

# Diffusion of He interstitial and di-He cluster at grain boundaries in $\alpha$ -Fe

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## Abstract

A systematic molecular dynamics study of the diffusion mechanisms of He interstitial and di-He cluster at two representative interfaces has been carried out in  $\alpha$ -Fe. The diffusion coefficient of a He interstitial and the effective migration energies were determined. The He atom diffuses along the  $\Sigma 11$  grain boundary one-dimensionally along specific directions, while it migrates two-dimensionally at low temperatures, and three-dimensionally at higher temperatures, in the  $\Sigma 3$  grain boundary. The di-He interstitial cluster can migrate rapidly along the  $\Sigma 3$  interface at low temperatures, but not at the  $\Sigma 11$  interface. It has been observed that a di-He interstitial cluster can kick out a self interstitial atom (SIA) at high temperatures, forming a  $\text{He}_2\text{V}$  complex. The SIA migrates rapidly near interfaces, whereas the  $\text{He}_2\text{V}$  complex is immobile at the temperatures considered. This small cluster may serve as the smallest nucleation for the formation of helium bubbles at interfaces.

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## 1. Introduction

It is well known that the first wall materials of a fusion reactor are exposed to high energy neutron irradiation, resulting in a high rate of helium production by  $(n, \alpha)$  reactions. Because of the extremely low solubility of He in metals, helium atoms tend to be trapped at defects that are produced in displacement cascades, such as vacancies, and strongly interact with grain boundaries (GB) and dislocations, which can produce significant changes in microstructure and mechanical properties, potentially embrittling the materials even at extremely

low concentrations [1,2]. High helium concentrations can lead to the formation of helium bubbles that enhance void swelling due to large increases in the cavity density [3], and produce surface roughening and blistering [4]. The formation of He bubbles both in bulk and GBs remains one of the most important issues in nuclear fusion technology. Thus, it is important to have a detailed knowledge of He diffusion in both bulk and GBs, that includes trapping and detrapping, the interaction of He with microstructures, the mobility of small helium–vacancy clusters, and the nucleation of helium bubbles.

Recently, a number of computer simulations have been employed to yield important understanding of He behavior in bcc metals [5–8] and fcc metals [9]. Their results have shown that the binding

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energies of an interstitial helium atom, an isolated vacancy and a self-interstitial iron atom to a helium–vacancy cluster do not depend much on cluster size, but rather on the helium-to-vacancy ratio in  $\alpha$ -Fe [5]. In order to understand the mechanisms responsible for the formation of He–vacancy clusters, the molecular dynamics (MD) method has been combined with kinetic Monte Carlo methods to study the migration and clustering of transmutant helium gas atoms in  $\alpha$ -Fe, with particular emphasis on the high mobility of small vacancy–He clusters [6]. Atomistic calculations also demonstrate the strong binding of He to GBs [7] in  $\alpha$ -Fe. Both substitutional and interstitial He atoms are trapped at GBs, with binding energies ranging from 0.5 to 2.7 eV and from 0.2 to 0.8 eV, respectively. In general, binding energy increases linearly with GB excess volume. However, the diffusion constant for He diffusion along an extended defect is expected to depend significantly on the type of extended sink (dislocations or GBs), which has been observed at different GBs in fcc Cu implanted with He [10]. The large variation in density and size of bubbles at different GBs may be correlated with the varying atomistic structures of the GBs, which suggests that the GB's structure is important for the diffusivity of He along GBs. In this paper, the diffusion mechanisms of He interstitials and their small clusters in grain boundaries will be studied using molecular dynamics (MD) methods.

## 2. Simulation methods

Most of the details of the methodology used in the calculations of the atomic arrangement of GBs have been previously described elsewhere [11,12]; thus, only the central principles are explained in this paper. The computational cell consists of two parallel sections having different orientations, forming the GB along their interface. The equilibrium structures of the GBs at 0 K are obtained by relaxation using molecular dynamics with an energy quench employing a viscous drag algorithm. Periodic ‘boundary conditions’ of the model are applied along the GB in the directions perpendicular to the normal direction of the GB plane, whereas a semi-rigid ‘boundary condition’ is applied in the direction normal to the GB [11]. The two GBs considered 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 [8]. The shape of the MD block is rectangular with dimension

$59.6 \text{ \AA} \times 66.0 \text{ \AA} \times 56.8 \text{ \AA}$  (18816 atoms) and  $57.5 \text{ \AA} \times 66.0 \text{ \AA} \times 56.8 \text{ \AA}$  (17978 atoms) for the  $\Sigma 3$  GB and  $\Sigma 11$  GB, respectively.

