

MIGRATION OF VACANCIES, HE INTERSTITIALS AND HE-VACANCY CLUSTERS AT GRAIN BOUNDARIES IN ALPHA-Fe – F. Gao, H. L. Heinisch and R. J. Kurtz (Pacific Northwest National Laboratory)*

OBJECTIVE

The objective of this work is to fundamentally understand the migration mechanisms of vacancies, He interstitials and small He-vacancy clusters at grain boundaries in α -Fe using the dimer method and long-time molecular dynamics.

SUMMARY

The dimer method for searching transition states has been used to systematically study possible migration paths of vacancies, He interstitials and He-vacancy (He/V) clusters at $\Sigma 11\langle 110 \rangle \{323\}$ and $\Sigma 3\langle 110 \rangle \{111\}$ grain boundaries (GBs) in α -Fe. Vacancies trapped at the GBs diffuse along the GBs with migration energies much less than that within the perfect crystal. Long-time dynamics simulations of diffusion pathways reveal that vacancies migrate one-dimensionally along the close-packed rows in the $\Sigma 3$ GB, and one-dimensionally in zigzag paths within the $\Sigma 11$ GB. Also, dimer saddle point searches show that He interstitials can diffuse along the GBs with migration energies of 0.4-0.5 eV, similar to those of individual vacancies at the GBs, and the corresponding mechanisms are determined. The rate-controlling activation energy for migration of a He-divacancy cluster in the GBs determined using the dimer method is about 0.9 eV, which is comparable to the migration energy for a He-divacancy cluster in bulk α -Fe.

PROGRESS AND STATUS

Introduction

The interactions of He impurities with microstructural features, such as dislocations and grain boundaries (GBs), can result in adverse effects on mechanical properties of metals and alloys. Thus, the formation of He bubbles both in bulk and at GBs remains one of the most important aspects in nuclear fusion technology. A detailed knowledge of He diffusion in both the bulk and at GBs, including the mobility of small helium-vacancy clusters and the nucleation of helium bubbles, is extremely important to quantitatively understand the fate of He atoms with respect to the microstructural features with which they interact.

Previously, molecular statics, molecular dynamics and the dimer method have been combined to study the fate of He atoms in the vicinity of dislocations [1, 2] and GBs [3, 4] in α -Fe. These results have demonstrated that both substitutional and interstitial He atoms are trapped at GBs, with binding energies ranging from 0.2 to 0.8 eV and from 0.5 to 2.7 eV, respectively. Molecular dynamics simulations have shown that the diffusion coefficient for He diffusion along an extended defect is expected to depend significantly on the type of extended sink (dislocation or GB). Also, the diffusion mechanisms strongly depend on the atomic structures of GBs as well as the temperatures [4]. In the present study, the detailed diffusion mechanisms and energy barriers of He interstitials and small He-vacancy clusters in two representative GBs are studied using the dimer method. In parallel, the migrations of vacancies in these GBs are studied using both the dimer method and long-time dynamics simulations to understand their possible contributions to the formation of helium bubbles.

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Computational Approach

The details of the methodology used in the calculations of the atomic arrangement of GBs have been previously described elsewhere [3, 4]. The two symmetric tilt GBs studied in the present work are $\Sigma 3\{112\}$ $\Theta=70.53^\circ$ and $\Sigma 11\{323\}$ $\Theta=50.48^\circ$, and their corresponding ground-state structures are shown in [5]. Periodic boundary conditions are applied in the directions parallel to the GB plane, whereas a semi-rigid boundary condition is applied in the direction normal to the GB. The dimension of the simulation cell is 33.3 Å x 36 Å x 32.4 Å, consisting of 3120 and 3247 atoms for the $\Sigma 3$ GB and $\Sigma 11$ GB, respectively.

The lowest energy configurations of a single He interstitial and a He_1V_2 cluster in each GB were determined by raising the lattice temperature to 1000 K, with simulation time up to about 10 ps, and then slowly cooling down to 0 K. The possible transitions starting from these stable configurations were systematically searched using the dimer method [6]. In all cases 100 dimer searches were carried out starting from each initial state. The end configuration that corresponds to the lowest energy barrier was used for the next set of dimer searches. This approach repeats until the He interstitial and He_1V_2 cluster migrate to positions which are equivalent to their original positions. In addition, long-time dynamics based on the dimer method [7] was employed to investigate the long-time behavior of a single vacancy in the GBs. The interatomic potentials describing the Fe-Fe, Fe-He and He-He interactions are the same as those used previously [4]. In the simulations of vacancy migration, the recently developed Fe-Fe potential by Mendeleev et al. [8] was also used to check the potential-sensitivity of its migration energy and path in both the bulk and GBs.

