Atomistic Simulations of Helium Clustering and Grain Boundary Reconstruction in Alpha-Iron

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Abstract

The accumulation and clustering of He atoms at $\Sigma 3$ $\langle 110 \rangle$ $\{112\}$ and $\Sigma 73b$ $\langle 110 \rangle$ $\{661\}$ grain boundaries (GBs) in bcc Fe, as well as their effects on GB reconstruction, have been investigated using atomic-level computer simulations. The accumulation of He atoms and the evolution of the GB structure all depend on local He concentration, temperature and the original GB structure. At a local He concentration of 1%, small He clusters are formed in the $\Sigma 3$ GB, accompanied by the emission of single self-interstitial Fe atoms (SIAs). At a He concentration of 5%, a large number of SIAs are emitted from He clusters in the $\Sigma 3$ GB and collect at the periphery of these clusters. The SIAs eventually form $\langle 100 \rangle$ dislocation loops between two He clusters. It is likely that impurities may promote the formation of $\langle 100 \rangle$ loops and enhance their stabilities in α -Fe. At a He concentration of 10%, the large number of emitted SIAs are able to rearrange themselves, forming a new GB plane within the $\Sigma 3$ GB, which results in self-healing of the GB and leads to GB migration. In contrast to the $\Sigma 3$ GB, He clusters are mainly formed along the GB dislocation lines in the $\Sigma 73b$, and the emitted SIAs are accumulate at the cores of the GB dislocations, leading to the climb of the dislocations within the GB plane. As compared to bulk Fe, a higher number density of clusters form at GBs, but the average cluster size is smaller. The product of cluster density and average cluster size is roughly constant at a given He level, is about the same in bulk and GB regions, and varies linearly with the He concentration.

Keywords: Grain boundary; atomistic simulation; nucleation of He clusters; bcc Fe

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1. Introduction

Because of the extremely low solubility of helium (He) in metallic materials, high concentrations of He created by nuclear transmutation reactions are known to induce the formation of He bubbles, that are associated with the pre-existing and radiation-induced defects and microstructural features such as dislocations and grain boundaries (GBs). In sufficient concentration He can significantly degrade the mechanical properties of materials. In particular, the nucleation and growth of He bubbles at GBs may lead to high-temperature embrittlement, which is manifested by severe loss of creep-rupture strength [1,2]. Production of He in structural materials employed in the fusion nuclear environment will be significant and represents one of the most challenging materials problems to resolve for fusion power generation. The nucleation of He bubbles at microstructural features in metals has been studied using experimental approaches and theoretical methods. Evans *et al.* observed the formation of He clusters at $\langle 100 \rangle$ GB dislocations of low angle tilt GBs in irradiated molybdenum [3]. Baskes *et al* [4] investigated the trapping of He at GBs in nickel using atomistic computer simulations and found that GBs are important trapping sites for He atoms. Furthermore, the size of bubbles at GBs in copper formed by He-implantation was found to increase with increasing GB energy [5], which underscores the importance of GB structure. The nucleation behaviour of He bubbles in single-crystal and nano-grain bcc molybdenum has been investigated using MD simulations [6]. These simulations showed that strong precipitation of He occurs at the GBs in nano-grain molybdenum and the density, size and spatial distribution of He bubbles vary with GB structure. Helium bubble nucleation at low-angle twist boundaries in gold has been investigated [7,8] and it was found that the GBs with well-defined structures (pure twist boundaries) could trap He atoms forming a super-lattice of small bubbles at GB dislocation nodes.

Reduced-activation ferritic/martensitic (RAF/M) steels are leading candidate structural materials for future fusion reactors and He concentrations on the order of 2000 appm will be produced by end-of-life. Consequently, the formation of He bubbles at GBs in steels or Fe has been widely investigated. Lane *et al.* [9] studied the He bubble

nucleation at GBs in a ternary austenitic steel after He implantation using transmission electron microscopy (TEM), while Randle *et al.* [10] investigated the interaction mechanisms of He bubbles with GBs in an austenitic steel using TEM. Dynamical interaction of He bubbles with GBs in Fe and Fe-9Cr was also studied by in situ electron microscopy and thermal desorption spectroscopy (TDS) [11]. Novel experimental techniques have been employed to characterize the transport and fate of He in RAF/M steels under fusion relevant He injection coupled with neutron-induced displacement damage [12]. In addition, molecular dynamics (MD) methods have been extensively employed to study the atomic-level processes of the He behaviour at GBs in bcc Fe. We have previously studied the diffusion mechanisms of He interstitials and di-He clusters at GBs in α -Fe using MD simulations [13-15]. We discovered that He atoms diffuse one-dimensionally along specific directions in the $\Sigma 11$ GB, whereas in the $\Sigma 3$ GB they migrate one-dimensionally at low temperature, two-dimensionally at intermediate temperature, and three-dimensionally at high temperature. The different migration behaviour of He in the two GBs indicates that He diffusivity is sensitive to the GB structure. Furthermore, the binding energies of He atoms to GBs in bcc Fe were found to increase with increasing excess volume of GB [16]. Terentyev *et al.* also studied the migration of a He interstitial in $\langle 110 \rangle$ tilt GBs in α -Fe [17], finding that GB atomic structure plays an important role in the accommodation, migration mechanism and diffusivity of He atoms.