The lowest energy configurations of a single He interstitial and a He di-interstitial 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. These stable configurations were used as the initial starting configurations for investigating the migration of He interstitials in the temperature range of from 600 to 1200 K. The 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, which is accurate in the limit of large simulation time. In the present simulations, considerable fluctuation in MSD is observed for all the temperatures considered. 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, as detailed in [8]. 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.

The Fe–Fe interaction is described by the potential developed by Ackland et al. [13] based on the Finnis–Sinclair formalism, while the Fe–He potential was fit to ab initio calculations of small He–Fe clusters by Wilson and Johnson [14]. A classical potential developed by Beck [15] was used to describe He–He interaction. The details of the potentials and cohesive energy of fcc He, and the formation energies of various defects and an interstitial He, as well as a substitutional He atom, are given in [7].

## 3. Diffusion of He interstitial in $\Sigma 3\{112\}$ and $\Sigma 11\{323\}$ GBs

The mean square displacements of a He interstitial are plotted as a function of time for the  $\Sigma 3$  GB in Fig. 1. All the MSDs increase with increasing time, and are approximately linear with time. However, there exist some large fluctuations in the MSD, which may lead to large errors in the estimation of activation energy for He diffusion. As described above, the trajectory of the He atom has been divided into  $N$  segments of equal time interval, and the number of segments depends on the time

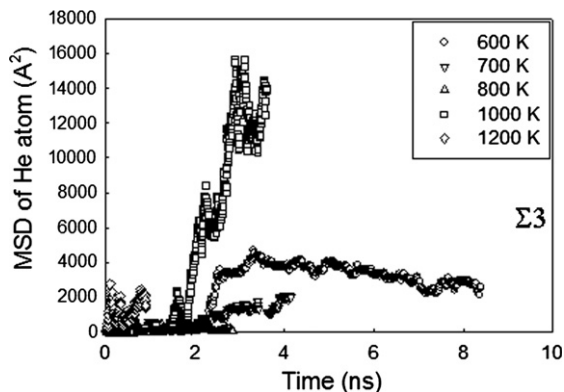


Fig. 1. Mean-square displacements (MSDs) of the He atom as a function of time for the temperature range between 600 and 1200 K on the  $\Sigma 3$  GB.

interval, which is varied from 10 to 500 ps. For simulation times up to several nanoseconds the diffusion coefficient can be estimated with high accuracy. During the simulation, a large number of He jumps are observed, but the dynamic processes occasionally involve the jumps of Fe atoms. However, the contribution of Fe jumps to the total MSD is negligible. The MSDs of the He interstitials in the  $\Sigma 11$  GB are somewhat smaller than that in the  $\Sigma 3$  GB, which may be associated with the atomic structures of the GBs. The diffusion coefficients estimated for the He interstitial in both GBs are given in Fig. 2 as a function of reciprocal temperature. The best fits of these results to the Arrhenius relation give the values of  $E_m$  and  $D_0$  to be  $0.22 \pm 0.06$  eV and  $1.49(\pm 0.54) \times 10^{-4}$  cm<sup>2</sup>/s for

