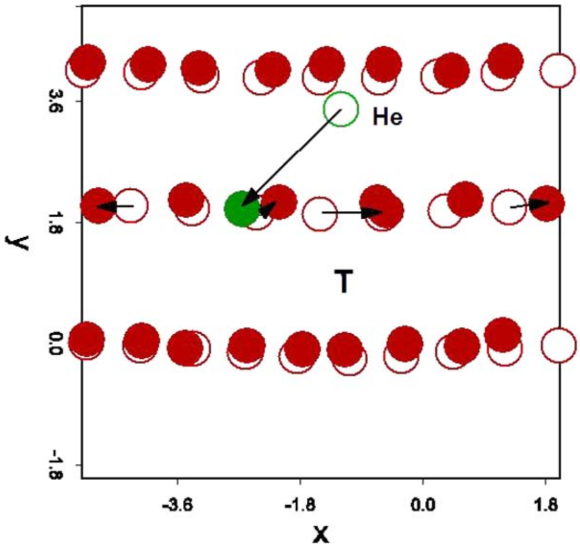

Fig. 3. The relaxation of an interstitial He atom into the crowdion interstitial configuration near the dislocation core. Open circles are the initial atom positions, and filled circles are the final atom positions. Arrows between open and filled circles connect the initial and final positions for atoms undergoing significant relaxation displacements. Some atoms along the crowdion that appear to be near the He atom but have no significant displacement are in different atom planes above or below the plane of the crowdion row.

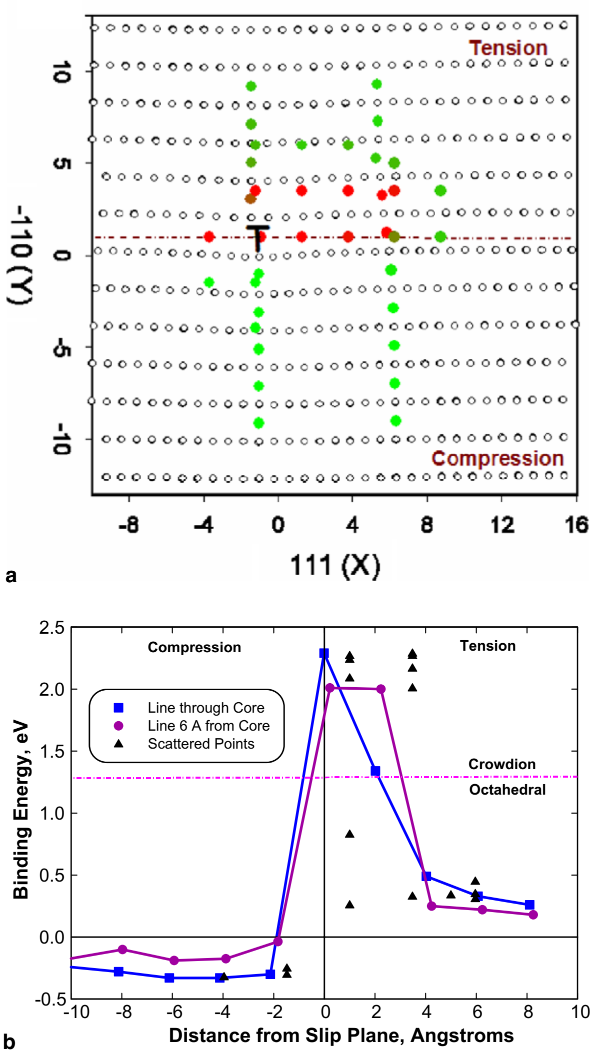

Fig. 4. (a) Locations of the initial position of a single interstitial He atom prior to relaxation. The open circles are Fe atom rows, and the filled, colored circles are the initial He atom positions. The dislocation line is along the z axis (into the page), and the z-components of all the He locations are approximately the same. At green locations the He atom relaxed to an octahedral site, and at red locations the He relaxed to a crowdion position. (b) Binding energies of relaxed interstitial He atoms as a function of their distance from the dislocation slip plane at the locations in 3(a). The points connected by lines are those lying along the two vertical lines of atom positions through the dislocation core and 0.5–0.6 nm from the core, respectively. Dimensions on axes are in Angstrom units. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