In our previous work, the clustering of interstitial He in bulk Fe as a function of He concentration was investigated using MD simulations [18]. At low He concentrations, self interstitial atoms (SIAs) emitted from He clusters remain attached to the clusters, while at higher He concentrations cluster-interstitial dislocation loop complexes with more than one He-V cluster are formed, in good agreement with experimental observations [19]. In the current study, we explore He accumulation in a $\Sigma 3 \langle 110 \rangle \{112\}$ and a $\Sigma 73b \langle 110 \rangle \{661\}$ GB compared to bulk bcc Fe using MD simulations at different local He concentrations and temperatures. Here we focus on the effects of GB structure, temperatures and He concentration on He clustering and the formation of dislocation loops, as well as GB structural evolution.

2. Simulation Procedure

In the present simulations, a modified version of the MOLDY computer code [20] is employed. The interatomic potentials by Ackland *et al.* [21] and Aziz [22] are used to describe the Fe-Fe and He-He interactions respectively, while the Fe-He interaction is described by the potential developed by Gao *et al.* [18], which is based on the electronic hybridization between Fe *d*-electrons and He *s*-electrons. The migration energy of a single He interstitial, as calculated with this potential, is consistent with that obtained by *ab initio* methods, and the binding energies of small He-V and He-He clusters are also in good agreement with those obtained by *ab initio* and other interatomic potential calculations. The diffusion properties of He interstitials and their clusters in bulk Fe have been studied using MD [23]. The results showed that small He clusters can migrate at low temperatures, but they can emit SIAs and are trapped by the resultant vacancy, forming He-vacancy (He-V) clusters, at higher temperatures.

Two symmetric tilt GBs are considered in this work, both with a common $\langle 101 \rangle$ tilt axis. The two GBs are $\Sigma 3 \{112\}$, $\Theta = 70.53^\circ$ and $\Sigma 73b \{661\}$, $\Theta = 13.44^\circ$. These two grain GBs have the same tilt axis, but different angles. $\Sigma 3 \langle 110 \rangle \{112\}$ with $\Theta = 70.53^\circ$ and $\Sigma 73b \{661\}$ with $\Theta = 13.44^\circ$ represent high and low angle tilt GBs, respectively. Their atomic structures are shown in Figs. 1(a) and (b), respectively. Periodic boundary conditions are imposed along the x and z directions, where crystal coordinates corresponding to the x, y and z directions in the two GB models are indicated in Fig. 1. Atoms in region F are rigidly fixed in their original positions, whereas the atoms in the region T are used to control temperature by performing a velocity rescaling every 200 time steps according to the difference between the current temperature and the desired temperature. Regions V indicate vacuum slabs. The thickness of each slab, except for region T, is larger than the cut-off distance of the interatomic potential (0.53 nm). A bulk Fe model is also simulated for comparison. The dimensions and the number of Fe atoms in each model are given in Table 1, along with the number of He atoms included to simulate 1%, 5%, and 10% local concentrations (see below).

The NVT (constant number of atoms, volume and temperature) ensemble is used in the present simulations with a time step of 1 fs. Initially, GB models are relaxed at 0 K and constant pressure with a molecular statics (MS) approach, and then the excess atomic volume (Ω_{xs}) of the two GBs is determined. The excess atomic volume (EAV) which can provide information about the width of the grain boundary is found to affect the He binding energy and accumulation in MD simulations. In addition, EAV may be also used in other simulation methods such as kinetic Monte Carlo. As shown in Figs. 1(c) and (d), the excess atomic volume of the $\Sigma 73\text{b}$ GB is about ten times larger than in the $\Sigma 3$ GB, particularly at the cores of the GB dislocations. Due to its extremely low solubility He is strongly attracted to regions of high EAV. From Figs 1(c) and 1(d) it is apparent that regions with elevated EAV occur within ± 0.4 nm of the $\Sigma 3$ GB plane, and ± 0.5 nm of the $\Sigma 73\text{b}$ GB. Helium atoms are inserted at random positions within these EAV regions to create local He concentrations of 1%, 5% or 10%. Here the local He concentration is defined as the number of He atoms to the number of Fe atoms within the EAV region. In order to compare results from the $\Sigma 3$ GB with those in bulk Fe He atoms at approximately the same concentration are randomly added to a region with a thickness of ~ 0.8 nm along the [001] direction in bulk Fe. The number of He atoms for all the models are given in Table 1. After He insertion, the cell is relaxed at 0 K to achieve a minimum energy configuration, followed by temperature rescaling to the required annealing temperature and held there for 1 ns. Models are annealed at temperatures of either 300, 600 or 800 K. Helium clustering is monitored by counting the number and size of He clusters defined as those that are within a distance of 0.2 nm of each other.

