

**DIFFUSION OF He INTERSTITIAL AND SMALL CLUSTERS AT GRAIN BOUNDARIES IN  $\alpha$ -Fe—**  
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**EXTENDED ABSTRACT** (submitted to the Journal of Nuclear Materials as part of the proceedings of the 12<sup>th</sup> International Conference on Fusion Reactor Materials, Santa Barbara, California, December 4–9, 2005)

A systematic molecular dynamics study of the diffusion mechanisms of He interstitial and their small clusters at two representative interfaces,  $\Sigma 11$  and  $\Sigma 3$ , has been carried out in  $\alpha$ -Fe. The diffusion coefficient of a He interstitial and the effective migration energies were determined, and the diffusion mechanisms of single interstitials and di-He interstitials are discussed in detail. 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 a smallest nucleation for the formation of helium bubbles at interfaces.

Most of the details pertaining to the methodology used in the calculations of the atomic arrangements of GBs have been described in detail elsewhere [1,2]. Two symmetric tilt GBs,  $\Sigma 3 \{112\} \Theta = 70.53^\circ$ ,  $\Sigma 11 \{323\} \Theta = 50.48^\circ$ , were employed to study diffusion of He interstitials and small clusters in the temperature range from 600 to 1200 K. The interatomic potentials used in this research have been described in detail previously [3]. 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. 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 where  $D_0$  is the pre-exponential factor and  $k_\beta$  is the Boltzmann constant.

$$D = D_0 \exp\left(-\frac{E_m}{k_\beta T}\right), \quad (1)$$

The mean square displacements of a He interstitial are determined as a function of time for the  $\Sigma 3$  and  $\Sigma 11$  GB using the method described above. 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. 3 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 pre-exponential factors,  $D_0$ , can be determined. The best fits of these results to Eq (1) give the values of  $E_m$  and  $D_0$  to be 0.28 eV and  $4.39 \times 10^{-4} \text{cm}^2/\text{s}$  for the  $\Sigma 3$  GB, and 0.34 eV and  $4.3 \times 10^{-4} \text{cm}^2/\text{s}$  for the  $\Sigma 11$  GB, respectively.

The migration mechanisms of He interstitials in GBs have been studied by analysis of the computer-generated trajectories. The result suggests that the He interstitial mainly migrates with one-dimensional behavior at low temperature. However, it has been observed that the migration path of the He interstitial changes from one-dimensional (1D) diffusion to two-dimensional (2D) diffusion in the interface plane at

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800 K and three-dimensional (3D) diffusion at higher temperatures in 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 [4]. 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 it can only move in the spaces between the three planes. These results demonstrate that interstitial He diffusion and the corresponding migration mechanisms depend significantly on the atomic structures of the GBs.

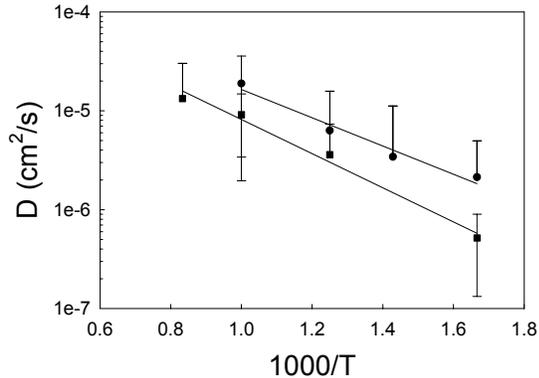


Fig. 1. Diffusion coefficients of He interstitial as a function of reciprocal temperature in the  $\Sigma 3$  and  $\Sigma 11$  GBs in  $\alpha$ -Fe, where reciprocal temperature is scaled by 1000.

Figures 2(a) and (b) show 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 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.

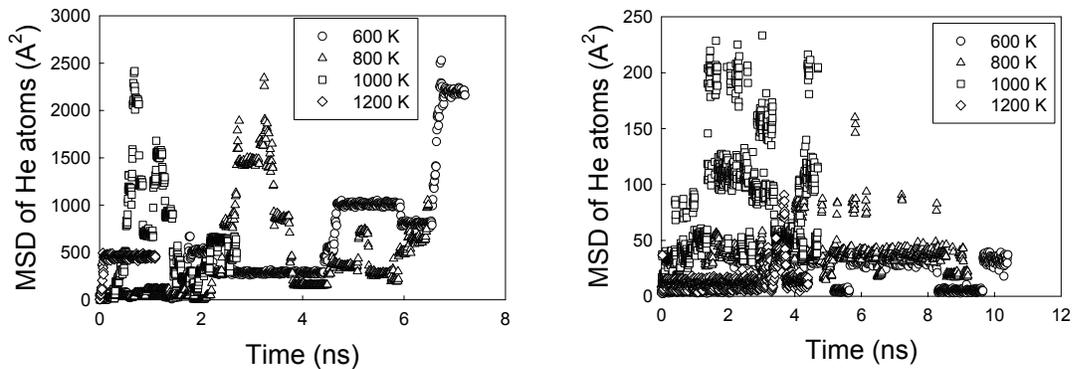


Fig. 2. Mean-square displacements of the di-He interstitial cluster as a function of time for the temperature range between 600 and 1200 K on (a) the  $\Sigma 3$  GB and (b) the  $\Sigma 11$  GB.

The 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 an 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.

Figure 3 shows the creation of a SIA that has a crowdion configuration along the  $[1\bar{1}1]$  direction, and two He atoms, where the vacancy between them is not plotted. The large dark spheres represent Fe atoms, the small gray spheres vacant sites and the large gray spheres He atoms. 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 concentrations at interfaces. 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. Similar to the simulations at 1200 K in the  $\Sigma 3$  GB, a SIA is also emitted by the di-He interstitial cluster in the  $\Sigma 11$  GB, 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.



Fig. 3. Atomic plot showing the emission of a self interstitial atom that forms a  $\langle 111 \rangle$  crowdion.

## Conclusions

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. The diffusion coefficient of a single He interstitial is calculated using the mean square displacements of He atoms, and the effective migration energies were determined to be 0.28 eV and 0.34 eV for  $\Sigma 3 \langle 110 \rangle \{112\}$  GBs, and  $\Sigma 11 \langle 110 \rangle \{323\}$ , respectively. 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 self interstitial atom, and 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  $\text{H}_2\text{V}$  complex may serve as a smallest nucleation site for the formation of helium bubbles at interfaces.

## References

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