

MODELING THE INTERACTION OF HELIUM WITH DISLOCATIONS AND GRAIN BOUNDARIES IN ALPHA-IRON—H. L. Heinisch, F. Gao, and R. J. Kurtz (Pacific Northwest National Laboratory)

OBJECTIVE

The objective of this research is to understand the fate of helium atoms produced in metals and alloys by the neutrons in a fusion reactor in part by studying the migration and diffusion mechanisms of He atoms in dislocations and grain boundaries in α -Fe using atomic-scale methods of molecular dynamics and statics.

SUMMARY

Molecular statics, molecular dynamics and the dimer method of potential surface mapping are being used to study the fate of helium in the vicinity of dislocations and grain boundaries in alpha-iron. Even at very low temperatures interstitial helium atoms can migrate to dislocations and grain boundaries, where they are strongly bound. The binding energies of helium to these microstructural features, relative to the perfect crystal, and the migration energies of helium diffusing within them have a strong correlation to the excess atomic volume that exists in these extended defects. Helium atom migration energies within the dislocations and grain boundaries studied are in the range of 0.4–0.5 eV. Helium “kick out” mechanisms have been identified within dislocations and grain boundaries by which interstitial helium atoms replace a Fe lattice atom, creating a stable He-vacancy complex that may be a nucleation site for a He bubble.

PROGRESS AND STATUS

Introduction

In the development of structural materials for nuclear energy production, including fission and fusion, the production and presence of helium (He) and its effects on the properties of structural materials under irradiation have long been a concern [1–4]. Computer simulations of He production, diffusion, trapping and clustering can provide valuable insights into the effects of He on the properties of nuclear materials. Although atomic-scale simulation of rare gases in metals has a history spanning half a century [5], progress has been spotty over the years. However, recently, interest in computational modeling of He-metal interactions and the development of relevant computational capabilities has increased significantly, primarily as part of the efforts to develop advanced materials that have minimum deleterious effects of He accumulation. The primary input information for these models is the interatomic potentials. In the past few years molecular dynamics (MD) simulations using Embedded Atom Method (EAM) type interatomic potentials have been performed to study He clustering [6,7] and He migration and interactions with extended defects [8–10] in α -Fe. Recent *ab initio* calculations [11,12] are providing new insights and quantitative information on He-Fe interactions.

According to MD modeling results single interstitial He atoms are extremely mobile in α -Fe, having migration energy of less than 0.1 eV in a perfect Fe crystal [9]. Interstitial He atoms are strongly trapped at vacancies, and they can also be trapped—less strongly but significantly—by features in the microstructure where there is much less excess volume than at a vacancy. Interstitial locations in and near grain boundaries (GBs) and dislocations can have sufficient excess volume to trap He atoms. The purpose of our modeling is to determine the binding energies of He to these extended defects and the migration energies of He within them, as well as to determine the kinetics of He clustering and the stability of He clusters in and near them.

Multiscale modeling, from *ab initio* computer simulations through analytical reaction rate theory computations, is required for comprehensive quantitative modeling of He disposition in an irradiated metal. Recently *ab initio* calculations are providing more critical information, but they are still restricted to atom configurations that comfortably fit within extremely small volumes and, usually, periodic boundary conditions, which limits their usefulness for studies of extended defects such as dislocations or grain

boundaries. MD suffers from a lack of realistic interatomic interactions, simply because much of the important physics of the interactions cannot be directly included. However, because of the large size of models that can be dealt with relatively efficiently, MD models can easily be applied to situations that include long-range fields and the essential features of large, non-symmetric defected regions of the material. It is often possible to tailor the potentials used in MD to more realistically represent some specific aspect(s) of the defect interactions--but with a concomitant loss of general applicability. Knowing which things to get exactly right and which details can be safely ignored--tempered by the possibility of even implementing these things quantitatively--is the essential dilemma of multiscale modeling.