The binding energy of a He interstitial to each GB was determined to quantify the relative effectiveness of each GB for trapping He. The binding energy is defined as:

$$E_{\text{B}}^{\alpha} = E_{\text{f}}^{\alpha} - (E_{\text{gb}}^{\alpha} - E_{\text{gb}}),$$

where E_{gb}^{α} is the energy of the GB with a He atom at site α , E_{gb} is the energy of the GB without a He atom, and E_{f}^{α} is the formation energy of a He atom at site α in bulk Fe. The binding energy of a He interstitial to each GB is shown in Fig. 2 as a function of distance from the GB plane. The binding of He to the $\Sigma 3$ GB is much weaker than to the $\Sigma 73\text{b}$ GB.

In order to be trapped by a GB the binding energy must, as a minimum requirement, exceed kT . The value of kT at the highest annealing temperature is about 0.065 eV. Inspection of the data in Fig. 2 reveals that He atoms must be closer than ~ 0.2 nm to the GB plane to be trapped by the $\Sigma 3$ GB, and ~ 0.6 nm from the $\Sigma 73b$ GB. Of course the capture distance is somewhat larger for each boundary at 300 K where the value of kT drops to about 0.025 eV. These results suggest that some of the He atoms initially placed within the EAV zone may escape and migrate away from the GB, particularly at the higher annealing temperatures.

To track the He atom concentration with time perpendicular to the GB plane, each simulation cell is divided into thin slabs in the y-direction each with a thickness of 0.12 nm. The He concentration in each slab, defined as the number of He atoms divided by the number of Fe atoms in the slab, is monitored over the course of the simulation. We also followed the He cluster density and average size within the GB plane. In this work a stable He cluster is defined as one that consists of three or more He atoms. This size is selected because a di-He cluster can dissociate at the higher temperatures simulated in this study. Figure 3 shows a typical plot of He cluster density and average size as a function of time for a simulation performed at 300 K with an initial 5% He concentration. The behaviour depicted in this graph is typical of all of the simulations performed here. It is evident that the He cluster density and average size evolve rapidly in the first ~ 100 ps of the simulation, and then they do not change much for the remainder of the simulation. In essence, nucleation of most of the He clusters occurs within this early stage of the simulation, followed by cluster growth. A rough estimate of the cluster nucleation time for He atoms randomly distributed within the EAV region can be obtained from the following equation:

$$t \gg x^2/2D$$

where t is time, x is the average initial He atom spacing and D is the bulk diffusivity. We assume He atoms diffuse one dimensionally, either toward or away from the GB. For a 1% He concentration at 300 K the value of x is about 1.1 nm and D is $\sim 3.4 \times 10^{-9}$ m²/s based on previous simulations [23]. This gives a time for cluster nucleation of ~ 180 ps, which agrees reasonably well with our simulation results, recognizing that this time will decrease at

higher He concentrations and higher temperatures. We note that our estimate of the nucleation time also depends on the He atom diffusivity. While He interstitials diffuse rapidly in bulk Fe, their diffusivity decreases considerably within the GB. Simulations performed by Deng *et al.* found the activation energy for He interstitials in a $\Sigma 3$ GB is 0.224 eV compared to 0.039 eV for diffusion in the bulk [23]. By density functional theory (DFT) calculations, Zhang *et al.* [24] also found that the GB diffusion of an interstitial He atom is always slower than its bulk diffusion, although the grain boundaries studied in that work are different from those in the current investigations. A more accurate estimate of the nucleation time would need to account for these factors.

We also briefly assessed the effects of the model size on He cluster evolution. Larger models of the $\Sigma 3$ GB were constructed for this assessment. In one model the GB area (x, z dimensions) was increased by $\sim 50\%$, and in the other model the GB area remained the same, but the model height (y dimension) was increased by $\sim 50\%$. The simulation time was similar for all models considered. No significant difference in the He cluster distributions after 1.0 ns simulation time was seen, which suggests that the cell sizes of the models used are large enough for the present studies.

3. Results and Discussion

3.1. $\Sigma 3$ GB with 1% He

After randomly inserting 1 % He into the EAV region of the $\Sigma 3$ GB the cell was quenched to 0 K and then annealed at 300, 600 or 800 K. During annealing at 300 K we found that most He interstitials in the EAV region migrate to the GB plane along the $\langle 100 \rangle$ direction in ~ 30 ps, but a few He atoms move away from the GB plane, migrating three-dimensionally. The He concentration distributions normal to the GB at different times at 300 K are shown in Fig. 4(a), where the blue solid straight line represents the GB plane. Fig. 4(a) clearly indicates that most He atoms have accumulated in the GB plane within 30 ps. Helium interstitials in the GB plane migrate easily with migration energy of about 0.22 eV along the $\langle 110 \rangle$ direction [23]. Also, two He atoms can join together, forming a stable He dimer (He_2) that migrates one-dimensionally along the $\langle 110 \rangle$ direction in the GB plane. A He atom can also join a He_2 cluster, forming a He_3 cluster. Similarly, the He_3 cluster also

