

**DIFFUSION OF He INTERSTITIALS IN GRAIN BOUNDARIES IN  $\alpha$ -Fe**—F. Gao, H. L. Heinisch, and R. J. Kurtz (Pacific Northwest National Laboratory)

**OBJECTIVE**

The objective of this research is to study the migration and diffusion mechanisms of He atoms in grain boundaries in  $\alpha$ -Fe using molecular dynamics and to assess the effects of different grain boundaries on activation energies and diffusion mechanisms of He interstitials.

**SUMMARY**

The migration and diffusion mechanisms of interstitial He atoms at two representative grain boundaries in  $\alpha$ -Fe,  $\Sigma 11\langle 110 \rangle \{323\}$  and  $\Sigma 3\langle 110 \rangle \{112\}$ , are studied using molecular dynamics. The migration of He atoms was followed for 10 – 30 ns, at temperatures between 600 and 1200 K. The diffusion coefficient of He atoms is calculated using the mean square displacements of He atoms, and the effective migration energies were determined to be 0.32 and 0.44 eV for  $\Sigma 11\langle 110 \rangle \{323\}$  and  $\Sigma 3\langle 110 \rangle \{112\}$  GBs, respectively. He interstitial diffuse quickly in the  $\Sigma 11$  GB with one-dimensional behavior along the GB directions, while it migrates one-dimensionally at low temperature, two-dimensionally at intermediate temperature and three-dimensionally at higher temperature in the  $\Sigma 3$  GB. The different activation energies and diffusion mechanisms in these two representative grain boundaries suggests that the varying atomic structures of the grain boundaries are important for the diffusivity of He.

**PROGRESS AND STATUS**

**Introduction**

It is generally accepted that grain boundaries provide fast diffusion paths for He atoms, and their accumulation in both bulk and GBs have major consequence for structural integrity of first-wall materials. However, the detail knowledge of He diffusion in both bulk and GBs, trapping and detrapping, interaction of He with microstructures, the importance of small helium-vacancy cluster mobility and helium bubble nucleation processes represent important scientific and technological issues, which demand computer simulations to obtain insight and fundamental understanding of the complex atomic-level processes of He atoms controlling microstructural evolution in advanced ferritic steels. We have initiated a systematic study to characterize the interaction of He with extended defects (dislocations and GBs) in a fusion relevant structural material such as ferritic steel. The grain boundary structures and binding He to GBs in  $\alpha$ -Fe have been explored previously using computer simulations [1]. Atomic calculations demonstrate strong binding of He to GBs in  $\alpha$ -Fe, and both substitutional and interstitial He atoms are trapped at GBs. We report here on the results of MD simulations of helium migration and its diffusion mechanisms in grain boundaries studied using molecular dynamics methods. The correlation of these results with the binding properties of He atom at GBs is also discussed.

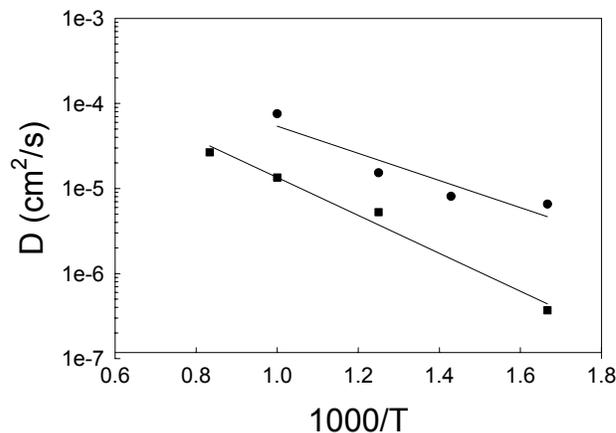
**Modeling**

The model consists of a two-part computational cell, rectangular in shape. The inner part, region I contains movable atoms, while region II supplies neighbors for region I, with a semi-rigid boundary condition. The equilibrium structures of GBs at 0 K are obtained via relaxation using molecular dynamics with an energy quench. The two grains are free to move and undergo homogenous displacement in all three directions, which occurs during relaxation via a viscous drag algorithm. Periodic boundary conditions are applied to the directions perpendicular to the normal direction of the GB plane. Two symmetric tilt GBs are employed to study He diffusion, all with a common  $\langle 101 \rangle$  tilt axis. The two GBs are  $\Sigma 3\{112\}$   $\Theta=70.53^\circ$  and  $\Sigma 11\{323\}$   $\Theta=50.48^\circ$ , consisting of 18816 and 17976 atoms, respectively. MD simulations of He diffusion were performed in the temperature range from 600 K to 1200 K, and the migration of He atoms were followed for 10 – 30 ns, which depends on temperature. The diffusivity and self-diffusion coefficient of He atoms can be determined from summation of the mean square