Time scales are important. *Ab initio* and static molecular interaction models have no time scale, and MD can model times of perhaps nanoseconds, usually at nearly unphysically high interaction rates. Kinetic Monte Carlo (KMC) methods can be used to model macroscopic time intervals, if only for a very small volume of material and a limited number of events. The quantitative details of each category of defect migration and interaction in KMC and analytical rate theory models must be supplied by lower scale models, e.g., *ab initio*, MD, or input from experiments.

Interatomic Potentials

The present work is aimed at determining the fundamental aspects of the interaction of helium atoms with the existing microstructural features, as well as radiation-induced microstructure changes in alpha-Fe (and eventually in ferritic steels for fusion power applications). In particular, we have studied He atom interactions with edge and screw dislocations as well as with several types of grain boundaries. Potentials for Fe-Fe, Fe-He and He-He suitable for use in MD simulations are needed for these studies. Our studies so far have been performed using the set of potentials consisting of the Fe-Fe potential of Ackland et al. [13], the Wilson and Johnson potential for Fe-He [14], and the He-He potential used by Beck [15]. These potentials were used by Morishita et al. [9,10] and others in studies of He bubble formation, and the Ackland potential has been widely used in other MD simulations of radiation damage and defect interactions in α -Fe. Thus, for consistency in comparing our simulations of He in grain boundaries and dislocations to that body of work, we have used them in the present simulations.

EAM potentials have functional forms with parameters that can be fitted to a set of material properties (usually for the perfect crystal and often to some defect configurations) determined by experimental measurements or *ab initio* calculations. There is no guarantee that any of the existing EAM potentials for Fe adequately represent all non-equilibrium or non-symmetric atom configurations. Mendeleev et al. [16] developed a number of EAM potentials for Fe that describes properties of both crystalline and liquid Fe. The various versions of the potential were fitted to different sets of measured and *ab initio*-calculated properties. These potentials are on average in better agreement with those properties than other EAM potentials for Fe. The Mendeleev Potential #2 appears to be the best for computation of defect properties of interest to the present study. We have re-done some of our He-dislocation calculations using the Mendeleev #2 potential for Fe-Fe. Results are compared and discussed below.

Calculations

He-Dislocation Interactions

He-dislocation interactions were studied by doing molecular statics to determine defect formation energies, and Dimer [17] calculations to determine transition state energies and configurations. Some MD simulations were also done to study the intermediate range behavior of interstitial He-dislocation interactions at low temperatures. Models of the $a/2[111]$ [-1-12] edge dislocation and the $a/2[111]$ screw dislocation were constructed using cylindrical computational cells, each containing a dislocation along (or parallel to) the cylinder axis and having periodic boundaries in the direction of the dislocation line, with fixed boundaries at the surface of the cylinder. See Fig. 1. All atoms in the cell were displaced according to the anisotropic displacement field of the dislocation, and the cell was relaxed to allow the dislocation core field to develop. To determine He defect formation energies, a He atom was placed at a specific

position within the relaxed cell and the cell was relaxed again. Starting from a specific relaxed configuration, Dimer calculations were performed to determine the energies, saddle points, and final configurations of all possible transitions. More details of how these calculations were performed are in [9]. To study He-core interactions MD simulations were performed for picoseconds at 100 K for single migrating He atoms near the edge dislocation core. To study the effects of different Fe-Fe potentials, separate test cells were constructed for the Ackland and Mendelev Fe-Fe potentials because their equilibrium lattice parameters for perfect Fe are slightly different (0.28665 nm Ackland; 0.28553 nm Mendelev).