migrates along the $\langle 110 \rangle$ direction, but not as quickly as a single He interstitial or the dimer. An Fe atom is displaced from its site by a He_4 cluster, forming a He_4VFe complex, but the emission of a SIA is not observed at 300 K. Further annealing of the system produces He_5 clusters, which spontaneously emit a $\langle 110 \rangle$ crowdion interstitial, and forms a stable He_5V cluster. To illustrate the evolution of small He-V clusters, the atomic configurations near the $\Sigma 3$ GB plane before and after annealing are shown in Figs. 4(b) and (c), where the upper image shows a view normal to the tilt axis and the lower image gives a view normal to the GB plane. Figure 4(c) shows that at the end of the simulation almost all the initial He has accumulated in the GB plane and formed small He clusters, He_n ($n=2-6$). In addition, at the periphery of He_5 and He_6 clusters, the Fe lattice is obviously distorted, which is indicated by the yellow circles in Fig. 4(c).

To understand the effect of temperature on He clustering simulations at 600 and 800 K were also performed. During early annealing at 600 K, most He interstitials migrate two-dimensionally into the GB plane along $\langle 110 \rangle$ and $\langle 111 \rangle$ type directions. The present results agree well with the migration behaviour of single He atoms in the same GB observed by Terentyev *et al.* [17], and our previous studies [13] with different empirical potentials. However, it should be noted that He atoms within the GB plane mainly migrate along the $\langle 110 \rangle$ direction, but with several deviations along the $\langle 111 \rangle$ direction. Also, several He atoms migrate away from the GB plane at 600 K, which is associated with the weak binding (i.e. increased capture distance) to the $\Sigma 3$ GB.

Small He clusters (He_2 , He_3) migrate quickly within the GB plane at 600 K without creating SIAs, whereas a He_4 cluster always emits a SIA, forming a He_4V cluster. The SIAs migrate only along the $\langle 111 \rangle$ direction. In contrast to the migration mechanisms of He atoms at 300 and 600 K, He interstitials migrate three-dimensionally toward the GB at 800 K. Moreover, He interstitials more easily migrate within the GB at 600 and 800 K, which increases the probability of forming clusters. Interestingly, the He cluster density was larger at 600 K and 800 K than at 300 K, the average cluster size was almost the same at all three temperatures. During annealing at 800 K emitted SIAs moved along both the

$\langle 111 \rangle$ and $\langle 110 \rangle$ directions. Large He clusters did not appear at 1% He concentration, even at 800 K. The largest He cluster consisted of only 7 He atoms. These results suggest that the $\Sigma 3$ GB is favorable for accumulating He atoms, but it impedes the growth of large He clusters, at least within the very short time scale of these simulations. The higher migration energies of He atoms and clusters, as compared to those in the bulk [18], and the decrease in migration dimensions (1D or 2D migration) in the $\Sigma 3$ GB may account for these observations.

3.2. $\Sigma 3$ GB with 5% He

In order to explore the effect of He concentration on cluster growth, and atomic rearrangements of GBs, higher He concentrations (5% and 10%) are considered for the $\Sigma 3$ GB. Figure 5 shows the temperature dependence of He clustering in the $\Sigma 3$ GB with 5% He after 1 ns annealing time. It is apparent that a large number of He clusters are formed at 300 K, as shown in Fig. 5(a), where the largest He cluster includes 15 He atoms. However, most Fe atoms remain in their original positions, and some SIAs are emitted, but remain bound to their cluster. With increasing temperature, larger He clusters are formed and more SIAs are emitted during the annealing. We found that He clustering at 600 and 800 K is similar. Compared to 300 K, He atoms migrate more rapidly within the GB, which leads to the formation of some large He clusters, as shown in Figs. 5(b) and (c). The largest He clusters at 600 and 800 K include 32 and 33 He atoms, respectively, which are significantly larger than those at 300 K. We also observe that the number of large He clusters at 600 and 800 K is greater than at 300 K. Also at 600 and 800 K several SIAs are emitted that collect around the periphery of the large clusters. To understand the nature of these SIA clusters the systems were quenched to 0 K for further analysis. This analysis indicates that the trapped SIAs form well-defined dislocation loops (an example is shown in Fig. 5(c) insert). Almost all of these confined dislocation loops have $\langle 100 \rangle$ Burgers vectors, rather than the $\langle 111 \rangle$ dislocation loops normally observed in high-energy displacement cascades in α -Fe [25]. Moreover, the population of these dislocation loops increases with increasing simulation time, and they always form between He clusters. In post-irradiation experiments interstitial dislocation loops with a Burgers vectors of $\langle 100 \rangle$ or $1/2\langle 111 \rangle$ are generally

