6.1 DIFFUSION OF He INTERSTITIALS AND He CLUSTERS IN α-Fe—H. Deng (Hunan University), F. Gao, H. L. Heinisch and R. J. Kurtz (Pacific Northwest National Laboratory)

OBJECTIVE

To study the diffusion properties of He interstitials and He clusters in the bulk and in grain boundaries of α-Fe with a newly developed Fe-He potential.

SUMMARY

The accumulation of He atoms in materials will significantly degrade the mechanical properties of materials; therefore, understanding the properties of He interstitials and their clusters in materials is of fundamental importance within a fusion reactor environment. The diffusion properties of single He interstitials and He clusters in the bulk and grain boundaries of α-Fe are being studied using molecular dynamics with a new Fe−He potential. It is found that the migration barrier for a single He interstitial in the bulk is very low, which is consistent with the result obtained using *ab initio* methods. Large He clusters can cause Fe self-interstitial atoms (SIA) to be formed, which can be trapped by the resulting vacancy, forming a He-vacancy complex. It is found that for He interstitials in grain boundaries (GBs), the He migration is one-dimensional in a Σ11 GB, while it is two-dimensional in a Σ3 GB at 600 K and three-dimensional at higher temperatures.

PROGRESS AND STATUS

Introduction

It is well known that first wall materials of a fusion power system will be exposed to a high concentration of He generated by (n, α) transmutation reactions caused by 14 MeV neutron irradiation [1]. Because of the extremely low solubility of He in materials, He atoms tend to be trapped at defects, such as vacancies, dislocations, and grain boundaries (GBs) [2, 3]. The accumulation of He atoms in materials results in the formation of He bubbles, which can lead to void swelling and produces low-temperature intergranular embrittlement, surface roughening, blistering, and premature creep rupture at high-temperatures [4]. These phenomena can significantly degrade the mechanical properties of materials, and they are strongly correlated to the diffusion of He defects and their interactions with microstructural features. Therefore, understanding of the migration and diffusion properties of He defects (single He interstitials and clusters) both in the bulk and GBs is of fundamental importance within a fusion reactor environment.

In early simulations, most studies of He behavior in Fe employed the repulsive Fe−He potential of Wilson and Johnson (WJ−potential) [6], which predicted the most stable He interstitial position to be in the octahedral configuration, in contrast to *ab initio* calculations [7–9] that demonstrated that a tetrahedral interstitial position is the most stable site. Recently, several new empirical potentials for Fe−He interaction have been developed [10–14], and all of these Fe−He potentials reproduced well the relative stability of He interstitials.

In our previous work, we have studied the diffusion properties of a He interstitial and a di-He cluster at grain boundaries in α-Fe [15–17]. Terentyev et al., also studied the migration of a He interstitial in <110> tilt grain boundaries in α -Fe [18], and found that the atomic structures of grain boundaries play an important role in the migration mechanism and diffusivity of He interstitials. More recently, Stewart et al., studied the formation and diffusion of He clusters and bubbles in BCC Fe [19]. However, the results obtained from these simulations are found to depend on the empirical potentials used in the Fe−He system. The details of different potentials have been described in a recent paper [20].

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Simulation Methods

In the present simulations the pair interaction and the many-body function for Fe−Fe are those of Ackland and Mendelev [21], and the pair potential for He−He interaction is the Aziz potential [22]. The new Fe−He potential developed at PNNL is used for describing the Fe−He interaction. Similar to the many-body potential formalism, the new Fe−He potential consists of a pair potential and an embedding function, and then the total energy of a Fe−He system can be written as:

$$U = \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} V(r_{ij}) + \sum_{i=1}^{N} F_s(\rho_s^i), \tag{1}$$

where the first term represents a repulsive pair potential and the second term is the many-body interaction that provides the contribution from the s-band electron density. The pair potential can be represented by a summation of cubic knot functions:

$$V(r) = \sum_{k=1}^{8} a_k (r_k - r)^3 H(r_k - r), \tag{2}$$

where $H(r_k - r)$ is the Heaviside function. The many-body interaction function is

$$F_s(\rho_s) = b_1 \sqrt{\rho_s} + b_2 \rho_s^{\ 2} + b_3 \rho_s^{\ 4}. \tag{3}$$