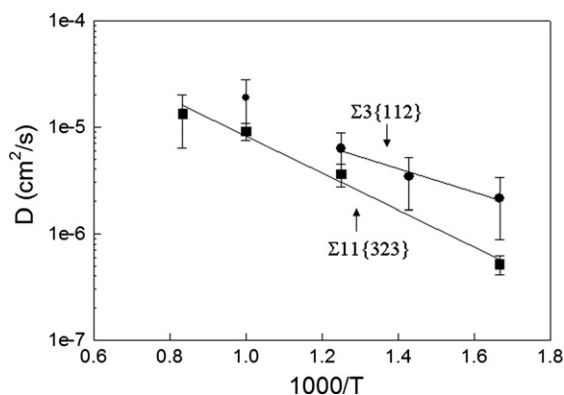


Fig. 2. Diffusion coefficients of He interstitial as a function of reciprocal temperature in the  $\Sigma 3$  and  $\Sigma 11$  GBs in  $\alpha$ -Fe, where reciprocal temperature is scaled by 1000 (the data at 1000 K for the  $\Sigma 3$  GB is not included in the calculation of effective migration energy because the He interstitial diffuses three-dimensionally).

the  $\Sigma 3$  GB, and  $0.34 \pm 0.08$  eV and  $4.3(\pm 0.96) \times 10^{-4}$  cm<sup>2</sup>/s for the  $\Sigma 11$  GB, respectively. It should be noted that the effective migration energy for an He interstitial at interfaces is generally larger than the value of 0.082 eV [6] in the bulk.

The migration mechanisms of He interstitials in GBs have been studied by analysis of the computer-generated trajectories. The detailed trajectories of the He interstitial in the  $\Sigma 3$  and  $\Sigma 11$  GB are found in [8]. The result generally suggests that the He interstitial mainly migrates with one-dimensional behavior at the temperatures considered. However, it has been observed that the migration path of the He interstitial changes from two-dimensional (2D) diffusion in the interface plane at the temperatures below 800 K to three-dimensional (3D) diffusion at higher temperatures in the  $\Sigma 3$  GB. This is expected because high temperatures lead to the dissociation of the He interstitial from the  $\Sigma 3$  GB. This behavior is consistent with its small binding energy, which is the lowest He binding energy among all the GBs calculated [7]. The dissociation at high temperatures allows the He interstitial to also migrate along  $\langle \bar{1}12 \rangle$  direction, resulting in 3D diffusion. In the  $\Sigma 11$  GB the He interstitial is strongly bound to the middle plane on which the initial starting position of the He interstitial is allocated, and can only move in the spaces between the three planes. It is of interest to note that the He interstitial migrates one-dimensionally along the  $\langle \bar{1}\bar{1}3 \rangle$  direction, even at higher temperatures. Although only two GBs have been considered in these diffusion simulations, the results demonstrate that interstitial He diffusion and the corresponding migration mechanisms depend significantly on the atomic structures of the GBs. The variation in diffusion mechanisms of He interstitials in GBs should have significant effects on He bubble nucleation at different GBs. The diffusion mechanisms of the He interstitial are different from that observed in the bulk, where a He interstitial migrates three-dimensionally.

#### 4. Diffusion of a di-He interstitial cluster in the interfaces

Fig. 3(a) and (b) shows the mean square displacements of a di-He interstitial cluster as a function of time for the  $\Sigma 3$  and  $\Sigma 11$  GB, respectively. In general, the migration behavior is more complicated than that of a single He interstitial observed above. In the  $\Sigma 3$  GB the MSDs increase generally with

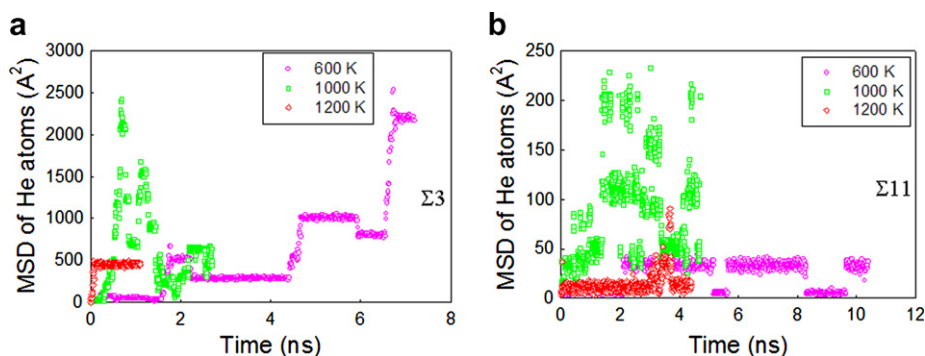


Fig. 3. Mean-square displacements (MSDs) of the di-He interstitial cluster as a function of time for the temperature range between 600 and 1200 K on (a) the  $\Sigma 3$  GB and (b) the  $\Sigma 11$  GB. The MSDs in the  $\Sigma 3$  GB are much larger than those in the  $\Sigma 11$  GB.