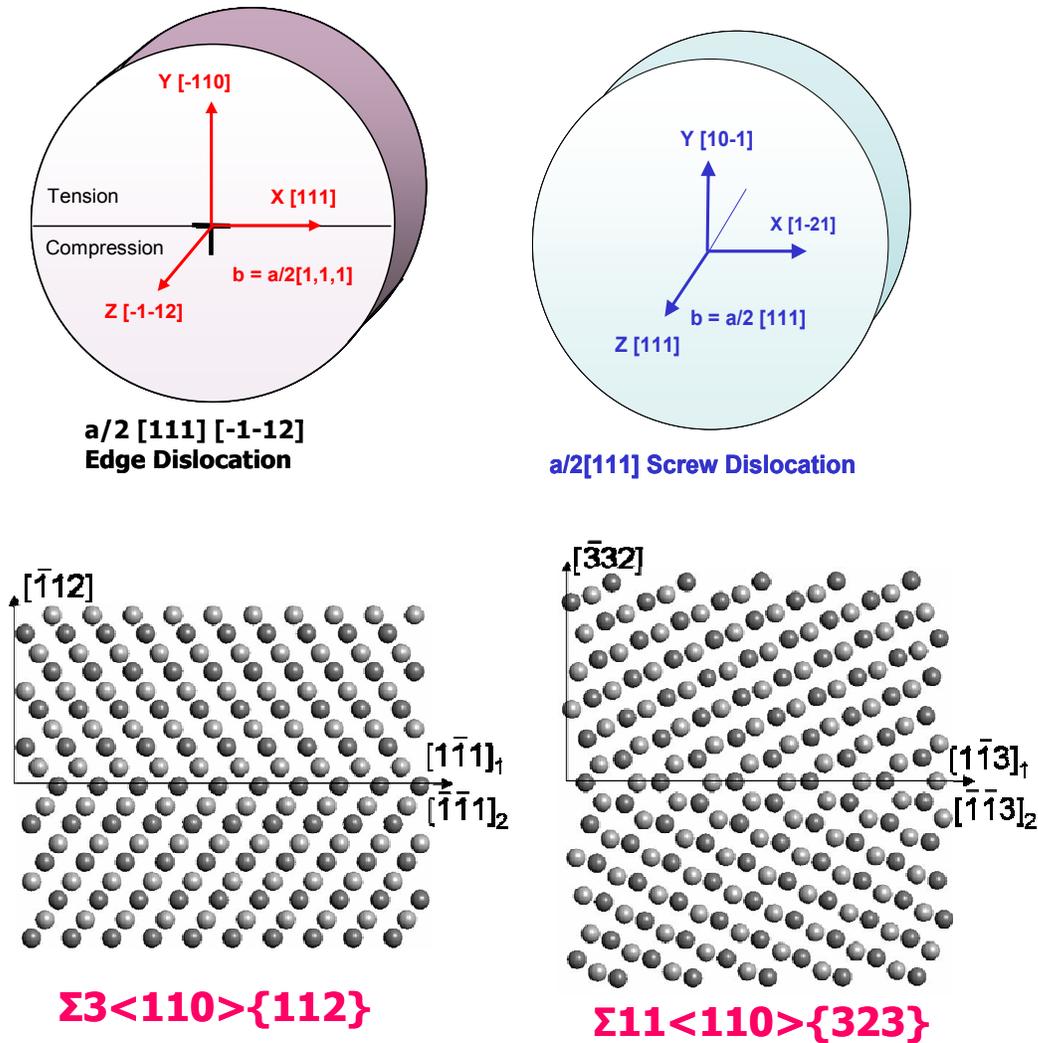


Fig. 1. Schematic drawings of the computational cells and orientations of the models of the $a/2 \langle 111 \rangle [-1-12]$ edge dislocation, the $a/2 \langle 111 \rangle$ screw dislocation, and the $\Sigma 3 \langle 110 \rangle \{112\}$ and $\langle 110 \rangle \{323\} \Sigma 11$ grain boundaries.