Results

The transition states of He interstitials, vacancies and HeV_2 clusters are searched in both the GBs using the dimer method, and the highest energy barrier along the lowest energy path is determined to be the corresponding activation energy for migration of a defect or a cluster. Table 1 summarizes the possible migration energies for He interstitials, vacancies and HeV_2 clusters in the $\Sigma 3$ and $\Sigma 11$ GBs, along with those in the bulk for comparison.

	E_m (eV)		
	He	V	He_1V_2
$\Sigma 3$	0.46	0.48 (0.38)	0.9
$\Sigma 11$	0.47	0.74 (0.61)	0.92
Bulk	0.08	0.78 (0.64)	1.13

Table 1 Migration energies of defects in both bulk and GBs, along with those of vacancies. Values in parenthesis were obtained using the new Mendeleev potential [8] for comparison.

He interstitial. The possible migration mechanisms for a He interstitial in the $\Sigma 3$ GB are shown in Figure 1(a). Initially, the He atom can migrate from one octahedral position below the GB plane to a similar position above the GB plane along the $[\bar{1}\bar{1}1]$ direction, as indicated by one of the arrows, overcoming an energy barrier of 0.46 eV. Then, the He atom can further migrate to an equivalent position below the GB plane with the same energy along the $[1\bar{1}\bar{1}]$ direction, but in a different atomic row, which results in the

net diffusion of the He atom along the $[\bar{1}\bar{1}\bar{1}]$ direction, denoted as path A. If the He migrates to a row above the GB plane along the $[\bar{1}\bar{1}\bar{1}]$ direction, and then migrates to a different location in its initial row along the $[\bar{1}\bar{1}\bar{1}]$ direction, the migration of the He atom leads to its net diffusion along the $[110]$ direction, which is denoted as path B. These two paths have the same migration energy and are equivalent, which may be associated with the typical atomic structure of the $\Sigma 3$ GB, and results in two-dimensional migration of He within the GB plane. Previously, molecular dynamics simulations revealed that the He atom migrates two-dimensionally at low temperature and three-dimensionally at higher temperatures in the $\Sigma 3$ GB [4]. The present dimer results are in excellent agreement with the previous MD simulations, and they now provide a physical explanation for the observed phenomena.

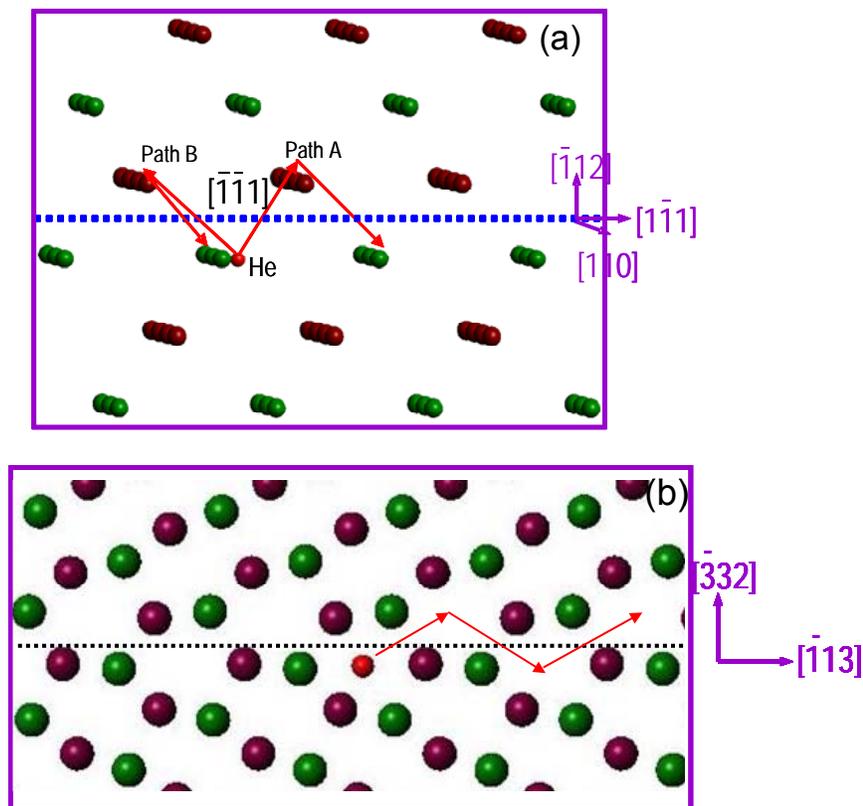


Figure 1. Possible migration paths of a He interstitial in (a) the $\Sigma 3$ GB and (b) the $\Sigma 11$ GB, where a small sphere represents the He atom and arrows indicate possible paths.

