He–V Cluster Nucleation and Growth in α -Fe Grain Boundaries

M.A. Tschopp^{a,*}, F. Gao^b, K.N. Solanki^c

^a*U.S. Army Research Laboratory, Aberdeen Proving Ground, MD 21005*

^b*University of Michigan, Ann Arbor, MI 48109*

^c*Arizona State University, Tempe, AZ 85287*

Abstract

The nucleation of helium (He) clusters and their growth in a monovacancy (V) eventually leads to the formation of He bubbles on grain boundaries and within the lattice for α -Fe, which can cause the macroscopic deterioration of material properties. The research objective herein is to model the nucleation and growth of small He clusters by calculating the formation/binding energetics of a single He atom to a He_nV cluster ($n = \{1-7\}$) and by capturing how the grain boundary affects this behavior in bcc α -Fe. The formation energies for 1–8 He atoms in a monovacancy are calculated at all potential grain boundary sites within 15 Å of ten select high angle grain boundaries. These results are combined with previously calculated vacancy formation energies and interstitial He formation energies to quantify how the local grain boundary structure impacts the binding of an interstitial He atom to a He_nV cluster. We find that, despite the large range of different local environments within the grain boundaries, it is nearly always energetically favorable for a nearby interstitial He atom to combine with either a monovacancy or a He_nV cluster to form a larger He_nV cluster, with a binding energy that can be much greater (as much as 100% greater) than in the bulk crystal. Furthermore, a model is presented that captures the formation and binding energies of the various He–V clusters while capturing the subsequent binding energies of different clusters/defects in the presence of grain boundaries – both of which are important when accounting for the total energetics pertaining to He–V cluster growth in the presence of the high angle grain boundaries.

*Corresponding author

Email address: mark.a.tschopp.civ@mail.mil (M.A. Tschopp)

Keywords: Helium–vacancy cluster, grain boundary, iron, interstitial, monovacancy, formation energy, binding energy

1. Introduction

The large amount of helium (He) produced in future fusion reactors presents a number of challenges pertaining to the fate of He and the formation of He bubbles [1, 2]. In particular, these challenges are defined by the underlying sequence of processes that emerge due to the presence of He: 1) due to its high mobility as an interstitial atom, He tends to first diffuse/segregate to internal lattice defects such as vacancies, dislocations, and grain boundaries; 2) subsequent nucleation and growth of He bubbles then occurs at these internal defects since He is easily trapped; and 3) these He bubbles can lead to a macroscopic deterioration of material properties, which includes void swelling, surface roughening and blistering, and high temperature intergranular embrittlement [*e.g.*, 3, 1, 2, 4, 5, 6, 7, 8, 9, 10]. These processes are ultimately related to the atomic-level interactions between He atoms and small He clusters with the metal lattice. Certainly, to fully develop predictive models for material behavior in these reactors under irradiation conditions requires simulation methods over multiple length and time scales, but the basic understanding of the initial stages of He segregation and cluster growth lies at the atomistic scale.

Atomistic simulations can provide information about the interaction between He, He clusters, and grain boundaries. While quantum mechanics and molecular dynamics simulations have been used to examine how He and He clusters affect single crystal lattice properties and physical properties in α -Fe [11, 12, 13, 14, 15, 16, 17, 18, 19], the grain boundary itself and its atomic configuration within these alloy systems plays a significant role in trapping point defects and various atomic species. Reduced activation ferritic/martensitic steels for fusion reactors may have high He concentrations (approximately 2,000 appm). The extremely low solubility of He in metals results in He bubbles forming in both the matrix (trapped by vacancies and dislocations) and the grain boundaries, as has been observed experimentally in a number of studies by TEM [20, 21, 22]. In fact, Li et al. [20] found that there is an approximately 10 nm-wide zone surrounding some grain boundaries where He bubbles were depleted (presumably because He is segregating to the boundary). Hence, understanding and modeling the interaction between He and grain boundaries is important. There have been a number of recent studies using both first principles and molecular dynamic simulations that

have examined how solutes, impurities, and point defects segregate to grain boundaries within bcc metals [23, 24, 25, 26, 27, 28, 29, 30, 31, 32]. In addition to this, there is a growing body of work that have focused on He interactions with grain boundaries [33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47]. These prior works have been significant for understanding the migration paths and mechanisms of He for a few boundaries using the dimer method [34, 36], understanding migration of interstitial He in different grain boundaries using molecular dynamics [37], understanding how the grain boundary strength is affected by He [38, 39, 46] or He bubbles [40], understanding the diffusion and stability of He defects in grain boundaries using first principles [41, 42], and understanding how He concentration is manifested within the GB [47]. For instance, Kurtz and Heinisch [33] used a Finnis–Sinclair potential (detailed in Morishita et al. [48]) to show that interstitial He is more strongly bound to the grain boundary core than substitutional He. Kurtz and Heinisch also found that the maximum He binding energy increases linearly with the grain boundary excess free volume, similar to prior work in fcc nickel [49]. In subsequent studies, Gao, Heinisch, and Kurtz [34] found a relationship between the maximum binding energy and grain boundary energy as well. Additionally, Gao et al. started to detail the diffusion trajectories of interstitial and substitutional He atoms along a $\Sigma 3$ and $\Sigma 11$ grain boundary and found that the dimensionality of migration of interstitial He may depend on temperature (e.g., in the $\Sigma 3(112)$ boundary). Some recent work has utilized first principles to quantify binding strengths of He and He–V clusters at the $\Sigma 5(310)$ symmetric tilt grain boundary [42] and have recently extended this work towards looking He cluster growth in two grain boundaries using both DFT and an empirical potential [46].