He-Grain Boundary Interactions

Simulations of He interactions within two tilt GBs, $\Sigma 3 \{112\}$ $\Theta = 70.53^\circ$ and $\Sigma 11 \{323\}$ $\Theta = 50.48^\circ$, were performed to study the diffusion of He interstitials and small clusters in the temperature range from 600 to 1200 K. Only the Ackland interatomic potential was used for Fe-Fe interactions. The MD migration

simulations were followed for 1–14 ns, depending on the temperature. The diffusivity, D , of He atoms can be determined from the sum of the mean square displacements (MSD) of He atoms. To accurately calculate the diffusion coefficient of He atoms, the method used here is based on decomposing the single trajectory into a set of shorter independent segments with equal duration, and then an average MSD, D_i (i indicates the i th time interval for the segment) for each segment, is calculated. The time interval of segments varies from 10 ps to 500 ps, and then D_i is averaged over all time intervals. With the diffusion coefficients of He atoms obtained at different temperatures, the activation energy for He migration in GBs, E_m , can be estimated from the Arrhenius Relation

$$D = D_0 \exp(-E_m / k_B T) \quad (1)$$

where D_0 is the pre-exponential factor, T is the absolute temperature, and k_B is the Boltzmann constant.

The mean square displacements of a He interstitial are determined as a function of time for the $\Sigma 3$ and $\Sigma 11$ GBs using the method described above. More details of how the He-GB simulations were performed are in [10]. Using the same techniques, interactions of He di-interstitials with these GBs have also been studied [19].

Results and Discussion

Dislocations

The binding energies and migration energies calculated for He near the edge and screw dislocations and in the grain boundaries described above are summarized in Fig. 2, which is a table of energies for various types of He defects arranged in relation to the energy scale in the far left column. The binding energy is defined as the difference of the formation energy of the He defect when it is in a perfect crystal and when it is in the dislocation or GB. Migration energies of He atoms near and within the dislocations are determined from Dimer analysis. The binding energies are very position dependent, and only maximum binding energies are reported in Fig. 2.

The maximum binding energy of single interstitial He atoms to the edge dislocation is 2.3 eV, with a maximum binding of 2.9 eV at the corner of a jog on the dislocation. The binding energies represent the differences in the formation energies of the stable defect configurations in the perfect and dislocated regions. As expected, interstitial He atoms approaching the core region on the tensile side of the edge dislocation migrate more favorably toward the dislocation line, initially as octahedral interstitials. An octahedral interstitial He placed about three Burgers vectors from the dislocation center has migration energy toward the center on the order of 0.2 eV. As excess volume increases, the He atom is more likely to occupy tetrahedral locations, ultimately going into the lowest energy interstitial configuration near the dislocation, which is a [111] crowdion. As a crowdion, the He preferentially migrates along the dislocation line, which is perpendicular to the crowdion direction, by hopping to crowdion positions in adjacent rows with a migration energy of 0.4–0.5 eV, depending on the initial position. The activation energy for He jumping out of the crowdion configuration to an octahedral interstitial site (as a first step of migrating away from the dislocation) is about 1.5 eV.

Binding energies of single interstitial He atoms to the screw dislocation are less than half that to the edge dislocation, and the He interstitials near the screw are never observed in the crowdion configuration. This is probably because the excess interstitial volume in the vicinity of the screw dislocation is significantly less than that found near the edge dislocation.