Figure 1(b) shows the possible migration paths of a He interstitial in the $\Sigma 11$ GB. Dimer searches indicate that the He atom can migrate from a tetrahedral position below the GB plane to a similar position above the GB plane, and this movement leads to the He atom diffusion along the $[\bar{1}\bar{1}\bar{3}]$ direction, as indicated by the arrows. This path is the lowest energy path, with an activation energy of 0.47 eV. Also, dimer searches reveal other possible transition states, but with much higher energies. These results suggest that the He atom migrates one-dimensionally along the $[\bar{1}\bar{1}\bar{3}]$ direction, but its path is zigzag along the interface in the same plane. The present dimer results are in good agreement with the previous MD studies [4]. The MD simulations suggest that the He interstitial is strongly bound to the middle plane on which the initial starting position of the He interstitial is located, and it can only move in the spaces between the three planes.

Vacancy: One of the components controlling He bubble nucleation and growth is the mobility of vacancies in both bulk and GBs. Both He atoms and vacancies can be deeply trapped by dislocations and GBs, and the fundamental understanding of their migrations within dislocations and GBs is important for multi-scale computer simulation of microstructural evolution under radiation conditions. The dimer searches find the lowest vacancy migration energy to be 0.48 eV in the $\Sigma 3$ GB, which is much smaller than that in the bulk (see Table 1). The surprising result is that the vacancy migrates one-dimensionally along the $\Sigma 3$ GB, as demonstrated in Figure 2(a), where the arrows indicate possible paths. A long-time dynamics simulation has also been carried out to study the vacancy migration, and it is found that the vacancy moves forwards and backwards along the $[1\bar{1}1]$ direction. This confirms that the vacancy migrates only one-dimensionally with a similar energy to that of a He interstitial in the $\Sigma 3$ GB. Figure 2(b) shows the possible mechanisms for a vacancy to migrate in the $\Sigma 11$ GB, and its path is a zigzag path along the interface, with strong bonding to the interface. One of the interesting results is that the vacancy migrates within a plane perpendicular to the interface, and the migration out of the plane requires much higher energy (~ 0.77 and 0.9 eV within the $\Sigma 3$ and $\Sigma 11$ GBs, respectively). These results suggest that the vacancies may migrate one-dimensionally at low temperatures and two-dimensionally at higher temperatures.

We have also used the new Fe potential recently developed by Mendeleev et al. [8] to study the vacancy migration in both GBs (included in Table 1), as included in the parenthesis. The migration mechanisms of the vacancies are very similar to those observed in the Ackland potential, i.e. the vacancy migrates one-dimensionally along the $[1\bar{1}1]$ direction in the $\Sigma 3$ GB, whereas its path is a zigzag path in the $\Sigma 11$ GB, with one-dimensional behavior along the $[\bar{1}13]$ direction, but with slightly smaller migration energies.

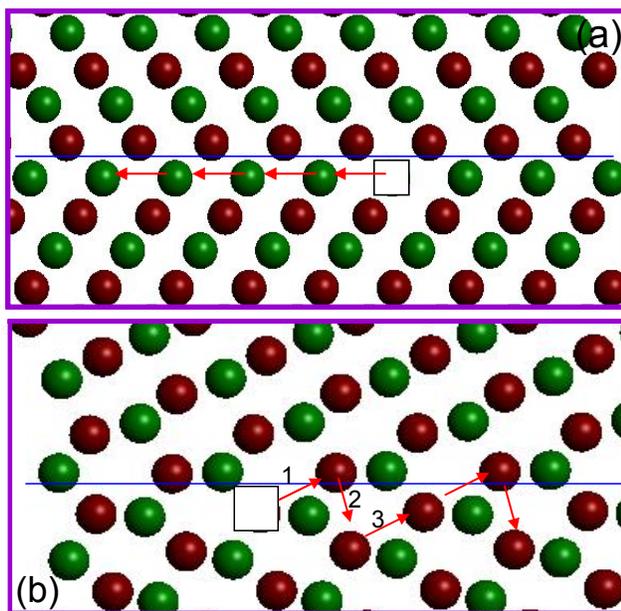


Figure 2. Possible paths of a trapped vacancy in (a) the $\Sigma 3$ GB and the $\Sigma 11$ GB, where the white squares represent vacancies and arrows indicate their movements along the GBs.