displacements (MSD) of He atoms and the mean square displacements of all atoms  $N$  in the simulation cell, respectively. With self-diffusion coefficients obtained at different temperatures, the activation energy for He migration in GBs,  $E_m$ , can be estimated from the Arrhenius relation. In all cases the set of interatomic potentials due to Ackland[2], Wilson and Johnson[3], and Beck[4] were used for the Fe-Fe, Fe-He and He-He interactions, respectively.

## Results

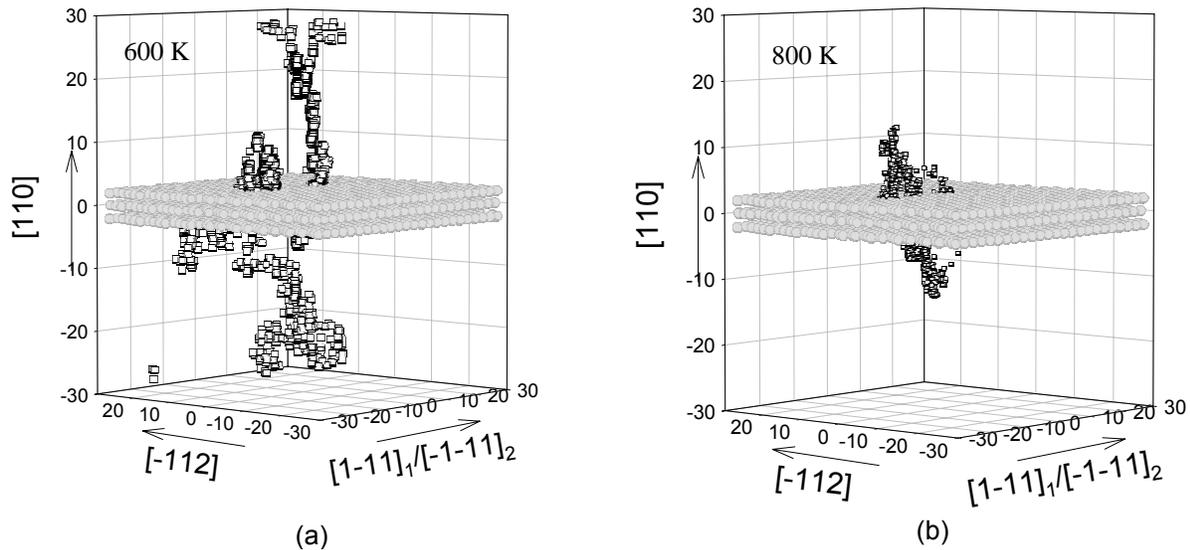
The lowest energy configurations of single He atom at the GBs were determined by the procedure described in the previous section. The most stable configuration of He interstitial in the  $\Sigma 3$  GB is found to form a  $\langle \bar{1}11 \rangle$  crowdion defect with Fe atoms, while a tetrahedral He interstitial is the most stable configuration in the  $\Sigma 11$  GB. These stable configurations are used as the initial starting configurations, and the migration of He interstitials was investigated at the temperature range of between 600 and 1200K. The mean square displacements (MSDs) of all the atoms and the He interstitial can be determined as a function of time. 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 diffusion coefficients estimated for the He interstitial in both GBs are given in Fig. 1 as a function of reciprocal temperature, where circle symbols represent the data calculated for the  $\Sigma 3$  GB and square symbols indicate the data obtained for the  $\Sigma 11$  GB. The data approximately follow an Arrhenius relationship, from which the corresponding activation energies,  $E_m$ , and preexponential factors,  $D_0$ , can be determined. The best fits to the data give the values of  $E_m$  and  $D_0$  to be 0.32 eV and  $2.15 \times 10^{-3} \text{ cm}^2/\text{s}$  for the  $\Sigma 3$  GB, and 0.44 eV and  $2.3 \times 10^{-3} \text{ cm}^2/\text{s}$  for the  $\Sigma 11$  GB, respectively. It should be noted that the data at 1200 K in the  $\Sigma 3$  GB is excluded for the evaluation of activation energy because the He interstitial dissociates from the GB at this temperature, migrating three-dimensionally. This is consistent with the small binding energy of He interstitials to the  $\Sigma 3$  grain boundary. The migration energies of He interstitials in GBs are slightly higher than that of He interstitials in the bulk (0.08 eV). In the bulk of Fe, a He interstitial has very high mobility, and can migrate from one tetrahedral site to another before becoming deeply trapped as a substitutional helium in a radiation-induced or thermal vacancy. The activation energies obtained in the present work suggest that He interstitials are very mobile in the GBs, and grain boundaries provide fast diffusion paths for He interstitials along some specific directions.