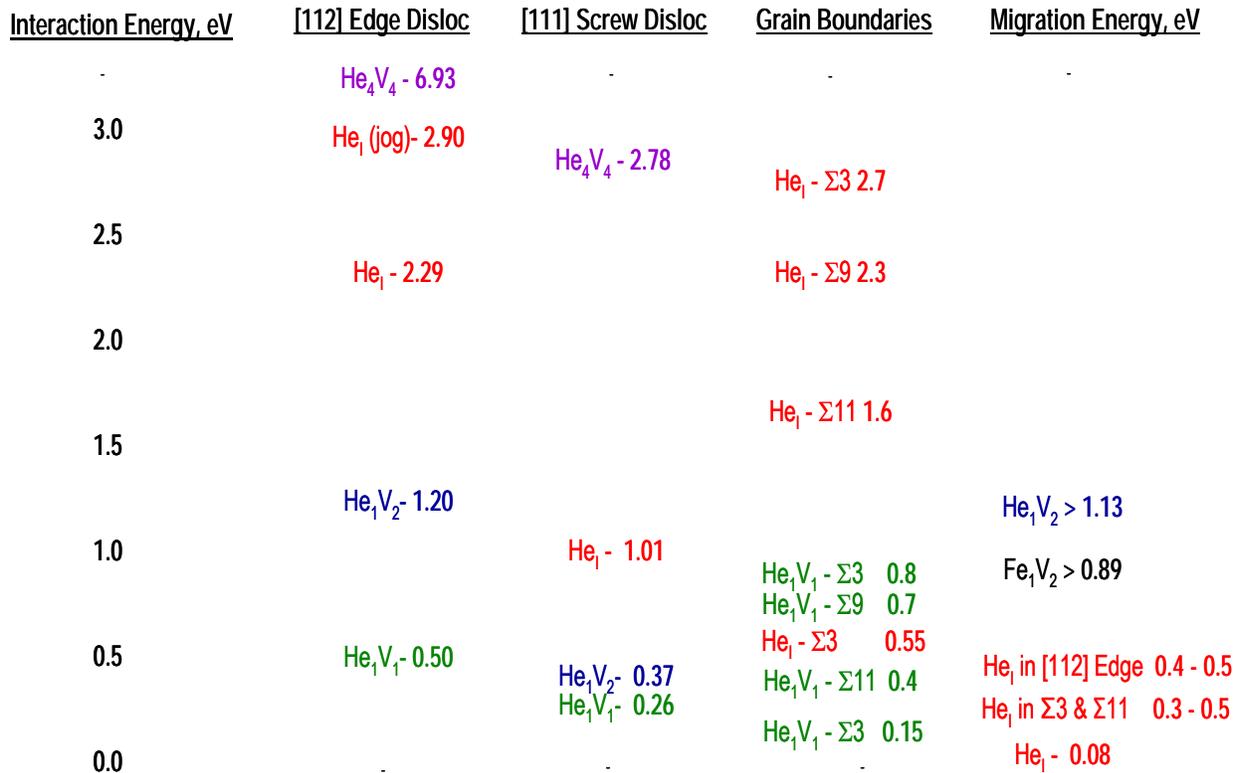


Fig. 2. A “map” of binding energies and migration energies in eV for He in dislocations and grain boundaries.

Entries in the binding energy part of the map are labeled according to the numbers of He and vacancies in the defect, He_iV_j. For example, He₁ is a single interstitial He atom and He₁V₁ is a substitutional He atom. The relative positions of the entries are related to the interaction energy scale on the left.

Grain Boundaries

The GBs do not have the long range fields associated with the single dislocations, but there is excess atomic volume dispersed throughout the boundary region that provides a sink for migrating interstitial He atoms. In the GBs the maximum binding energies of interstitial He atoms are somewhat less than in the dislocations, and they vary with the boundary type and orientation. See Fig. 1. Interstitial He has a binding energy to the Σ3 GB of 0.55 eV, and the dimensionality of its migration is temperature dependent. In the high temperature MD simulations [10], the interstitial He atom migrates one-dimensionally within the Σ3 GB at lower temperatures, and two-dimensionally above 800 K. At 1200 K the He atom was observed to migrate out of the GB three-dimensionally, reflecting the relatively smaller binding energy of He to the Σ3. He atoms have a higher binding energy to the Σ11 GB, and He atom migration is observed to be one-dimensional within the GB throughout the 800-1200 K temperature range studied. The migration energies of He atoms within the grain boundaries are in the range of 0.3–0.5 eV, depending on the He atom location and defect type.