found in bcc Fe [26, 27]. In general, computer simulations using various Fe potentials have revealed that interstitial loops with $\mathbf{b} = 1/2\langle 111 \rangle$ are more stable than those with $\mathbf{b} = \langle 100 \rangle$ [28]. It is not surprising that displacement cascades in Fe always produce $1/2\langle 111 \rangle$ interstitial loops, which exhibit high mobility at ambient temperature [25]. Based on extensive MD simulations of the interaction between $1/2\langle 111 \rangle$ clusters, different mechanisms for the nucleation and growth of $\langle 100 \rangle$ dislocation loops visible by transmission electron microscopy (TEM) have been proposed [29,30]. However, a systematic MD investigation of reactions involving glissile $1/2\langle 111 \rangle$ interstitial loops showed that the formation of a $\langle 100 \rangle$ segment occurred as a reaction product, but a perfect $\langle 100 \rangle$ loop was not formed [29]. The lack of perfect $\langle 100 \rangle$ loop formation is supported by *in situ* TEM studies in pure Fe that show coalescence between two $1/2\langle 111 \rangle$ loops into a larger $1/2\langle 111 \rangle$ loop [27]. Using the self-evolving atomistic kinetic Monte Carlo method, Xu et al. [30] pointed out that formation of $\langle 100 \rangle$ loops involves a directly atomic interaction between two $1/2\langle 111 \rangle$ loops, and does not follow the conventional assumption of dislocation theory. Here, we have shown that in the presence of large He clusters $\langle 100 \rangle$ dislocation loops with a $[112]$ habit plane can be readily formed, and they remain stable up to 800 K. It is also likely that impurities may promote the formation of $\langle 100 \rangle$ loops in α -Fe, enhance their stabilities, and inhibit them from transforming into $1/2\langle 111 \rangle$ dislocation loops. In experiments, after helium implantation, two sets of interstitial dislocation loops, with Burgers vectors of $1/2\langle 111 \rangle$ and $\langle 100 \rangle$, were identified using TEM in oxide dispersion strengthened ferritic steel [31]. This result indicates that the formation of $\langle 100 \rangle$ loops in iron may be associated with the presence of helium.

3.3. $\Sigma 3$ GB with 10% He

When the He concentration increases to 10%, He atoms rapidly diffuse toward the GB plane at all the three temperatures investigated. Instead of forming spherical shaped clusters they adopt a platelet-like cluster configuration. As a result, a large number of SIAs are emitted. We found that the He cluster geometries and GB atomic configurations after

1.0 ns annealing were similar for all three temperatures, thus only results for 800 K were analysed in detail and shown here in Fig. 6(a).

It is interesting to note that a number of large He clusters are formed, but without GB deformation, contrary to the 5% He results presented above (see Fig. 5(c)), even if a large number of SIAs are emitted early in the simulation. To further understand the effect of emitted SIAs on GB structure, the evolution of the GB as a function of the time was examined. Fig. 6(b) shows several snapshots of the GB structure where only Fe atoms are displayed for clarity. Before annealing it can be seen that some SIAs are created due to the locally high He levels, but the GB structure is not significantly distorted. After 3 ps of annealing, a large number of He clusters are formed, which results in the creation of many SIAs. These SIAs migrate quickly and collect at the periphery of each cluster. The GB structure is significantly deformed, and it appears highly disordered as shown in Fig. 6(b). Further annealing leads to rearrangement of the disordered Fe atoms within the GB, and at about 10 ps GB reconstruction occurs, where a new atomic layer forms above the original GB plane, which is clearly shown in the final snapshot. We also observed that some single He atoms and small He clusters migrate quickly within the GB plane and are absorbed by large He clusters. The final result of the reconstruction process is that the GB plane migrates up one atomic plane in the $[\bar{1}12]$ direction. Although the time evolution of GB reconstruction depended somewhat on temperature, the formation of an extra atomic layer above the original GB plane was observed at all temperatures investigated. The process of GB reconstruction observed here may share similar attributes with the point defect mediated GB migration and sliding discovered by Borovikov *et al.* in simulations of tungsten GBs subjected to extreme mechanical stress [32]. This will be a topic for future investigations.

A summary of our results for the $\Sigma 3$ GB as a function of He concentration is presented in Fig. 7. It is apparent that He cluster density and average size do not depend strongly on temperature, as shown in Figs 7(a) and 7(b). The cluster density and average size are much more sensitive to the initial He concentration, although cluster density appears to plateau at 5% He, Fig. 7(a). It is anticipated that an inverse relationship may exist between cluster density and average cluster size so that as cluster density increases the average cluster size decreases. We tested this hypothesis by plotting the product of cluster

density and average cluster size against the initial He concentration, which we anticipated would be approximately a constant. The results, displayed in Fig 7(c), show that this product is indeed a constant, confirming our expectation, and it depends linearly on the He concentration.