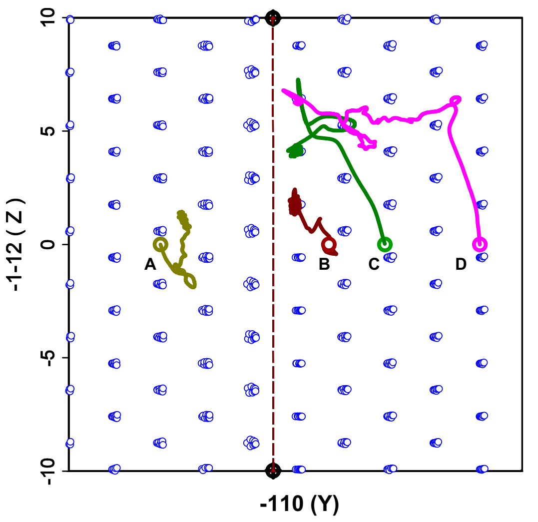

Fig. 5. Trajectories of interstitial He atoms starting from various unstable locations near the edge dislocation (core center along vertical line). The figure is a superposition of four separate trials with a single He atom. The tension side of the dislocation is on the right side of the line, compression on the left.

cantly smaller binding energies that decrease with distance from the dislocation. Near the core on the tension side the binding energies decrease more rapidly perpendicular to the slip plane than along the slip plane.

To investigate the attraction of interstitial He atoms to the edge dislocation in the vicinity of the core, MD simulations at a lattice temperature of 100 K were performed for individual interstitial He atoms starting at various distances from the dislocation, three on the tension side and one on the compression side. Fig. 5 shows a composite of their individual trajectories. In these cases, interstitial He atoms beginning up to 1 nm from the dislocation core on the tension side migrate to the layer of atoms nearest the slip plane, and become crowdion interstitial defects. Within a simulated time of less than 2 ps each of the He atoms had reached its final position in the atom layer nearest the core, where it remained trapped for the remainder of the simulation (up to 8 ps). It should be mentioned that in each case the interstitial He atom was assigned no initial velocity, but it started its trajectory at a location that was not an equilibrium interstitial position, so it immediately received some kinetic energy due to its interaction with surrounding Fe atoms. This may be the cause of significant migration of He along the direction of the dislocation line $[-1\,-1\,2]$ in trials C and D.

The He interstitial starting on the compression side migrated a short distance to a minimum energy position in an octahedral site, where it stayed for the remainder of the 3 ps run. This may seem somewhat surprising, given that the binding energy of He on the compression side is negative. On the other hand, dimer analysis indicates that the migration energy between octahedral sites in the vicinity of the dislocation on the compression side is on the order of 0.25 eV for transitions away from the slip plane, which would not be easily activated within 3 ps at 100 K. A migration mode along the direction of the dislocation line with an activation energy of about 0.1 eV was also identified, which is apparently the action taken by the He interstitial on the compression side during this short simulation.

The binding energies of relaxed interstitial He atoms to the dislocation can be associated with the excess interstitial volume at the various initial interstitial locations. In Fig. 6 the He binding energy is plotted as a function of excess interstitial volume for locations lying on the line through the dislocation core and along the line about 0.5–0.6 nm from the core, as depicted in Fig. 4(a). There is apparently a strong correlation between excess volume and binding energy for nearly all of the interstitial locations tested. However, in two of the tested locations with excess volume less than 0.0002 nm^3 the binding energy is greater than 2 eV, much higher than the correlation implied by the other data points would predict. These two outlying data points correspond to initial interstitial locations on and near the slip plane at 0.5–0.6 nm from the dislocation core.

It is clear that He interstitials are strongly trapped on the tension side of edge dislocations, so it is unlikely they can easily migrate away from the dislocation at temperatures less than about 800 K. However, it may be possible for interstitial He atoms to migrate along the dislocation core. The dimer method was applied to trapped He interstitials to determine the migration pathways and migration energies for diffusion near the edge dislocation. An interstitial He, initially in the crowdion configuration very near or in the dislocation core, is found to migrate along the dislocation line by jumping to a crowdion position in an adjacent close-packed row with a migration energy of about 0.4–0.5 eV, depending on its initial position and the jump direction.