Two interstitial He atoms placed in close proximity in the Σ3 GB migrate one-dimensionally as a di-interstitial He cluster at temperatures of 600–1000K without dissociation [19]. At 1200 K an interesting phenomenon is observed in that the di-interstitial He cluster “kicks out” an Fe atom and occupies the resulting vacancy, forming a very stable, stationary He₂V defect. The Fe atom becomes a crowdion interstitial that quickly migrates along the [1–11] interface axis one dimensionally. A similar kick out

mechanism is observed at 1200 K in the $\Sigma 11$ GB, where the kicked out Fe atom migrates within the GB as a [110] dumbbell. Depending on its long-term stability, the He₂V defect might be the smallest He bubble nucleus.

Comparing Interatomic Potentials

Results of calculations of some Fe and He defect formation energies using the Mendeleev version of the Fe-Fe potential were compared to the values obtained using the Ackland Fe-Fe potential, with the same Fe-He potentials for both cases. Table 1 gives the values of the He octahedral and tetrahedral interstitial formation energies and the He binding energies in a crowdion interstitial position near the edge dislocation. These results are also compared to results of *ab initio* calculations [11]. The formation energies using the Mendeleev potential are somewhat smaller than those using the Ackland potential, but in both cases the octahedral position is more stable than the tetrahedral, in contrast to the *ab initio* results. The magnitude of the difference is greater for the Mendeleev potential than for the Ackland potential. Evidently, the relative stability of these two He interstitial positions is not strongly influenced by the Fe-Fe interaction. Very recently Seletskiaia et al. [18] have shown results of similar calculations using a new empirical Fe-He potential fitted to results of *ab initio* calculations. The close agreement of their results using the empirical and *ab initio* methods indicates that the stability of the He interstitial in Fe is, not surprisingly, most strongly influenced by the Fe-He potential. Based on this success, it will be very interesting to incorporate the new Fe-He potential function into our further studies of He in dislocations and grain boundaries.

Table 1. Comparison of He interstitial formation energies in eV at octahedral and tetrahedral sites calculated in this study using Ackland[13] and Mendeleev[16] versions of EAM Fe-Fe interatomic potentials. The MD results are compared to results of *ab initio* calculations for these configurations by Seletskiaia et al. [11].

	<u>Ackland</u>	<u>Mendeleev</u>	<u><i>ab initio</i></u>
He Octahedral	5.25	4.99	4.60
He Tetrahedral	5.33	5.13	4.37

The results of our simulations indicate that the behavior of interstitial He within dislocations and GBs is strongly influenced by the excess volume found in the atomic arrangements of these extended defects. Moreover, the excess volume in the defected Fe lattice is determined solely by the Fe-Fe interatomic interactions, and the Mendeleev Fe-Fe potential #2 is fitted to many properties of Fe, including the *ab initio* values of self-interstitial atoms [16]. It is tempting to think that one could predict the behavior of He in any configuration of extended defects based solely on the magnitude and spatial distribution of excess volume in that configuration. However, according to results using the new Fe-He empirical potential [18], the response of He atoms to the atomic arrangements they experience in Fe appears to depend strongly on the He-Fe interactions. On the other hand, all the tests of this new He-Fe potential were performed on configurations where the excess volume is negative. It would be of great interest to have results of *ab initio* calculations performed for atom configurations containing excess volume that is representative of that found in dislocations or GBs.

Conclusions

Molecular dynamics simulations have been performed for binding energies and migration energies of He in dislocations and grain boundaries. He is strongly trapped in regions of excess volume found in these extended defects. Details of the trapping and migration mechanisms of He observed in these simulations will be corroborated in further simulations using the latest interatomic potentials based on results of *ab initio* calculations. These simulations provide essential elements of the defect interaction information required for multiscale modeling of the fate of He in α -Fe.

Acknowledgements

This research is supported by the US Department of Energy, Office of Fusion Energy Sciences, under Contract DE-AC06-76RLO 1830.

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