There are still a number of unresolved issues relating to how He interacts with grain boundaries, though. In our previous work [43, 44], we extended these studies by focusing on one He atom in interstitial or substitutional sites interacting with grain boundary sites, as well as multiple He atoms in a monovacancy. Moreover, we incorporated a larger range of grain boundary structures than had previously been done to understand both the average grain boundary behavior, the individual grain boundary behaviors, and how the local environment influences the formation and binding of He atoms/clusters. However, while these focused on these individual He atom/clusters and the energetics of their interaction with the grain boundary, another aspect that has been relatively untouched is how to partition the energy for the binding of two He atoms/clusters within the boundary. That is, the binding energy of adding an additional He atom to a He–V cluster has been calculated for the single crystal lattice, but this same calculation

in the grain boundary environment is more difficult; this calculation is confounded with the binding of each individual He atom/cluster to a particular grain boundary site, which requires the simulations performed in Tschopp et al. [43, 44] to partition appropriately. While experiments suggest that this binding behavior is indeed energetically favorable (i.e., He bubbles preferentially grow rather than distribute into small clusters), is it energetically more favorable than in the lattice? less favorable? by how much? how can this information be captured (model form)? Answering the questions utilizing the following methods can help to account for the complete energetic landscape of the beginning stages of He–V cluster nucleation and growth in the presence of grain boundaries.

Therefore, the research objective of the present work is to explore the growth of He–V clusters by calculating the binding energy of a single interstitial He atom to a He_nV cluster ($n = \{1-7\}$) to form a larger He–V cluster and to understand how the grain boundary affects this binding behavior in bcc α -Fe. This approach utilizes an iterative approach that has been previously applied to systematically quantify the interactions between point defects, carbon, hydrogen, and He with Fe grain boundaries [31, 32, 30, 29, 43, 44]. Herein, this approach is applied along with using multiple different starting positions, or instantiations, about each site to more precisely probe the energy landscape for ten select grain boundaries. In this paper, we present this approach for eight He_nV clusters and we explore how the grain boundary structure impacts additional He atoms binding to these He_nV clusters using molecular static calculations. A number of interesting new findings emerge from the present study. We find that, despite the large range of different local environments within the grain boundaries, it is nearly always energetically favorable for a nearby interstitial He atom to combine with either a monovacancy or a He_nV cluster to form a larger He_nV cluster. This work significantly enhances our understanding of the energetics involved with how the grain boundary structure interacts with He_nV clusters and how ultimately this may affect He (re-)combination and embrittlement near grain boundaries in polycrystalline steels.

2. Simulation Methodology

The interaction between interstitial He and He–V clusters at every site within 15 Å of the grain boundary center (866 total sites) is investigated for ten low order coincident site lattice grain boundaries ($\Sigma 3, \Sigma 5, \Sigma 9, \Sigma 11, \Sigma 13$) in the $\langle 100 \rangle$ and $\langle 110 \rangle$ symmetric tilt grain boundary (STGB) systems (139,426 simulations total). The molecular static calculations were performed

with a modified version of MOLDY [50, 51, 52] and the grain boundary generation utilized the following [31, 32]: 1) a bicrystal computational cell with 3D periodic boundary conditions, 2) a minimum distance between grain boundaries of 12 nm, 3) multiple initial configurations with rigid body translations and an atom deletion criterion, 4) the Polak-Ribière conjugate gradient energy minimization, and 5) the Ackland and Mendelev [53] interatomic potential for Fe. Multiple replications of the simulation cell (greater than $4a_0$) were used in the grain boundary tilt and period directions to minimize any effect of periodic boundaries on the He binding/formation energies, resulting in cell sizes on the order of 4660–9152 Fe atoms ($\Sigma 13(510)$ and $\Sigma 11(113)$, respectively). The Fe–He interatomic potential fit by Gao et al. [54] to ab initio calculations using an s-band model is used herein. This interatomic potential has shown good agreement with DFT results for vacancy (less than 4 vacancies) and He formation energies in different grain boundary sites and grain boundaries [41]. The present study uses vacancy [32], interstitial He [43], and He_nV cluster [44] formation energies calculated in prior studies, which often required multiple starting configurations (20) at each grain boundary site to reasonably approximate the minimum (formation) energy He configurations. Further details of the simulation methodology are provided within the Supplemental Material and our previous work [43, 44]. The formation and binding energies for the different grain boundaries and He clusters are shown in the Appendix. Figures A1 and A2 show the binding/formation energies and how they evolve with spatial position.