3.4. $\Sigma 73b$ GB

The same methodology was used to explore the affects of GB structure on He accumulation and clustering by performing the same set of simulations on the $\Sigma 73b$ GB. As shown in Figs. 1(b) and (d), the $\Sigma 73b$ boundary consists of an array of GB dislocations parallel to the x-direction, which contrasts sharply with the low excess volume twin structure of the $\Sigma 3$ GB. The $\Sigma 73b$ GB has much greater excess volume and, consequently, the interstitial He atom binding energies are considerably greater than for the $\Sigma 3$ GB, Fig. 2. A series of annealing simulations were done at 300, 600 and 800 K with 1% He. Similar to the $\Sigma 3$ GB simulations, almost all He atoms aggregate at the GB dislocation core regions within a very short time, but some He atoms are able to migrate along the GB dislocation line direction. However, He atoms seldom congregate to form large clusters in the $\Sigma 73b$ GB at 300 K, as compared to the clustering found in the $\Sigma 3$ GB, as illustrated in Fig. 8(b). Only one He_3 cluster forms after annealing at 300 K, where the three He atoms are roughly aligned with the dislocation line (indicated by yellow circles in Fig. 8(b)). The time evolution of the He distribution normal to the GB plane is shown in Fig. 8(c), where the solid blue straight line represents the GB plane. Unlike the $\Sigma 3$ GB, the He distribution normal to the $\Sigma 73b$ GB does not change significantly with time. The number of He atoms that are able to move by pipe diffusion increases at higher temperature, which results in the formation of more small He clusters (He_3) at 800 K. Even with increased mobility many He atoms still remain as single interstitials, instead of forming clusters, which contrasts with the results in the $\Sigma 3$ GB. This suggests it is more difficult to form large clusters in the $\Sigma 73b$ GB because He atoms are strongly bound to the large excess volume regions associated with GB dislocation cores [16], and they are effectively constrained to migrate

one-dimensionally. As shown in Figs. 1(c) and (d), the maximum excess volume in the $\Sigma 73b$ GB is about ten times larger than in the $\Sigma 3$ GB, which provides strong trapping. In addition, it is observed that a single He at the core of a GB dislocation is able to displace an Fe atom from its site, and form an Fe-V-He complex. The aggregation of these complexes at GB dislocations distorts the GB structure and limits clustering.

The atomic configurations for the 5% He level after 1 ns annealing at 300 and 800 K are shown in Figs. 9(a) and (b), respectively. At this He concentration some large He clusters are formed, especially at 800 K. The number of large clusters increases with increasing temperature, and some form spherical shapes at 600 or 800 K (see Fig. 9(b)) in contrast to the platelet-like clusters observed at 300 K. Emitted SIAs mainly collect at the cores of the GB dislocations.

Lastly, at a 10% He concentration, He atoms rapidly diffuse to the GB for all temperatures considered, resulting in the formation of many large He clusters with platelet-like structures. A large number of SIAs are created due to these clusters, which leads to significant GB structural changes. Structures of the $\Sigma 73b$ GB before and after annealing at different temperatures are shown in Fig. 10. We find that SIAs aggregate at the cores of the GB dislocations, causing those dislocations to climb in the x-direction, but He atoms do not climb with the GB dislocations. This phenomenon is different from that seen in the $\Sigma 3$ GB, where the SIAs caused a different form of GB motion. The dislocations comprising the $\Sigma 73b$ GB enhance formation of small He clusters, but impede their growth. These results clearly demonstrate that He clustering, emission of SIAs, and formation of SIA clusters or loops strongly depend on initial GB structure.

3.5. Comparison of GB and Bulk Fe

It is instructive to compare the clustering behaviour of He in bulk Fe with that in Fe GBs to characterize the differences between these two important regions of the microstructure. The accumulation and clustering He in bulk Fe with local He concentrations of 1%, 5% and 10% at 600 K are investigated using a model similar in size to those used for the GB simulations, see Table 1. As observed before, He atoms move quickly at 600 K, but three-dimensionally, in contrast to their behaviour in the GBs.

Helium distributions as a function of time in the bulk and the $\Sigma 3$ GB with a 1% He concentration are shown in Figs. 11 (a) and (b), respectively. The bulk Fe He distribution widens at 0.03 ns, while it becomes sharper in the $\Sigma 3$ GB. With increasing simulation time, some He atoms aggregate to form clusters in the bulk, but some still remain as single interstitials. By comparison in the $\Sigma 3$ GB most He atoms migrate to the GB, and only a few escape. These results suggest that the GBs significantly enhance He accumulation and clustering.

Figure 12 summarizes the He clustering behaviour in bulk Fe and for both Fe GBs as a function of simulation temperature at a 5% He concentration. Note cluster density is highest for the $\Sigma 73b$ GB and lowest for bulk Fe, Fig. 12(a). The cluster density does not vary much with simulation temperature, although there may be a slight tendency toward decreasing cluster density with increasing temperature. The average cluster size was largest in bulk Fe and smallest in the $\Sigma 73b$ GB. As with cluster density, cluster size only weakly depends on temperature. A slight trend toward increasing size with temperature is evident, Fig. 12(b). Given the general lack of temperature sensitivity of the cluster density and average cluster size, it is not surprising that the product of these two parameters is nearly constant over all simulation temperatures, Fig. 12(c). Furthermore, this product is approximately the same for both GBs and bulk Fe. Across all simulation temperatures the value of this parameter ranged from a low of 3.1 clusters/nm² to a high of 4 clusters/nm², with an average value of 3.7 clusters/nm². The constancy of this parameter may be due to the fixed amount of He present in our simulations. In a real fusion system He is constantly generated and is free to flow to the deepest traps. Since the product of number density and average cluster size strongly depends on the He concentration, it is logical to expect that the local He concentration will be higher in the vicinity of GBs compared to bulk Fe.