**Fig. 1. Diffusion coefficients of He interstitial as a function of reciprocal temperature in  $\Sigma 3$  and  $\Sigma 11$  GBs in  $\alpha$ -Fe, where reciprocal temperature is scaled by 1000.**

The migration mechanisms of He interstitials in GBs have been studied by carefully analysis of the computer-generated trajectories. The trajectories of the He interstitial in the  $\Sigma 3$  GB are shown in Fig. 2(a)

for the temperature of 600 K, where gray spheres represent Fe atoms in three (110) atomic planes. The middle plane is the plane containing the initial starting site of the He interstitial. At 600 K, the He interstitial mainly migrates along the  $\langle 110 \rangle$  direction that is parallel to the tilt axis, but some displacements are observed along the  $\langle \bar{1}\bar{1}1 \rangle$  direction. This can be also demonstrated by plotting the components of the MSD along  $\langle 110 \rangle$ ,  $\langle \bar{1}\bar{1}1 \rangle$  and  $\langle \bar{1}\bar{1}2 \rangle$  directions as a function of time, and the large increase in the MSD is due to the contribution of the  $\langle 110 \rangle$  component. These results suggest that the He interstitial mainly migrates with one-dimensional behavior at low temperature. However, the migration path of the He interstitial changes from one-dimensional (1D) diffusion to two-dimensional (2D) diffusion with increasing temperature. The trajectories of the He interstitial at 800 K are shown in Fig. 2(b). The further increase in temperature (up to 1200K) leads to the dissociation of the He interstitial from the  $\Sigma 3$  GB because of its small binding energy to that GB. In fact, the He interstitial has the lowest binding energy in the  $\Sigma 3\{112\}$  shown in Fig. 2, among all the GBs calculated.[1]. Dissociation from this GB allows for the He interstitial to also migrate along the  $\langle \bar{1}\bar{1}2 \rangle$  direction, resulting in three-dimensional (3D) diffusion. It is important to point out that the activation energy obtained for He migration in the  $\Sigma 3$  GB is an effective activation energy. The temperature dependence of the MSD along different directions suggests that the migration barrier along the  $\langle 110 \rangle$  direction should be lower than that along the  $\langle \bar{1}\bar{1}2 \rangle$  direction.

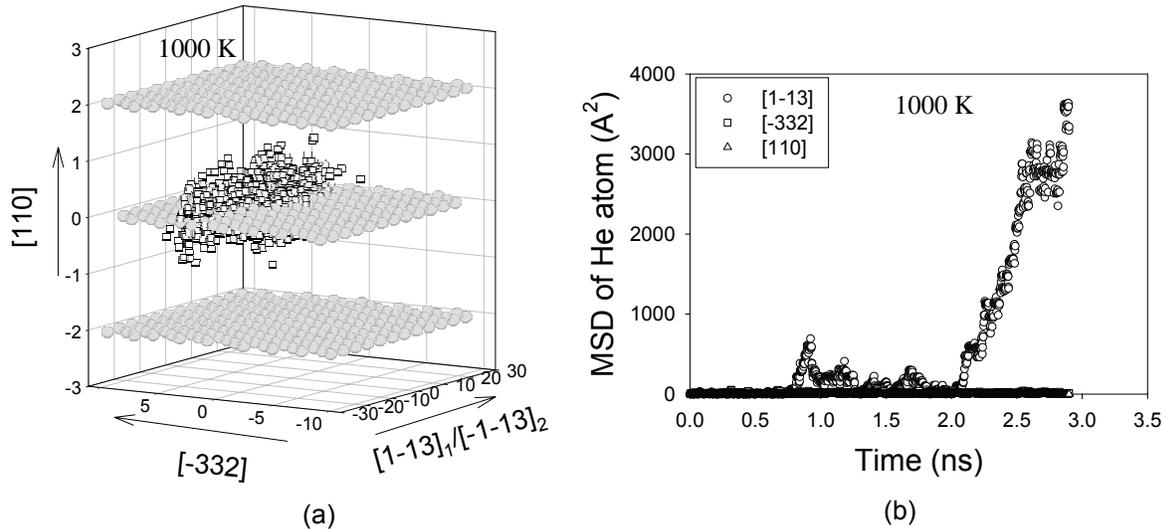


**Fig. 2. Trajectories of He interstitial at 600 K (a) and at 800 K (b) in  $\Sigma 3$  GB, where three (110) atomic planes at the boundary are presented, as indicated by light spheres.**