He₁V₂ cluster: The most stable configuration for a He₁V₂ complex in the GBs is found to be two first neighbor vacancies, with a He atom located between them, as shown in Figure 3(a). This configuration is slightly different from the most stable configuration of the He₁V₂ cluster in the bulk, where the He atom is substitutional He, but slightly displaced from one vacancy along the line between the two vacancies. To understand the migration of a He₁V₂ cluster within GBs, the dimer searches of transition states were first carried out to study its migration in the bulk. The results show that there exist a number of possible

transition states. The lowest transition state corresponds to the He jumping from one vacancy to the other with an activation energy of 0.02 eV for first neighbor vacancies, but this energy increases to 0.66 eV for second neighbor vacancies. The migration of the He_1V_2 cluster is dominated by the vacancy migration, rather than by the He atom, i.e. it is a vacancy mechanism. The migration energy is determined to be about 1.13 eV. Fu and Willaime [9] studied the migration of a He_1V_2 cluster in the bulk using *ab initio* methods, and they found that the He_1V_2 cluster can migrate as a unit over appreciable distance via substitutional He-vacancy mechanisms, with an activation energy of 1.17 eV. The mechanisms and migration energy obtained in the present study are in excellent agreement with their results.

Figure 3 shows the migration mechanisms of a He_1V_2 cluster in the $\Sigma 3$ GB, and its path is a rotational path within the interface. Starting with the stable configuration, the He atom diffuses into the nearest vacancy site above the GB plane, and becomes a substitutional He. At the same time, an Fe atom close to one of the two vacancies below the GB plane diffuses into this vacancy site, resulting in a configuration where the He atom and the vacancy are in second neighbor positions, as exhibited in Figure 3(b). The arrows in Figure 3(a) indicate the movements of the He atoms and vacancies, and it should be noted that the migration behavior of the He_1V_2 cluster follows a collective motion. However, these defects are strongly bound to the interface, and the possible dissociation from the interface requires much higher energy. The further diffusion of an Fe atom above the GB plane to the vacancy and of the He atom to a nearest-neighbor site lead to the formation of a configuration similar to the initial configuration, but with different direction. This collective motion is indicated by the arrows in Figure 3(b). There are two possible migration paths for the configuration in Figure 3(c), one back to its original position in Figure 3(a) and another resulting in its migration along the $[\bar{1}1\bar{1}]$ direction. Similar to the migration of a vacancy, these collective motions eventually lead to one-dimensional migration along the interface, with a corresponding migration energy of 0.9 eV. It should be emphasized that these collective motions occur within a plane perpendicular to the interface, and out-of-plane migration of the He_1V_2 cluster is not observed, or it may require much higher energy. Similar behavior of the He_1V_2 cluster in the $\Sigma 11$ GB is observed, and its migration energy is about 0.92 eV. It is noted that the migration energy of a He_1V_2 in the GBs is similar to that in the bulk, but the migration mechanisms are completely different. In the bulk, the He_1V_2 cluster can migrate three dimensionally, while it migrates only one-dimensionally via the substitutional He-vacancy migration mechanism within the GBs.

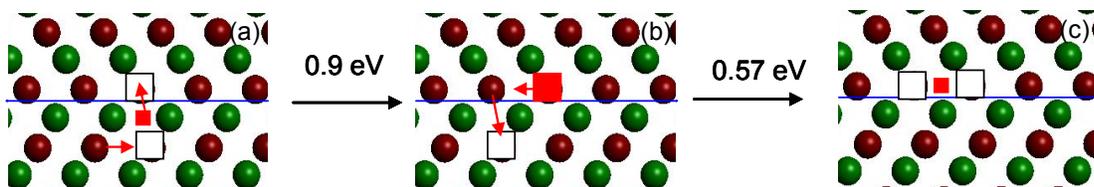


Figure 3. Migration mechanism of a HeV_2 cluster, where the arrows indicate the collective motion of Fe and He atoms, resulting in its one-dimensional migration along the $\Sigma 3$ GB.

Summary

The possible migration paths and mechanisms of vacancies, He interstitials and He-vacancy (He/V) clusters at $\Sigma 11$ and $\Sigma 3$ GBs are studied by combining dimer saddle point searches and long-time dynamics in alpha-Fe. In contrast to the three-dimensional migration behavior of vacancies in the perfect crystal, they migrate one-dimensionally along close-packed rows in the $\Sigma 3$ GB and one-dimensionally in zigzag paths within the $\Sigma 11$ GB. He interstitials can diffuse along the GBs with migration energies of 0.4-0.5 eV, similar to those of individual vacancies at the GBs. There are two equivalent paths for a He interstitial within the $\Sigma 3$ GB plane, leading to its two-dimensional migration, but there is only one possible path in the $\Sigma 11$ GB. The migration energy of a He-divacancy cluster in the GBs using the dimer method is determined to be about 0.9 eV, and the corresponding migration mechanism shows that its path is a rotational path within the GBs, but its collective motion exhibits one-dimensional migration parallel to the GB plane.

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