3.6. Relationship to experiments

It should be emphasized that the present simulations model only the nucleation and early growth stages of He bubbles for a fixed quantity of He. We do not include vacancies and self-interstitial atoms in our simulations, so the effects of displacement damage are not treated. Consequently, our simulation results most closely correspond to conditions created during He implantation experiments at a depth from the surface where He atoms come to rest in the sample. A typical SRIM calculation for an implantation experiment shows that negligible Frenkel pairs are created at the end of the He implantation range. In addition, caution should be exercised in comparing the present results with experimental observations because we do not model long-time migration of He atoms and clusters so the coalescence and growth of He bubbles to time scales achievable in experiments is not fully captured.

Given the above caveats some comparisons can be made with recent experimental observations. Bubble formation at 55 grain boundaries in He implanted Cu has been examined [33]. The results of this investigation showed trends opposite to those found in our simulations. Helium bubbles in Cu grain boundaries tended to be larger than in the grain interior and bubble size was found to increase with increasing grain boundary energy [33]. The observed trend was rationalized in terms of He diffusivity in a grain boundary relative to the bulk. It was assumed that He diffusivity increases with increasing grain boundary excess volume or energy [33], which does not correspond to the conditions in our simulations (see below).

More recent He-implantation experiments on a nanostructured ferritic alloy display a somewhat different trend than the results on Cu. Helium was implanted at 673 K to fluences up to 6.75×10^{21} He/m² in an effort to explore the effects of high levels of He produced in a potential fusion first-wall structural material [34]. The helium bubble

distribution in the ferrite matrix was compared to distributions at grain boundaries, dislocations, and coarse precipitates. The results of this study showed that for the lowest fluence investigated the average diameter of He bubbles located in grain boundaries was 1.45 nm compared to 2.15 nm for bubbles in the ferrite matrix [34]. At higher fluence the difference in bubble size changed. At a dose 3.3 times larger than the lowest dose the average diameter of grain boundary He bubbles was slightly larger than matrix bubbles (3.86 nm versus 3.46 nm), and this trend continued at the highest dose where the average diameter of grain boundary He bubbles was 4.29 nm compared to 4.04 nm for matrix He bubbles [34]. The authors speculated that He trapping at grain boundaries might have been aided by enhanced diffusivity in this region. While number densities were not reported, the authors stated that a high density of He bubbles along grain boundaries was found [34].

In the present simulations we find a higher number density of He clusters form at grain boundaries than in bulk Fe with smaller cluster sizes. These results can be understood in terms of reduced He diffusivity and increased trapping efficiency at grain boundaries relative to the bulk. Recent computer simulations of the diffusion of He atoms and clusters in bulk and grain boundaries in Fe employing the same potentials used in this investigation show that, for the range of temperatures simulated, interstitial He diffuses more slowly in a grain boundary than it does in the matrix [23]. The implication of reduced He mobility is an increase in cluster number density and reduced average cluster size since the bubble growth rate is slower. In addition, the higher trapping efficiency of large excess volume grain boundaries should promote a larger number density of He clusters compared to low excess volume grain boundaries and bulk Fe, which is what we observe in this work. The

behavior of the very low excess volume $\Sigma 3$ grain boundary is similar to bulk Fe and markedly different from the high excess volume $\Sigma 73b$ grain boundary.

4. Conclusions

The accumulation and clustering of He at the $\Sigma 3$ $\langle 110 \rangle \{112\}$, $\Sigma 73b$ $\langle 110 \rangle \{661\}$ GBs in α -Fe and bulk Fe have been studied using molecular dynamics simulations at different He concentrations and temperatures. The accumulation of He atoms, He clustering, and the evolution of GB structure all depend on the local He concentration, temperature and the original GB structure. Compared to bulk Fe, a higher number density of clusters form at GBs, but the average cluster size is smaller.

At a low He concentration (1%) in the $\Sigma 3$ GB the minimum He cluster size enabling the emission of a SIA consists of four He atoms at temperatures higher than 600 K. The largest size of He clusters slightly increases with increasing temperature, but the number of the He clusters increases more rapidly with temperature in the $\Sigma 3$ GB. In contrast, for the $\Sigma 73b$ GB, He atoms rapidly migrate to the GB dislocations, and they seldom form large He clusters, even at 800 K, which may be due to the strong trapping of He atoms at the cores of the GB dislocations.