increasing time for the temperatures of 600, 800 and 1000 K, but there exist significant fluctuations. During the simulation, a large number of He jumps are observed, and the di-He interstitial cluster mainly migrates along a  $\langle 110 \rangle$  direction in the plane containing the interface, which is similar to that observed for a single He interstitial. It should be noted that this direction is perpendicular to the interface axis. The di-He interstitial cluster mainly migrates one-dimensionally within the interface for all the temperatures considered, suggesting its strong bonding to the interface (the binding energy is estimated to be 1.4 eV). The migration behavior of the di-He interstitial cluster is slightly different from that of the single He interstitial which can change its migration path from 2D diffusion to 3D diffusion, depending on the temperature. The dissociation of the two He atoms is not observed at any of the temperatures considered.

One very interesting result observed for the migrating di-He interstitial cluster is that the MSD at 1200 K initially increases as time advances, but it is almost constant during subsequent simulations. A detailed atomic analysis of this situation reveals that the migrating di-He interstitial cluster causes a Fe atom to be ‘kicked out’ from its lattice site, resulting in the creation of a vacancy and a self interstitial atom (SIA). The SIA immediately migrates away from the di-He interstitial cluster, and this leads to the formation of a  $\text{He}_2\text{V}$  complex. The SIA diffuses rapidly along the  $[1\bar{1}1]$  direction that is parallel to the interface axis, and the diffusion behavior is similar to that of a SIA in the bulk Fe. However, in the bulk a SIA migrates mainly along a single  $\langle 111 \rangle$  direction, but it can easily change orientation from one  $\langle 111 \rangle$  direction to another, which leads to three-dimensional diffusion at high temper-

ature. In the  $\Sigma 3$  GB the SIA migrates only along the interface axis even at high temperatures, and this may be due to the strong binding of a SIA to the interface. A similar kick-out mechanism is also observed for the simulation temperature of 1000 K at about 1.7 ns. After a SIA is kicked out from its lattice site, the  $\text{He}_2\text{V}$  complex is observed to be very stable, and the subsequent simulations only involve the configuration changes of the complex without significant diffusion. Thus the  $\text{He}_2\text{V}$  complex might serve as a smallest nucleation object for bubble formation at interfaces, but this needs to be confirmed by simulating the diffusion of He atoms with different He concentration. In the present simulations, the diffusion coefficients of a di-He interstitial cluster cannot be estimated from the MSDs because the high temperature simulations result in the generation of a Frenkel pair.

The MSDs in Fig. 3(b) shows that significant diffusion of the di-He interstitial cluster does not occur for the  $\Sigma 11$  GB at the temperatures of 600 and 1200 K. Although a number of jumps are observed at 1000 K, the MSDs are much smaller than those obtained in the  $\Sigma 3$  GB. This may imply that the mobility of the di-He interstitial cluster in the  $\Sigma 11$  is lower than that in the  $\Sigma 3$  GB, and activation energy is higher. Similar to the simulations at 1200 K in the  $\Sigma 3$  GB, a SIA is emitted by the di-He interstitial cluster, and the SIA diffuses away from the cluster within a very short simulation time, resulting in the formation of a  $\text{He}_2\text{V}$  complex. In general, the SIA mainly migrates along the interface with  $\langle 110 \rangle$  migration mode. The  $\text{He}_2\text{V}$  complex is essentially immobile and may serve as a smallest nucleation object for bubbles formation at the interface, as discussed above. Again, the MSDs obtained do not provide sufficient data for evaluating the

diffusion coefficients of a di-He interstitial cluster and the corresponding activation energy in the  $\Sigma 11$  GB. The dimer method may be applied to calculate the activation energy barriers for a di-He interstitial cluster and the energy required for the emission of a SIA, which needs further investigations.