These functions are of the same forms as those for the Fe−Fe interaction [21]. For the mixed-pair density, we have employed the 1s-type and 4s-type Slater functions for He and Fe [23], respectively. The detailed fitting process and potential parameters have been described elsewhere [20]. In the 's-band model', the contribution to the total energy from s-electrons is very small, but it cannot be ignored here.

The diffusion properties are obtained using molecular dynamics simulations. The positions $r_i(t)$ of all the atoms at time t are recorded and the mean-square displacement (MSD) is

$$MSD = \langle |r_i(t) - r_i(0)|^2 \rangle = \frac{1}{N} \sum_{i=1}^{N} |r_i(t) - r_i(0)|^2, \tag{4}$$

where N is the total atomic number and '<···>' denotes averaging over all the atoms. The diffusion coefficient (D) can be obtained with the Einstein-Smoluchowski relation:

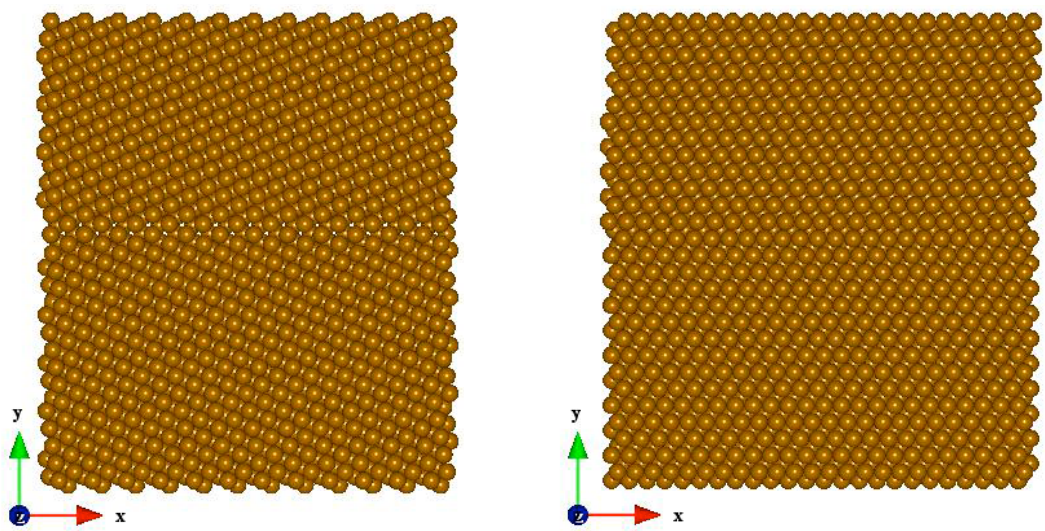
$$D = \lim_{t \to \infty} \frac{MSD}{q_i t} = \lim_{t \to \infty} \frac{1}{q_i t} \langle |r_i(t) - r(0)|^2 \rangle, \tag{5}$$

where q_i is a numerical constant that depends on the dimensionality such that q_i = 2, 4, or 6 for the one-, two- or three-dimensional diffusion, respectively. The relation of the migration energy (E_m) to the diffusion coefficient D is based on the Arrhenius equation:

$$D = D_0 \exp(-E_m / k_B T). \tag{6}$$

The E_m and D can be obtained by fitting the diffusion coefficient to equation (6) over a range of temperatures.