The binding energy of He atoms/clusters to each other and how this changes in the grain boundary environment uses formation energies to compute whether there is an energetic advantage/disadvantage for two defects being in near proximity to one another. There are three different binding energies that are relevant to He_nV cluster nucleation and growth in the grain boundary:

1. interstitial He binding to the grain boundary at site α ,
2. He_nV cluster binding to the grain boundary at site α , and
3. interstitial He atom binding to a He_{n-1}V cluster to form a He_nV cluster at site α .

The binding energy of interstitial He atoms, di-interstitial He atoms, and He_nV clusters (i.e., the aforementioned items 1 and 2) with the grain boundary is the primary focus of recent publications [43, 44]. However, the change in the binding energy of adding an interstitial He atom to a He_nV cluster in the presence of the grain boundary (i.e., the aforementioned item 3, which

quantifies the attraction/repulsion nature of this reaction) is also relevant to the growth of HeV clusters. This binding energy is given by:

$$E_b^{He^\alpha \rightsquigarrow He_n V^\alpha} = \left(E_f^{He_{n-1} V^\alpha} + E_f^{He^\alpha} \right) - E_f^{He_n V^\alpha}, \quad (1)$$

where $E_f^{He^\alpha}$ is the formation energy of an interstitial He atom at site α in the absence of the $He_n V$ cluster, and $E_f^{He_n V^\alpha}$ is the formation energy of a $He_n V$ cluster with n He atoms (or $n - 1$ He atoms, as in parentheses of Eq. 1). The remainder of this work explores how Equation 1 changes as a function of position near the grain boundary (i.e., changing site α); this calculation is more complex than previous work [43, 44] as it involves the binding energy of interstitial He and $He_n V$ to the grain boundary as well as with each other. Of the 20 different starting configurations for each interstitial He or $He_n V$ cluster, the minimum formation energy (and maximum binding energy) is used in the present analysis.

3. Results

The $He_n V$ cluster formation energies for every site are required to calculate the binding energy of an additional He atom. This formation energy distribution changes with the number of He atoms in the monovacancy; Figure 1 is a) a plot of the $He_n V$ formation energy as a function of the number of He atoms in the $He_n V$ cluster and b) a probability distribution plot of the $He_n V$ cluster formation energy. In Figure 1a, the shaded red area denotes the band of values for all E_f data; the shaded blue area highlights the band of E_f for those sites that were >10 Å away from the center of the GB (bulk values). The individual E_f points are also plotted with an expanded view of the $He_n V$ formation energy distributions in Figure 1b. Additionally, percentile lines were added every 2% (dotted) and 10% (dashed) to show how the formation energy distribution changes with increasing n He atoms in the $He_n V$ cluster. Since all percentile lines are plotted in Figure 1a, it is apparent that most percentile lines lie within the bulk region (blue) with approximately 20–40% of sites having lower formation energies than in the bulk, due to the grain boundary; this is even more apparent in the probability distribution plot where the deviation between formation energies in the grain boundary and in bulk sites is shown by the separation between the two curves for each $He_n V$ cluster. Notice that 0 He atoms is also plotted in Figure 1a; this refers to the vacancy formation energies over the same sites (from Ref. 31, 32). The negative deviation from the bulk formation energies is the binding energy, which increases with increasing n He atoms

in a monovacancy. There is also a linear trend in the formation energies, as would be expected. Previous work [44] has shown that there is some degree of linear correlation between formation energies of He_nV clusters (in general, $R > 0.70$ for $n = 1 - 8$), which decreases with an increase in the difference in the number of He atoms in the He_nV clusters. As might be expected, as the size of the He_nV cluster increases, the interaction volume of the He_nV cluster increases (dilatation) and this results in a lower dependence on the immediate local environment (e.g., shifting behavior from predominantly first nearest neighbors to including second nearest neighbors and beyond).

However, the He_nV energies in Figure 1 alone are not sufficient to calculate the energy contribution of adding an additional interstitial He atom to the cluster, though. There are three important interactions: 1) between the interstitial atom and the grain boundary; 2) between the He_nV cluster and the grain boundary; and 3) between the interstitial He and the He_nV in the grain boundary environment. For the binding energy calculation of adding an interstitial He atom to a He_nV cluster at grain boundary site α (Eq. 1), the reference states for the interstitial He and the He_nV cluster must be at site α . So, using a reference state of interstitial He in the bulk would confound the binding energy calculation with the influence of both items 1 and 3 above. The analysis hereafter uses values from Figures A1 and A2 to develop a model for He bubble nucleation and growth.