## 5. Summary

The diffusion of He interstitials and small He clusters along the  $\Sigma 11\langle 110 \rangle\{323\}$  and  $\Sigma 3\langle 110 \rangle\{112\}$  GBs in  $\alpha$ -Fe has been studied using molecular dynamics methods. From the diffusion coefficient of a single He interstitial, the effective migration energies were determined to be 0.22 eV and 0.34 eV for  $\Sigma 3\langle 110 \rangle\{112\}$  and  $\Sigma 11\langle 110 \rangle\{323\}$  GB respectively. The single He interstitial diffuses in the  $\Sigma 11$  GB with one-dimensional migration along the  $[1\bar{1}3]$  direction, whereas it migrates two-dimensionally at low temperatures, and three-dimensionally at higher temperatures in the  $\Sigma 3$  GB.

The MSDs of a di-He interstitial cluster in the  $\Sigma 3$  GB are much larger than those in the  $\Sigma 11$  GB, which is consistent with the fact that the di-He interstitial cluster is mobile in the  $\Sigma 3$  GB at low temperatures. At higher temperature in both the  $\Sigma 3$  and  $\Sigma 11$  GBs the di-He interstitial cluster can kick out a lattice atom, creating an SIA and a di-He-vacancy complex. The SIA migrates rapidly along the interfaces, with  $\langle 111 \rangle$  crowdion and  $\langle 110 \rangle$  migration mechanisms in the  $\Sigma 3$  and  $\Sigma 11$  GBs, respectively. The two He atoms and a vacancy form a  $\text{He}_2\text{V}$  complex and its mobility is very low. The  $\text{He}_2\text{V}$  complex may serve as a smallest nucleation site for the formation of helium bubbles at interfaces. The different activation energies and different diffusion mecha-

nisms of the single He interstitial in these two representative grain boundaries suggest that the varying atomic structures of the grain boundaries are important for the diffusivity of He interstitials.

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## References

- [1] E.E. Bloom, *J. Nucl. Mater.* 258–263 (1998) 7.
- [2] H. Ullmaier, *Nucl. Fus.* 24 (1984) 1039.
- [3] K. Farrell, P.J. Maziasz, E.H. Lee, L.K. Mansure, in: H. Ullmaier (Ed.), *Fundamental Aspect of Helium in Metals*, *Radiat. Eff.*, vol. 78, 1983, p. 1.
- [4] S.J. Zinkle, N.M. Ghoniem, *Fusion Eng. Des.* 51&52 (2000) 55.
- [5] K. Morishita, R. Sugano, B.D. Wirth, T. Diaz de la Rubia, *Nucl. Instrum. and Meth. B* 202 (2003) 76.
- [6] B.D. Wirth, E.M. Bringa, *Phys. Scr. T* 108 (2004) 80.
- [7] R.J. Kurtz, H.L. Heinisch, *J. Nucl. Mater.* 329–333 (2004) 1199.
- [8] F. Gao, H.L. Heinisch, R.J. Kurtz, *J. Nucl. Mater.* 351 (2006) 133.
- [9] M.I. Baskes, V. Vitek, *Metall. Trans. A* 16 (1985) 1625.
- [10] P.A. Thorsen, J.B. Bilde-Sørensen, B.N. Singh, *Mater. Sci. Forum* 207–209 (1996) 445.
- [11] R.J. Kurtz, R.G. Hoagland, J.P. Hirth, *Philos. Mag. A* 79 (1999) 665.
- [12] R.J. Kurtz, R.G. Hoagland, J.P. Hirth, *Philos. Mag. A* 79 (1999) 683.
- [13] G.J. Ackland, D.J. Bacon, A.F. Calder, T. Harry, *Philos. Mag. A* 75 (1997) 713.
- [14] W.D. Wilson, R.D. Johnson, *Rare Gases in Metals*, in: P.C. Gehlen, J.R. Beeler Jr., R.I. Jaffee (Eds.), *Interatomic Potentials and Simulation of Lattice Defects*, Plenum, 1972, p. 375.
- [15] D.E. Beck, *Mol. Phys.* 14 (1968) 311.