For simulations of the diffusion of He interstitials and He-clusters in the α –Fe bulk, MD boxes of $14a_0 \times 14a_0 \times 14a_0$ with 5488 Fe and $20a_0 \times 20a_0 \times 20a_0$ with 16000 Fe atoms are used, where a_0 is the lattice constant (2.8553Å) of perfect BCC Fe. The time step is chosen to be 1 fs for the molecular dynamics (MD) simulations with the NVT ensemble. The total simulation time for a single He interstitial diffusion is about 2.85 ns, but different MD times for He clusters are used, depending on the cluster size. Two GBs (Σ3{112} and Σ11{323}) have been studied, where periodic boundary conditions were imposed along the *x* and *z* directions, but nonperiodic boundary conditions were applied along the *y* direction [24]. The atomic structures of the two symmetric tilt GBs in α-Fe are Σ3 {112} Θ = 70.53° and Σ11 {323} Θ = 50.48° with a common <101> tilt axis, as shown in Fig. 1. The block size of Σ3 is 59.35Å × 65.74Å × 56.53Å with 18816 Fe atoms, and that of Σ11 is 56.82Å × 65.74Å × 56.53Å with 17976 Fe atoms.



(a) (b)

Fig. 1. Atomic structures of two GBs in α-Fe. (a) Σ11{323}: x → [1 -1 3], y→ [-3 3 2], z→ [110]; and (b) Σ3{112}: x→ [1 -1 1], y→[-1 1 2], z→[1 1 0].

Results and Discussion

It has been found that single He interstitials can migrate easily the Fe matrix. At a given temperature, these He interstitials are subject to a random displacement from their original positions and the trajectories can be tracked during the atomic-scale simulations. The MSD analysis can be used to extract reliable values of the diffusion coefficient D with enough simulation time, and then the migration energy can be obtained by the Arrhenius equation. In the present work, the diffusion properties of single He interstitials and He-clusters in α–Fe have been studied using classic molecular dynamics and MSD analysis, as described below. For He-clusters, the trajectories of the centers of mass were tracked. The temperatures used are different for single He interstitials and He clusters because the He_2-cluster will dissociate, whereas the He_x-clusters (x > 2) will create Fe self-interstitials at high temperatures (as discussed below). For a single He interstitial, the migration behaviour is simulated at 200 ~ 700 K at 100 K intervals. As an example, the MSD of a He interstitial migrating at 500 K is shown in Fig. 2, from which it can be seen that the MSD increases with the diffusion time (as long as 2.85 ns) and shows a linear-like relation.

Single He interstitials migrate three-dimensionally along the different directions, but they can move forward or backward along one direction until they change their direction; thus the MSD is not always linear with the simulation time during a long-time diffusion process. Here the diffusion coefficients are obtained using the so-called trajectory time decomposition (TTD) technique [25], which decomposes a single long trajectory of interstitials or clusters into a sequence of short independent trajectory segments.

Based on the Arrhenius equation and the MSD calculated with the TTD technique, the migration energy and diffusion coefficient for a single He interstitial are 0.039 eV and 1.55×10^{-8} m^2/s, respectively, as shown in Fig. 3 and Table 1. The migration energy is slightly smaller than the value of 0.058 eV calculated by the dimer method [20], which is in good agreement with the migration energy of 0.06 eV determined by *ab initio* calculations [8]. With different empirical Fe−Fe and Fe−He potentials, Stewart et al. [11] studied the diffusion property of single He interstitials in α-Fe, and found that the diffusion rates are similar (2.23 ~ 9.64 $\times10^{-8}$ m^2/s) and the migration energies are 0.107, 0.043, and 0.062eV with different Fe−He potentials (Wilson potential [6], ORNL potential [10] and Juslin-Nordlund potential [12], respectively). However, the above results indicate that the migration barrier of a He interstitial in the Fe matrix is very low, and it is slightly underestimated in the dynamics simulations with the new Fe−He potential.