The binding energies of an interstitial He atom joining with a He-V cluster (or a vacancy for the case of a He_1V cluster) to produce a He_nV cluster ($E_b^{\text{He}\rightsquigarrow\text{He}_n\text{V}^\alpha}$ in Equation 1) can be plotted against the number of He atoms in the He_nV cluster. Of course, this binding energy may change based on the local environment of the He_nV cluster. This local environment will also change the interstitial He formation energy, so previously computed values [43] are also used for the subsequent calculations. In Figure 2 and in Supplemental Data, the binding energy data for the 866 sites within all ten GBs is analyzed for each He_nV cluster ($n = 1-8$) in several ways. A number of different elements are displayed in Figure 2. First, the shaded red area denotes the band of values for all $E_b^{\text{He}\rightsquigarrow\text{He}_n\text{V}^\alpha}$ data; the shaded blue area highlights the band of $E_b^{\text{He}\rightsquigarrow\text{He}_n\text{V}^\alpha}$ for those sites that were >10 Å away from the center of the GB (bulk values). Second, the individual $E_b^{\text{He}\rightsquigarrow\text{He}_n\text{V}^\alpha}$ points are also plotted. Last, additional lines were added to show how the distribution of binding energies change with increasing n He atoms in the He_nV cluster (i.e., percentiles of the entire binding energy distribution).

There are several interesting findings exhibited in Figure 2. First, we analyze and discuss the binding energies of the region far from the grain

Figure 1: (a) The He_nV cluster formation energies plotted against the number of He atoms in the He_nV cluster for all sites (red) and for bulk lattice sites (defined by >10 Å away from boundary, in blue). The 2% and 10% percentile lines indicate the percentage of sites with formation energies different from the bulk single crystal energies. (b) Probability distribution plots of the He_nV cluster formation energies for GB sites versus bulk sites.

boundary (>10 Å). The energy associated with an interstitial He atom migrating to a vacancy to form He₁V is much higher (2.34 eV) than interstitial He atoms migrating to a He_{1-7}V cluster to form a He_{2-8}V cluster (≈ 1.3 eV, in agreement with Ref. 54). This result is in agreement with previous empirical potential [55, 56] and DFT results [13]. However, unlike the other empirical potentials, there does not exist a large decrease in the binding energy after six He atoms in a He-V cluster, in agreement with Gao et al.’s results [54]. Rather, there is a slight dilatation that is observed to occur when a cluster contains more than four He atoms and a compact He octahedron has been observed in clusters with six atoms, which are local maxima in the binding energy curve in the bulk sites. Additionally, we find that the variability in this binding energy of an additional He atom increases with increasing n in the formed He_nV cluster, but the data still follows the general trend observed by Gao and coworkers [54].

Next, we analyze and discuss the binding energies of all sites (including the grain boundary region). Most notably, almost all of the binding energies are positive (a total of 3 binding energies are negative for He₁V and He₂V cluster formation). So, even despite the large range of different local environments within the grain boundaries, the present simulations show that it is almost

always energetically favorable for a nearby interstitial He atom to combine with either a monovacancy or a He_nV cluster to form a larger He_nV cluster. Interestingly, when comparing the range of binding energies (shaded regions), the binding energies for the grain boundary region have values to both sides of the bulk values, with a greater percentage on the lower side of that obtained in the bulk (as denoted by the percentile lines in Figure 2). The most extreme case is the binding energy associated with an interstitial He atom binding to a monovacancy (for $n = 1$ in Fig. 2), which is a maximum in the bulk region and has a number of sites in the grain boundary region (approximately 30% of all sites explored) with binding energies lower than those in the bulk. This finding suggests that an interstitial He atom combining with a monovacancy to produce a He_1V cluster is no more energetically favored in the grain boundary environment than in the single crystal lattice, even though there

Figure 2: Binding energy of an additional interstitial He atom binding to a He_nV cluster to form a He_{n+1}V cluster as a function of n . Red represents all sites and blue represents the bulk sites ($> 10 \text{ \AA}$). The change in binding energies for particular sites is shown as various dotted/dashed lines for 2% and 10% percentile lines.

is an energetic driving force for interstitial He atoms and monovacancies to migrate to the grain boundary (i.e., still a positive binding energy). As is apparent, this is not the case for He–V clusters once they are formed within the grain boundary – there can certainly be an additional energetic driving force (over that in the bulk) for interstitial He atom within the boundary to combine with existing He_nV clusters. This is accentuated the most for an interstitial He atom combining with a He_7V cluster to form a He_8V cluster – for He_8V clusters, there are more sites with binding energies above those in the bulk than below those in the bulk ($\approx 30\%$ of sites are above bulk binding energies compared to $\approx 20\%$ below, i.e., Figure 2). The other observable trend is that the lower and upper extreme values of the binding energies tend to increase with increasing size of the cluster (aside from interstitial He binding with a monovacancy to form a He_1V cluster), even though the mean binding energy values tend to stay fairly constant with increasing cluster size.

Some questions about the role of local grain boundary structure naturally arise. First, do the same grain boundary sites always have the highest or lowest $E_b^{\text{He}\sim\text{He}_n\text{V}^\alpha}$ energies? In short, no. The sites of the five largest binding energies for each He_nV cluster are identified to track $E_b^{\text{He}\sim\text{He}_n\text{V}^\alpha}$ for all other He_nV clusters. This sort of analysis found that sites with the highest binding energies for one He_nV cluster may have much lower binding energies (as much as a 1 eV decrease) when combining with the next interstitial He atom. In other words, the degree of deviation from the bulk binding energies is not only a function of the initial local grain boundary environment, but is also very much a function of the number of He atoms in the existing He_nV cluster, suggesting that the local He–V cluster geometry may play a role as well.