At 5% He concentration, a number of large He clusters, with platelet-like shapes, are formed in the $\Sigma 3$ GB, which leads to the emission of many SIAs that collect at the cluster periphery. At 600 and 800 K these SIAs are able to form $\langle 100 \rangle [112]$ dislocation loops that are trapped between He clusters. It is proposed that impurities may play an important role in stabilizing $\langle 100 \rangle$ dislocation loops in α -Fe. In the $\Sigma 73b$ GB, a large number of He clusters are mainly formed along the GB dislocation lines and the emitted SIAs are accumulate at GB dislocation core regions, leading to the climb of these dislocations within the GB plane.

When the local He concentration increases to 10%, He atoms form many large clusters, which causes emission of a large number of SIAs. These SIAs can rearrange to form an extra atomic plane above the original GB plane within the $\Sigma 3$ GB, resulting in the self-healing of the GB deformation caused by SIAs accumulation and leading to the GB

migration. In the $\Sigma 73b$ GB the climb of the GB dislocations is also observed and it is more significant at high temperatures.

The He cluster density and average cluster size do not strongly depend on temperature for the range of simulation temperatures considered in this work, but do depend sensitively on the local He concentration. The product of cluster density and average cluster size is roughly constant at a given He level, is about the same in bulk and GB regions, and varies linearly with the He concentration.

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Table 1. Dimensions (nm) of simulation models, number of Fe atoms and number of He atoms randomly placed within the EAV region to produce a 1, 5, or 10% local concentration relative to the number of Fe atoms in that region.

Model Type	x	y	z	No. of Fe atoms	No. of He atoms for 1%	No. of He atoms for 5%	No. of He atoms for 10%
$\Sigma 3$	8.41	7.90	8.07	45,560	54	270	540
$\Sigma 73$	10.35	7.00	8.07	48,000	72	360	720
Bulk	8.57	8.57	8.57	54,000	54	270	540

Figure Captions

- Figure 1. Atomic structures and model geometries of (a) $\Sigma 3$ {112} and (b) $\Sigma 73b$ {661} GBs, where light blue and dark blue spheres correspond to atoms in the two adjacent atom layers along the tilt axis. The function of sub-regions marked V, F and T are described in the text. The corresponding excess atomic volumes for the $\Sigma 3$ {112} and $\Sigma 73b$ {661} GBs are presented in (c) and (d), respectively.
- Figure 2. Binding energy of interstitial He to $\Sigma 3$ and $\Sigma 73b$ GBs as a function of distance from the GB plane.
- Figure 3. He cluster density and average size as a function of time for the $\Sigma 3$ GB at 300K with an initial 5 % He concentration.
- Figure 4. He concentration profile at different times within the $\Sigma 3$ GB plane, for an initial He concentration of 1% within the EAV region (a), and atomic configurations of the $\Sigma 3$ GB plane showing the He distribution at (b) 0.0 ns and (c) 1.0 ns, where the green and white spheres represent Fe and He atoms, respectively.
- Figure 5. Atomic configurations near the $\Sigma 3$ GB plane with 5% He after 1.0 ns annealing at (a) 300, (b) 600 and (c) 800 K, where the orientations are the same as those in Fig. 2(c). The insert shows a $\langle 100 \rangle$ dislocation loop, where the He atoms are omitted.
- Figure 6. Atomic configurations near the $\Sigma 3$ GB plane with 10% He at 800 K; (a) after 1.0 ns annealing and (b) four snapshots showing the structural evolution of the GB as a function of simulation time, where the white solid line in the first and last snapshot show the location of the GB plane. Helium atoms are omitted for clarity and the orientations are the same as in Fig. 2(c).

- Figure 7. (a) He cluster density, (b) average size and (c) cluster density*average size as a function of He concentration for the $\Sigma 3$ GB at 300, 600 and 800 K.
- Figure 8. Atomic configurations of the $\Sigma 73b$ GB plane with 1% He concentration at (a) 0.0 ns and (b) 1.0 ns. Total He concentration profile normal to the $\Sigma 73b$ GB plane at different times (c).
- Figure 9. Atomic configurations of the $\Sigma 73b$ GB plane with 5% He concentration after 1.0 ns annealing at (a) 300 K and (b) 800 K, where the orientations are the same as those in Fig. 8(a).
- Figure 10. Structure of the $\Sigma 73b$ GB with 10% He concentration: (a) initial configuration, and at (b) 300 K, (c) 600 K and (d) 800 K after 1.0 ns annealing, where is viewed normal to the tilt axis, and the He atoms are omitted.
- Figure 11. Distribution of total He concentration at different times within the $\Sigma 3$ GB plane (a) and bulk (b) of α -Fe with 1% He concentration at 600 K along the y direction. (c) He cluster density within the GB plane and (d) average size of He clusters in the $\Sigma 3$ GB and bulk with 1%, 5% and 10% He concentrations at 300 K, where the solid symbols and open symbols are for the $\Sigma 3$ GB and bulk, respectively.
- Figure 12. (a) He cluster density, (b) average size and (c) cluster density*average size as a function of temperature in bulk Fe and for both $\Sigma 3$ and $\Sigma 73b$ GBs at an initial 5% He concentration.

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