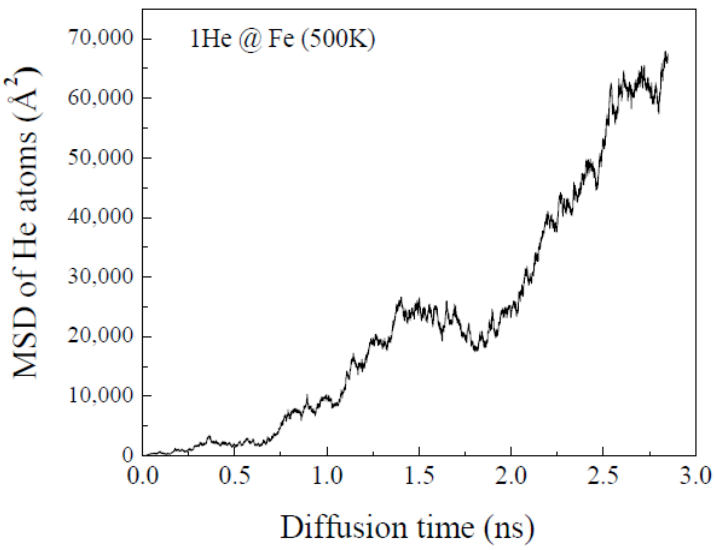


Fig. 2. MSD of a single He interstitial diffusing in Fe matrix as a function of time at 500 K

Table 1. Migration barriers and diffusion coefficients of He interstitial and clusters in α-Fe

Cluster	Migration Energy (eV)	Diffusion Coefficient (10^{-8} m^2/s)
1 He	0.039	1.55
2 He	0.090	1.47
3 He	0.097	1.10
4 He	0.103	0.45

For a He_2-cluster, it was found that the two He atoms will dissociate completely into two He interstitials when the temperature is higher than 400 K, and thus the MSDs were calculated at temperatures between 200 K and 400 K. As shown in Fig. 3 and Table 1, the migration energy and diffusion coefficient for a He_2-cluster are 0.090 eV and 1.47×10^{-8} m^2/s, respectively. No SIA formation is observed for a He_2-cluster diffusing in the Fe matrix.

When the size of a He cluster is larger than 3, it is always observed that an Fe SIA is created by the He cluster at the temperatures higher than 600 K. Fig. 4 shows a typical MSD for He_3-cluster migration in an Fe matrix at 700 K. The MSD increases quickly with increasing simulation time, but remains constant when an SIA is formed. Then the He-vacancy complex appears, and the He cluster is trapped by the vacancy. It is of interest to find that although the center of mass of the He-vacancy cluster does not change with time, the He atoms rotate quickly around the vacancy. However, when the Fe SIA moves

close to the He-vacancy cluster, recombination of the SIA with the vacancy occurs. During this process, the He cluster becomes mobile again, and it can quickly migrate in the Fe matrix, leading to an increase of the MSD, as indicated by the hatched region in Fig. 4. The processes of SIA formation and recombination with the vacancy within the He-vacancy cluster occurred several times during the present simulation. The minimum temperature for creating a SIA depends on the size of He cluster, and it is found that the larger the size, the lower the formation temperature. For example, a He_3-cluster can create a SIA when the temperature is 700 K or higher; a He_4-cluster creates a SIA when the temperature is higher than 400 K; a He_7 or larger causes SIA formation even if the temperature is as low as 100 K, which suggests that the large cluster is almost immobile in the Fe matrix over the temporal scale explored in these simulations.

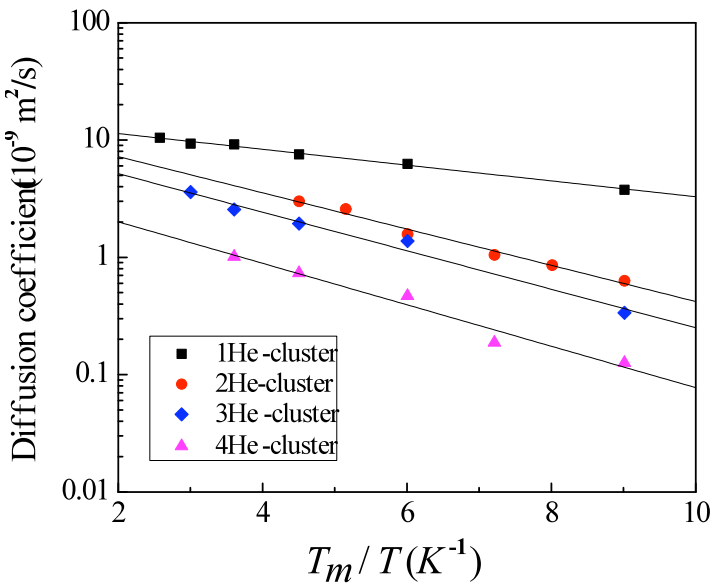


Fig. 3. Arrhenius plots for a single He atom and He clusters to diffuse in Fe matrix