Expanding further along this line, one hypothesis that can be tested is whether $E_b^{\text{He}\sim\text{He}_n\text{V}^\alpha}$ is correlated between the different He–V clusters for a particular site (and local grain boundary environment). To test this theory, the linear correlation coefficient R for $E_b^{\text{He}\sim\text{He}_n\text{V}^\alpha}$ is calculated for all sites and grain boundaries (Table 1). R is often used to compare the degree of linear correlation between two datasets, where $R = 1$ indicates a perfect positive correlation, $R = -1$ indicates a perfect negative correlation, and $R = 0$ indicates no correlation. As can be seen from Table 1, there is some degree of correlation ($R = \{0.734\text{--}0.901\}$) between $E_b^{\text{He}\sim\text{He}_n\text{V}^\alpha}$ for He_nV clusters with $n \leq 4$, but this correlation decreases substantially (down to $R = 0.215$) as n increases. Another way to examine this correlation is to perform a rank transformation, whereby the $E_b^{\text{He}\sim\text{He}_n\text{V}^\alpha}$ are sorted and

assigned a ranking, which is then correlated – however, this resulted in R values that were much closer to 0 ($R < 0.1$, i.e., no linear correlation).

Table 1: Linear correlation coefficients R for the binding energy of an additional interstitial He atom to a He_nV cluster over all GB sites.

Cluster	He_1V	He_2V	He_3V	He_4V	He_5V	He_6V	He_7V	He_8V
He_1V	1.000	0.901	0.872	0.803	0.519	0.640	0.316	0.256
He_2V	–	1.000	0.906	0.734	0.453	0.578	0.231	0.215
He_3V	–	–	1.000	0.791	0.525	0.621	0.281	0.260
He_4V	–	–	–	1.000	0.633	0.706	0.382	0.309
He_5V	–	–	–	–	1.000	0.542	0.447	0.348
He_6V	–	–	–	–	–	1.000	0.496	0.391
He_7V	–	–	–	–	–	–	1.000	0.498
He_8V	–	–	–	–	–	–	–	1.000

Figure 3 displays the spatial distribution of binding energies for He_nV clusters for the ten $\langle 100 \rangle$ (top rows) and $\langle 110 \rangle$ (bottom rows) symmetric tilt grain boundaries. The grain boundaries in this figure are arranged in order of increasing misorientation angle (top to bottom) for each symmetric tilt grain boundary system. The characteristics of these scatter plots are similar to those in the Appendix (Figures A1 and A2) in terms of the boundaries being ordered in terms of misorientation angle (from top to bottom) and tilt systems ($\langle 100 \rangle$, $\langle 110 \rangle$) for direct comparison. The He_nV cluster listed above in the final cluster size, i.e., an interstitial He atom combined with a He_{n-1}V cluster to form a He_nV cluster. However, the colorbar is scaled differently. In this colorbar, white refers to the bulk $E_b^{\text{He} \rightsquigarrow \text{He}_n\text{V}^\alpha}$ energies, blue refers to degree of negative deviation from this bulk value (down to +0%, i.e., 0 eV), and red refers to the degree of positive deviation from this bulk value (up to +100%). First, there are general trends for all grain boundaries and structures. The most noticeable trends are that $E_b^{\text{He} \rightsquigarrow \text{He}_n\text{V}^\alpha}$ approaches bulk energies as the distance from the grain boundary center increases and that $E_b^{\text{He} \rightsquigarrow \text{He}_n\text{V}^\alpha}$ is less attractive than in the bulk (large amount of blue). The lower formation energies of He_nV clusters may, in part, contribute to the lower attraction of interstitial He and He_nV clusters. In contrast to the formation/binding energies in Figures A1 and A2, though, the largest binding energies are not necessarily along the center or 1st layer of the GB plane, but rather are dispersed throughout the grain boundary region. As noted earlier, there is a noticeable symmetry to the binding energies about the grain boundary plane as well. Second, for a specific He_nV

cluster (i.e., each column), the $\Sigma 3(112)$ twin boundary again has a behavior similar to the bulk, irrespective of the size of the He_nV cluster, in contrast to the other boundaries. In other boundaries (not the $\Sigma 3(112)$ twin), it is evident that there is a slight shift in the binding energies. For instance, the $\Sigma 11(332)$ boundary visually has binding energies closer to bulk than the $\Sigma 3(111)$ boundary does; this bias for these two boundaries is noticeable for all He clusters as well. Last, for a specific grain boundary (i.e., each row), the general behavior is that $E_b^{\text{He}\rightsquigarrow\text{He}_n\text{V}^\alpha}$ increases with respect to the bulk $E_b^{\text{He}\rightsquigarrow\text{He}_n\text{V}^\alpha}$, as denoted by the gradual shift in the per-site contour colors from blue towards red. That is, in general, as the He_nV cluster size increases, the binding of an additional He atom to a He–V cluster is more likely to be near or above the bulk binding energy.