The trajectories of He interstitials and their MSD along three independent directions in the  $\Sigma 11$  GB at 1000 K are shown in Figs. 3(a) and (b), respectively. Similar to the plots in Fig. 2, only three atomic planes normal to the tilt axis are presented in Fig. 3(a). Although the He interstitial can move in the spaces between three planes, it is strongly bound to the middle plane on which the initial starting position of the He interstitial is allocated. It is of interest to note that the He interstitial migrates one-dimensionally along the  $\langle 1\bar{1}3 \rangle$  direction, even at higher temperature. Also, the MSD in Fig. 3(b) indicates that the He interstitial migrates only along  $\langle 1\bar{1}3 \rangle$ , giving rise to the increase in the MSD.

Although only two GBs have been used in these simulations of the diffusion of He interstitials, the results have indeed demonstrated that He diffusion and the corresponding migration mechanisms depend significantly on the atomic structures of the GBs. Earlier studies showed that there is a strong correlation between the binding energy of an interstitial He atom and the excess atomic volume in the GB [1]. The  $\Sigma 3$

GB has the smallest excess atomic volume and the smallest maximum binding energy for He. In the  $\Sigma 3$  GB He atoms demonstrate an ability to migrate three-dimensionally, including hopping out of the boundary into the matrix. On the other hand, the  $\Sigma 11$  GB has about eight times more excess volume, He atoms have binding energy three times greater than in the  $\Sigma 3$  GB, and they are restricted to one-dimensional migration within the GB. One might expect that this variation in diffusion mechanisms of He interstitials in GBs should have significant effects on bubble nucleation at different GBs.



**Fig. 3.** (a) Trajectories of He interstitials at 1000 K in a  $\Sigma 11$  GB, where three (110) atomic planes are presented, as indicated by light spheres, and (b) MSD of He interstitials along  $\langle 1\bar{1}3 \rangle$ ,  $\langle \bar{3}32 \rangle$ , and  $\langle 110 \rangle$  directions at the same temperature.

## Conclusions

Helium diffusion along the GBs in  $\alpha$ -Fe has been studied using molecular dynamics methods, and two grain boundaries,  $\Sigma 11\langle 110 \rangle\{323\}$  and  $\Sigma 3\langle 110 \rangle\{112\}$ , were used for the current investigations. The migration of He atoms were followed for 10–30 ns, at temperatures between 600 and 1200 K. The diffusion coefficient of He atoms is calculated using the mean square displacements of He atoms, and the effective migration energies were determined to be 0.32 and 0.44 eV for  $\Sigma 11\langle 110 \rangle\{323\}$  and  $\Sigma 3\langle 110 \rangle\{112\}$  GBs, respectively. We found that in the  $\Sigma 11$  GB, where excess volume is larger and He binding energy is high, He atoms easily diffuse one-dimensionally along specific directions, with a few directional changes observed at higher temperatures. However, He atoms migrate one-dimensionally at low temperature, two-dimensionally at intermediate temperature and three-dimensionally at higher temperature in the  $\Sigma 3$  GB, where excess atomic volumes are smaller and the binding energy of a He atom is lower. The different activation energies and diffusion mechanisms in these two representative grain boundaries suggests that the varying atomic structures of the grain boundaries, particularly regarding excess atomic volume, are important for the diffusivity of He atoms.

## References

- [1] R. J. Kurtz and H. L. Heinisch, J. Nucl. Mater. 329–333 (2004) 1199.
- [2] G. J. Ackland, D. J. Bacon, A. F. Calder, and T. Harry, Philos. Mag. A75 (1997) 713.
- [3] W. D. Wilson and R. D. Johnson: Interatomic Potential and Simulation of Lattice Defects, Plenum, (1972) 375.
- [4] D. E. Beck, Mol. Phys. 14 (1968) 311.