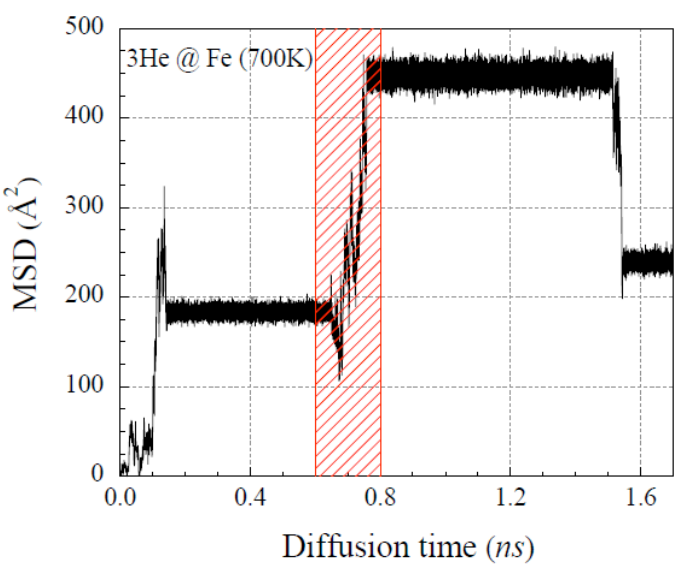
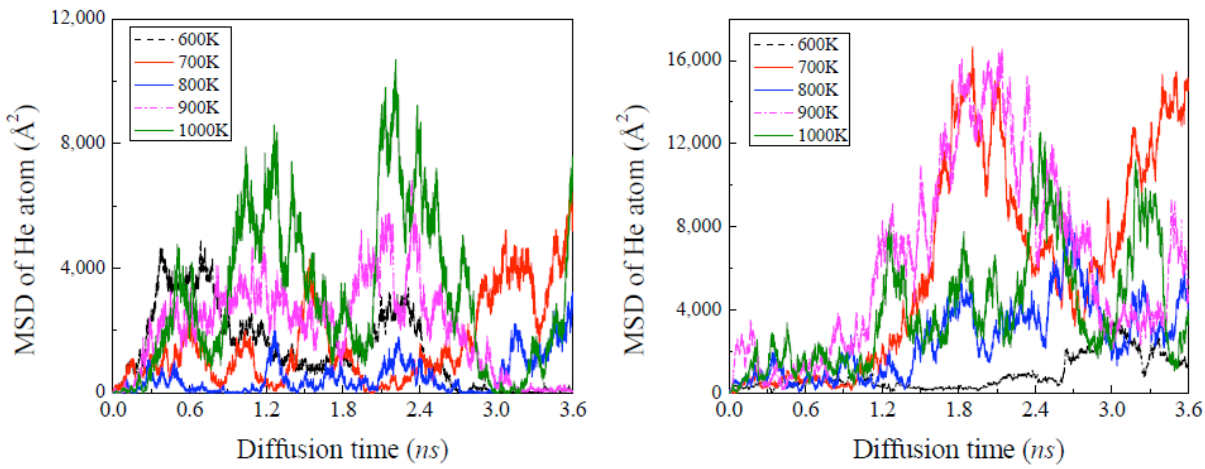


Fig. 4. MSD of a He_3-cluster diffusing in Fe matrix as a function of time at 700 K