Figure 3: The binding energies of an interstitial He atom to combine with a He_{n-1}V cluster (i.e., $E_b^{He \rightsquigarrow He_n V^\alpha}$ in Equation 1) in various sites for all ten high angle grain boundaries (upper rows – $\langle 100 \rangle$ GBs, lower rows – $\langle 110 \rangle$ GBs). The atoms are colored by the binding energy, which is scaled between zero and the maximum binding energy over all GBs and GB sites.

4. Discussion

4.1. Atomistically-Informed Model of the Growth of He_nV Clusters

One of the objectives of the present study is to model the initial stages of growth of a He–V cluster in the presence of the grain boundary. Modelling the growth of He–V clusters first requires a model of the binding of He–V clusters to the grain boundary; the binding between an additional He atom and the He–V cluster (i.e., the growth of the He cluster) is then readily obtained from such a model, as discussed in Section 4.2. First, an analytic model of the energetics of the interaction between He and the grain boundary as a function of distance from the GB center was fit using atomistic information gleaned from the (100,000+) simulations. The energies were fit to the Gaussian-based model outlined in Tschopp et al. [44], which has the form of

$$E_b(x) = c_1 \exp\left(-\left(\frac{|x|}{c_2}\right)^{c_3}\right), \quad (2)$$

where c_1 , c_2 , and c_3 are model constants. This form is chosen because the symmetric nature of the GB formation and binding energies as a function of distance resembles a normal distribution. The normal distribution curve is recovered from Eq. 2 when $c_3 = 2$; c_1 now modifies the height of the normal distribution and c_2 modifies the width of the normal distribution. The c_3 term modifies the slope of the transition region (i.e., diffuse or sharp transition). The c_3 term was modified herein such that it can be a real number (i.e., instead of restricting it to an even integer), which was necessary to capture the gradual transition of slope with increasing number of He atoms in the cluster. However, given the variability in binding energies due to the varying local environment of the grain boundary (e.g., see Figure A3), $c_3 = 2$ is used for the remaining analysis (and varying c_3 is discussed in Appendix 5.2).

Equation 2 is applied to the various He_nV clusters to capture the evolution of the binding and formation energies as a function of the distance for a general high angle grain boundary. Hence, the atomistic energies from all grain boundaries in this study were used for the model except for the $\Sigma 3\{112\}$ GB, which is excluded because of its drastically different binding/formation energy behavior with respect to the He_nV clusters. Table 2 lists the constants c_1 and c_2 for the model ($c_3 = 2$) as well as the FWHM values. It should be noted that the choice of boundaries may affect the parameters. However, different permutations of boundaries are tested and it is found that this factor only slightly affects the model parameters. When all permutations of 8 of the 9 boundaries are used, this results in standard deviations that

are on average less than 1.0% of c_1 and c_2 . Recall that the $\Sigma 3\{112\}$ GB is excluded because previous work [44] shows that this boundary has formation and binding energies of He–V clusters that are very similar to energies in the single crystal. When all permutations of 8 of the 10 boundaries (i.e., including the $\Sigma 3\{112\}$ GB) are used, the constant c_1 decreased by 6.8% to better capture the low He_nV binding energies of the $\Sigma 3\{112\}$ GB, while c_2 only slightly changing ($<0.1\%$).

The last column in Table 2 lists the formation energies of the various He_nV clusters and defects – the present model can be easily modified with the formation energy in the bulk, E_f^{bulk} , to obtain the formation energies for these He-related defects, i.e.,

$$E_f(x) = E_f^{bulk} - E_b(x). \quad (3)$$

The constants can be used to model the behavior of the binding and formation energy as a function of distance for all of the He_nV clusters discussed herein, which is shown in Figure 4a. As is also apparent from the evolution of the constants in Table 2, the binding energy increases as a function of the number of He atoms n (i.e., c_1), the width increases with an increase in n (also evident by the increase in the FWHM intersection points [black diamonds], i.e., proportional to c_2). Also, Figure 4b plots the model

Table 2: Parameters for binding energy for $\text{He}_{\{0,1,\dots,8\}}\text{V}_{\{0,1\}}$ as a function of distance (Eq. 2) for a general high angle grain boundary for model with $c_3 = 2$.

Defect	c_1 (eV)	c_2 (Å)	c_3 (unitless)	FWHM (Å)	E_f^{bulk} (eV)
V	0.5	3.5	2	5.8	1.7
He_{int}	1.4	4.3	2	7.2	4.4
He_1V	0.6	2.7	2	4.5	3.7
He_2V	1.3	3.4	2	5.6	6.8
He_3V	2.1	3.6	2	5.9	9.9
He_4V	2.7	3.8	2	6.3	12.9
He_5V	3.7	4.2	2	6.9	16.0
He_6V	4.3	4.4	2	7.4	19.0
He_7V	5.3	4.8	2	8.0	22.0
He_8V	6.4	5.1	2	8.4	25.1

fit for the binding energies of interstitial He and vacancies in the presence of a general high angle grain boundary. This plot shows that the binding energy for a vacancy with the grain boundary is much lower than that for an interstitial He atom, indicating that there is a larger driving force for interstitial He atoms to migrate to the boundary.