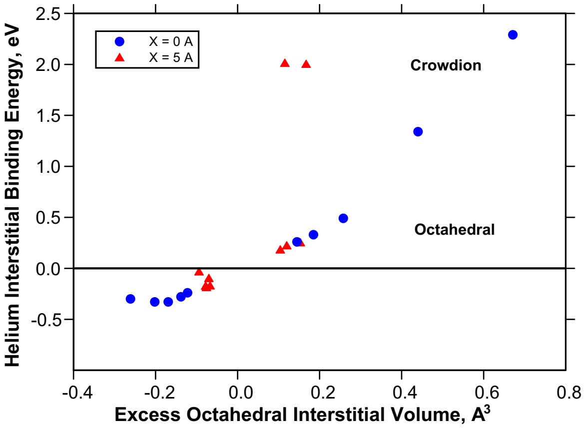

Fig. 6. Binding energy in eV of an interstitial He atom to an edge dislocation in α-Fe as a function of excess interstitial volume in Å^3. Values are shown for He atoms at positions along a line through the core ($X = 0$) and at 5–6 A from the core ($X = 5$) as depicted in Fig. 3(a).

4. Discussion

As expected, both substitutional and interstitial He atoms have positive binding energies on the tension side of the dislocation and negative binding energies on the compression side. Within about 2 Burgers vectors of the core on the tension side of the dislocation, interstitial He atoms relax to $\langle 111 \rangle$ crowdion configurations in atom rows perpendicular to the dislocation, along the direction of the Burgers vector. These configurations exhibit the strongest He binding energy, with a maximum value of 2.3 eV. Self-interstitial atoms in Fe have also been observed to be trapped in the form of $\langle 111 \rangle$ crowdions on the tension side of this edge dislocation in atomistic simulations by Kuramoto et al. [17] and Kamiyama et al. [18], using Finnis–Sinclair potentials. They attributed the stability of the crowdion to effects of the dislocation field.

As demonstrated in low temperature MD simulations and substantiated by dimer calculations, the He crowdion configurations formed in the core on the tension side of the dislocation remain centered on the He atoms, and the crowdions themselves are bound to the dislocation. If the crowdion could migrate away from the dislocation in the usual way, by a series of replacements along the close-packed atom row, this action would leave the He atom behind as a substitutional atom. However, this has not been observed. Instead, the energetically preferred migration mechanism of He crowdions trapped by the dislocation is for the He atom to hop from one crowdion position in a close-packed row to another crowdion position in an adjacent close-packed row. Thus, the He crowdion migration is perpendicular to the crowdion direction and along the direction of the dislocation line with a migration energy of 0.4–0.5 eV.

In a perfect Fe lattice (no dislocation) the He crowdion configuration was found to be unstable relative to the octahedral position. Thus, the existence of excess volume such as that in and near the core of the dislocation is evidently a prerequisite for formation of the very stable He crowdion. Indeed, He atoms placed at octahedral sites more than about 0.5 nm (2 Burgers vectors) from the dislocation core remained in their octahedral sites upon relaxation.

The formation of stable He crowdions in and near the core of the dislocation can be correlated with excess volume, but the correlation depends somewhat on the He position relative to the dislocation, especially the positions in Fig. 4(a) mentioned above that lie some distance from the dislocation. Evidently, excess interstitial volume at a single location is not the only driver for He crowdion formation. Perhaps excess volume smeared out over several neighboring shells of atoms can also lead to formation of stable crowdion configurations. This remains a problem for further investigation.

Interstitial Fe atoms placed in octahedral sites near the dislocation also take advantage of the effects of excess volume to relax to stable crowdion positions. It is also interesting to note that when a small amount of additional energy is added to the system initially, say by starting a relaxation with the interstitial atom initially displaced somewhat from the perfect octahedral location, a different relaxed configuration is often obtained by either He or Fe interstitial atoms that are initially two or three atom rows from the dislocation line. In this alternate case when the octahedral He or Fe interstitial atom is relaxed, it replaces a lattice atom in the nearest row toward the dislocation line, and the Fe atom displaced from that row becomes a crowdion in the next row nearer the dislocation line. This 'chain of replacements' effectively transfers the crowdion disturbance to the region of greatest excess volume.