Due to the fact that the time for creation of a SIA from a large He cluster (with more than five He atoms) at low temperature is very short (~5 ps), and the cluster is trapped by the vacancy, the MSDs for these large He clusters are very difficult to obtain. Considering the SIA formation temperature, the MSDs have been obtained from 200 - 600 K, or 200 - 500 K for the He_3 and He_4 clusters, respectively. The migration energies and diffusion coefficients are shown in Table 1 and Fig. 3, and they are determined to be 0.097 and 0.103 eV, and 1.10×10^{-8} and 0.45×10^{-8} m^2/s for the He_3 and He_4 cluster, respectively. In the report of Stewart et al., [19], the diffusion coefficients and migration energies of He_x-clusters (x = 1~ 6) were also calculated using the ORNL three-body potential. The diffusion coefficients are similar with those obtained in the present study, but the migration energies are slightly higher. There are also other differences between Stewart's and our results. In our calculations, for example, the He_2-cluster will dissociate completely when the temperature is higher than 400 K, and the large He_x-cluster (x > 4) will create a Fe SIA in very short time (less than 100 ps) and be trapped by the vacancy even at temperatures much lower than 700 K (at which the emission of a SIA occurs in their simulations). Thus, we cannot obtain the MSDs for these clusters at this temperature.

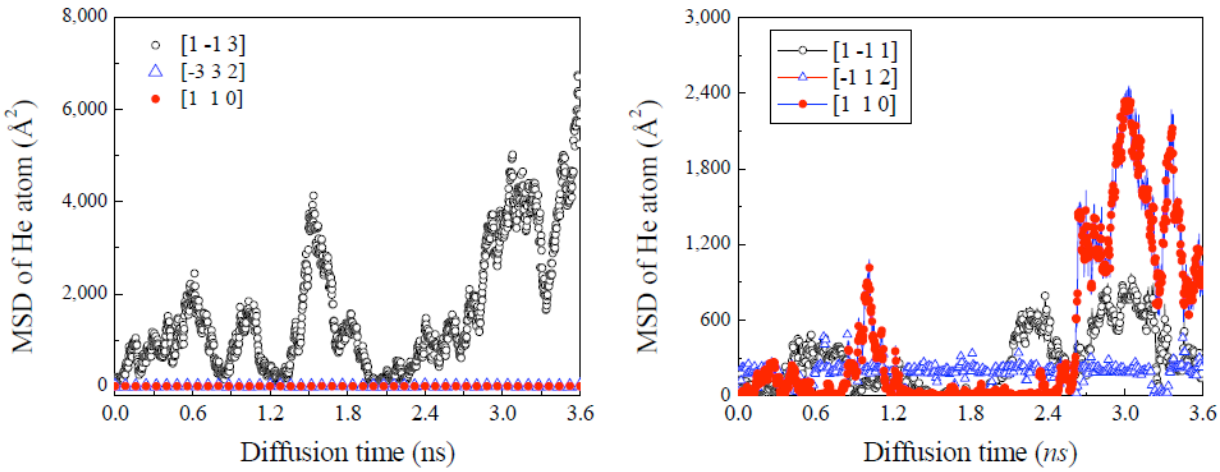
Both Σ11 and Σ3 GBs have a common <110> tilt axis and are used to study the effect of GB structure on He diffusion. The lowest energy configurations of a single He interstitial at the GBs were determined by an annealing simulation at 1000 K for 10 ps using molecular dynamics and then, slowly cooling down to 0 K [15]. The configurations of He_x-clusters at the GBs were determined by the same method. These configurations were used as starting configurations for calculating MSDs during the diffusion of He interstitials and their clusters. The results of the MSDs for a single He interstitial to diffuse at Σ11 and Σ3 GBs at different temperatures (600 ~ 1000 K) are shown in Fig. 5(a) and (b), respectively.