Figure 4: Model evolution of (a) He_nV binding energies and (b) interstitial He and vacancy binding energies as a function of distance for all grain boundaries except the $\Sigma 3\{112\}$ GB. The lines are the least-squares fit of the model (Eq. 2) to the atomistic data with the constants c_1 and c_2 given in Table 2. The black diamonds indicate the intersection point for the FWHM calculation. The dotted lines in (b) correspond to the He_nV energies in (a).

4.2. Model Extension for Binding Energies of Interstitial He with He-V Clusters

Linking atomistic information to Equation 2 is subsequently used to calculate the binding energy behavior of different defects or clusters within a general high angle grain boundary. For instance, to calculate this binding energy, the formation energies of He_nV clusters and interstitial He are required (and the vacancy formation energy for $n = 1$), which are directly calculated from Equations 2 and 3 with constants/energies from Table 2. Figure 5 plots the evolution of the binding energy of an interstitial He atom to a He_{n-1}V cluster to form a He_nV cluster for $n = 1-8$ (i.e., $\text{He} \rightsquigarrow \text{He}_n\text{V}$), which is examined herein. These curves represent the evolution of this binding energy and is the general behavior for the individual atomic simulation results shown in Figure 3. For instance, it is helpful to reexamine the trends in

Figure 3. First, it is apparent that the binding energies associated with the formation of the He_1V cluster are all below the bulk behavior (i.e., recall that white is bulk behavior and blue is below this). Second, it is also apparent that as n increases, there is a tendency for some binding energies in the grain boundary transition region to have larger binding values than in the bulk single crystal (i.e., red indicates energies that are larger than in the bulk). Third, the transition between these two extremes is around He_4V ; $n \leq 4$ is mostly binding energies below bulk and $n \geq 5$ is a mixture of binding energies above and below the bulk values. Now, compare these individual atomistic simulation results to those in Figure 5. The model captures these qualitative trends quite well. For example, the model for the binding energy of $\text{He} \rightsquigarrow \text{He}_1\text{V}$ predicts all binding energies below the bulk values while $\text{He} \rightsquigarrow \text{He}_8\text{V}$ predicts a transition region with values above bulk

Figure 5: Model evolution of binding energy of an interstitial He atom to a He_{n-1}V clusters to form He_nV clusters, which are based on the models in Figure 4. The numbers are used to indicate n for the He_nV cluster that forms (e.g., ‘1’ indicates an interstitial He atom combining with a vacancy to produce He_1V cluster).

energies. Moreover, the transition between these two behaviors occurs at $\text{He} \rightsquigarrow \text{He}_4\text{V}$. Last, the bulk binding energies are captured exactly, because the bulk formation energies are used in the calculation. For example, the large difference in bulk binding energies between He_1V and the remaining He–V clusters ($\text{He}_{\{2,3,\dots,8\}}\text{V}$), as shown in Figure 2, is evident in Figure 5.

The significance of the model described by Equation 2 is that the aforementioned model can subsequently be used to link atomistic energies to both formation and binding energies of defects within a grain boundary environment. In addition, this model can be fit by either utilizing the energies from a large number of simulations, as herein, or utilizing a limited amount of higher accuracy grain boundary energies, as may be the case for quantum mechanics simulations. In this work, we have shown that this model captures the formation and binding energies of the various He–V clusters and also captures the subsequent binding energies of different clusters/defects in the presence of grain boundaries – both of which are important when accounting for the total energetics pertaining to He–V cluster nucleation growth in the presence of the high angle grain boundaries.

5. Conclusions

The nucleation and growth of He clusters in a monovacancy eventually forms larger He bubbles on grain boundaries and within the lattice for $\alpha\text{-Fe}$. Herein, the formation/binding energetics of a single He atom to a He_nV cluster ($n = \{1-7\}$) is calculated to understand how the grain boundary affects this binding behavior in bcc $\alpha\text{-Fe}$. The challenge herein is that there is already a binding energy of the He–V clusters to the grain boundary itself that must be removed to compare how the local grain boundary environment affects the binding energy of subsequent He atoms growing the He_nV cluster. Calculating this binding energy value required the formation energies for 1–8 He atoms in a monovacancy at all potential grain boundary sites within 15 Å of ten select grain boundaries ($\langle 100 \rangle$ and $\langle 110 \rangle$ low Σ symmetric tilt grain boundaries) along with interstitial He and vacancy formation energies. Several conclusions can be made.

The first conclusion is that the binding energy of an additional He atom in a He_nV cluster is significantly affected by the grain boundary environment when compared to the same cluster in the bulk. That is, an interstitial He atom combining with a monovacancy to produce a He_1V cluster is no more energetically favored in the grain boundary region than in the single lattice; in fact, approximately 30% of grain boundary sites (< 10 Å) have binding energies that are actually lower than those in the bulk environment. This

leads to an interesting point; while it is energetically favorable for He-V clusters to be located at most grain boundary sites, there is actually a lower binding energy for an additional He atom in the boundary than in the bulk. However, there is a gradual transition of this behavior with increasing size of the He_nV cluster. For a He atom combining with a He_7V cluster to produce a He_8V cluster, there are many more sites with binding energies above the bulk lattice energies ($\approx 30\%$) than below ($\approx 20\%$), with binding energies up to 4 eV (compared to approximately 1.3 eV in bulk). Moreover, despite the large range of different local environments within the grain boundaries, it is nearly always energetically favorable for a nearby interstitial He atom to combine with either a monovacancy or a He_nV cluster to form a larger He_nV cluster.