Table 1 contains a summary of interaction energies of He-related point defects with ⟨1 1 2⟩ edge dislocations in α-Fe. Substitutional He atoms near the edge dislocation have a binding energy to the dislocation of 0.5 eV relative to substitutional He in the perfect Fe lattice. The migration energy of a substitutional He bound to a dislocation has not been determined, but substitutional He atoms in or near an edge dislocation are likely to be relatively immobile, facilitating the formation of He clusters. Interstitial He atoms are strongly bound to the dislocation with a maximum binding energy of 2.3 eV in these simulations, requiring temperatures on the order of 800 K to dissociate from the dislocation. Some of the highly mobile He interstitials produced under irradiation will be quickly trapped at edge dislocations where they can migrate along the dislocations at temperatures on the order of 200 K in so-called 'pipe diffusion.' The He migration energy of 0.4–0.5 eV along the dislocation is in the same range as the migration energy for interstitial He atoms within $\sum 3$ and $\sum 11$ grain boundaries determined from results of long-time molecular dynamics simulations [12].

Table 1
Helium interaction energies with edge dislocations in α-iron

Defect	Binding energy, eV to edge dislocation	Migration energy, eV	
		Perfect Fe	Dislocation
Substitutional He	0.50	–	–
Interstitial He	2.3	0.08	0.4–0.5
He_1V_2	1.2	>1.1	–

5. Conclusions

The results of these simulations indicate that interstitial He atoms are either repelled from or trapped at edge dislocations in α-Fe, depending on the direction of approach. Near the dislocation core on the tension side He is strongly trapped as a crowdion with 1–2 eV greater binding energy than as an octahedral interstitial, and in this form He atoms can migrate along the dislocation with a migration energy of 0.4–0.5 eV.

Acknowledgements

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References

[1] E.E. Bloom, J. Nucl. Mater. 85&86 (1979) 795.
[2] H. Ullmaier, Nucl. Fus. 24 (1984) 1039.
[3] R.L. Klueh, D.J. Alexander, J. Nucl. Mater. 218 (1995) 151.
[4] D.S. Gelles, J. Nucl. Mater. 283–287 (2000) 838.
[5] G. Henkelman, H. Jónsson, J. Chem. Phys. 111 (1999) 7010.
[6] W.D. Wilson, R.D. Johnson, Interatomic Potential and Simulation of Lattice Defects, Plenum, 1972, p. 375.
[7] W.D. Wilson, M.I. Baskes, C.L. Bisson, Phys. Rev. B 13 (1976) 2470.

[8] W.D. Wilson, C.L. Bisson, M.I. Baskes, Phys. Rev. B 24 (1981) 5616.

[9] K. Morishita, R. Sugano, B.D. Wirth, J. Nucl. Mater. 323 (2003) 243.

[10] K. Morishita, R. Sugano, B.D. Wirth, T. Diaz de la Rubia, Nucl. Instrum. and Meth. B 202 (2003) 76.

[11] R.J. Kurtz, H.L. Heinisch, J. Nucl. Mater. 329–333 (2004) 1199.

[12] F. Gao, H.L. Heinisch, R.J. Kurtz, J. Nucl. Mater., in press, doi:10.1016/j.jnucmat.2006.02.015.

[13] G.J. Ackland, D.J. Bacon, A.F. Calder, T. Harry, Philos. Mag. A 75 (1997) 713.

[14] D.E. Beck, Mol. Phys. 14 (1968) 311.

[15] T. Seletskaia, Y. Osetsky, R.E. Stoller, G.M. Stocks, Phys. Rev. Lett. 94 (2005) 046403.

[16] G. Voronoi, J. Reine Angew. Math. 134 (1908) 198.

[17] E. Kuramoto, K. Ohsawa, T. Tsutsumi, J. Nucl. Mater. 283–287 (2000) 778.

[18] H. Kamiyama, H. Rafii-Tabar, Y. Kawazoe, H. Matsui, J. Nucl. Mater. 212–215 (1994) 231.