(a) (b)

Fig. 5. The MSDs of a He interstitial diffusing along the different directions at Fe GBs as a function of time. (a): Σ11 GB and (b) Σ3 GB

In the Σ11 GB it is found that He interstitial migration is mainly along the $[1\bar{1}3]$ direction, as shown in Fig. 6a, which means that the He interstitial migrates one-dimensionally. The same phenomena have been observed at all the temperatures considered here. Based on the MSDs with TTD analysis, the diffusion coefficients were determined, and they obey an Arrhenius relation (Eq. (6)), as shown in Fig. 7. The best-fit migration barrier (E_m) and pre-exponential factor (D_0) are 0.172 eV and 4.26×10^{-8} m^{-2}/s, respectively. It is of interest to note that the present D_0 agrees well with that of our previous calculations, but the migration energy, E_m, is lower than determined previously [15, 16].



(a) (b)

Fig. 6. The MSDs of a He interstitial diffusing along different directions; (a) Σ11 GB at 700 K and (b) Σ3 GB at 600 K

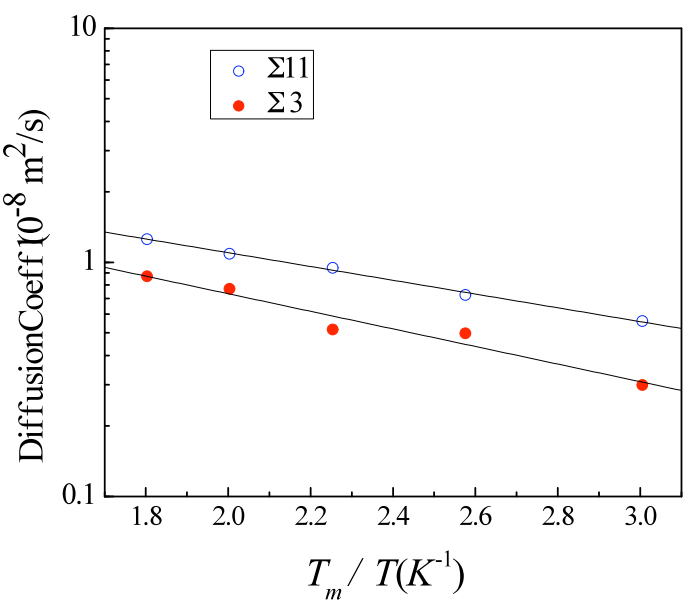


Fig. 7. Arrhenius plots for a single He interstitial diffusing at Σ11 and Σ3 GBs in α-Fe

In the Σ3 GB, it is found that the He interstitial can migrate along both the [110] and [1$\bar{1}$1] directions at 600 K, as demonstrated by the MSDs in Fig. 6b, which means that He migration is two-dimensional at low temperatures. When the temperature is higher than 700 K, the migration behavior of the He interstitial changes from two-dimensional diffusion to three-dimensional diffusion. The present results agree well with those of Terentyev et al. [18] and our previous results [16] with different empirical potentials, where it was found that He atoms migrate two- and three-dimensionally at low and high temperatures, respectively. The diffusion coefficients have also been determined using MSD and TTD analysis and they obey an Arrhenius relation, as shown in Fig. 7. The best-fit E_m and D_0 are 0.224 eV and 4.14×10^{-8} m^{-2}/s, respectively. Also the present D_0 agrees well with those of both Terentyev et al. [18] and our previous simulations with different potentials [15, 16]; and the present E_m agrees well with that of Terentyev et al. [18], but it is slightly lower than our previous result [15, 16].

Conclusions

Based on the present calculations, it is clear that a single He interstitial in Fe has very high mobility because of a very low migration barrier. Large He-clusters will create an SIA and are trapped by the resulting He-vacancy complex. The migration energies of He interstitials in Fe GBs are higher than those of He interstitials in bulk Fe. The migration of He interstitials in Σ11 and Σ3 GBs is relative to the special directions in the GBs, which suggests that the GBs may provide fast diffusion paths for He migration. An He interstitial migrates one-dimensionally along the Σ11 GB, while it migrates two-dimensionally at temperatures lower than 600 K and three-dimensionally at higher temperatures in the Σ3 GB.

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