The second conclusion is that the binding energies for an additional He atom are larger away from the grain boundary center as the size of the He_nV cluster increases. A model of mean behavior of the binding energies of the different He_nV clusters, interstitials, and vacancies with the grain boundary sites was used to calculate the binding energy of an additional He atom throughout the grain boundary region. The model results show that the binding energies of an additional He atom are significantly higher than those in bulk for larger He_nV clusters ($n \geq 5$) that are located away from the grain boundary center ($\approx 5 \text{ \AA}$), which qualitatively agrees with the binding energies plotted against the spatial location of the original grain boundary site. Hence, there are two important energetic considerations for nucleation and growth of He_nV clusters: the binding energy of the clusters themselves with the grain boundary [43, 44] and the binding energy of additional He atoms growing the He_nV clusters, which has been shown in this study.

Acknowledgments

F.G. is grateful for the support by the US Department of Energy, Office of Fusion Energy Science, under Contract DE-AC06-76RLO 1830.

References

- [1] E. E. Bloom, J. T. Busby, C. E. Duty, P. J. Maziasz, T. E. McGreevy, B. E. Nelson, B. A. Pint, P. F. Tortorelli, and S. J. Zinkle. Critical questions in materials science and engineering for successful development of fusion power. *Journal of Nuclear Materials*, 367–370:1–10, 2007. [2](#)
- [2] S. J. Zinkle and J. T. Busby. Structural materials for fission & fusion energy. *Materials Today*, 12(11):12–19, 2009. [2](#)

- [3] H. Ullmaier. The influence of helium on the bulk properties of fusion-reactor structural-materials. *Nuclear Fusion*, 24(8):1039–1083, 1984. [2](#)
- [4] T. Yamamoto, G. R. Odette, H. Kishimoto, J. W. Rensman, and P. F. Miao. On the effects of irradiation and helium on the yield stress changes and hardening and non-hardening embrittlement of similar to 8cr tempered martensitic steels: Compilation and analysis of existing data. *Journal of Nuclear Materials*, 356(1-3):27–49, 2006. [2](#)
- [5] H. Trinkaus and B. N. Singh. Helium accumulation in metals during irradiation - where do we stand? *Journal of Nuclear Materials*, 323(2-3):229–242, 2003. [2](#)
- [6] L. K. Mansur and W. A. Coghlan. Mechanisms of helium interaction with radiation effects in metals and alloys - a review. *Journal of Nuclear Materials*, 119(1):1–25, 1983. [2](#)
- [7] R. E. Stoller. The influence of helium on microstructural evolution - implications for dt fusion-reactors. *Journal of Nuclear Materials*, 174(2-3):289–310, 1990. [2](#)
- [8] R. Vassen, H. Trinkaus, and P. Jung. Diffusion of helium in magnesium and titanium before and after clustering. *Journal of Nuclear Materials*, 183(1-2):1–8, 1991. [2](#)
- [9] B. van der Schaaf, D. S. Gelles, S. Jitsukawa, A. Kimura, R. L. Klueh, A. Moslang, and G. R. Odette. Progress and critical issues of reduced activation ferritic/martensitic steel development. *Journal of Nuclear Materials*, 283–287:52–59, 2000. [2](#)
- [10] E. Getto, Z. Jiao, A. Monterrosa, K. Sun, and G.S. Was. Effect of pre-implanted helium on void swelling evolution in self-ion irradiated {HT9}. *Journal of Nuclear Materials*, (0):–, 2015. [2](#)
- [11] C. C. Fu and F. Willaime. Ab initio study of helium in alpha-fe: Dissolution, migration, and clustering with vacancies. *Physical Review B*, 72(6):064117, 2005. [2](#)
- [12] C. C. Fu and F. Willaime. Interaction between helium and self-defects in alpha-iron from first principles. *Journal of Nuclear Materials*, 367:244–250, 2007. [2](#)

- [13] T. Seletskaya, Y. N. Osetsky, R. E. Stoller, and G. M. Stocks. Calculation of helium defect clustering properties in iron using a multi-scale approach. *Journal of Nuclear Materials*, 351(1-3):109–118, 2006. [2](#), [8](#)
- [14] H. L. Heinisch, F. Gao, R. J. Kurtz, and E. A. Le. Interaction of helium atoms with edge dislocations in alpha-fe. *Journal of Nuclear Materials*, 351(1-3):141–148, 2006. [2](#)
- [15] H. L. Heinisch, F. Gao, and R. J. Kurtz. Atomistic modeling of helium interacting with screw dislocations in alpha-fe. *Journal of Nuclear Materials*, 367:311–315, 2007. [2](#)
- [16] X. T. Zu, L. Yang, F. Gao, S. M. Peng, H. L. Heinisch, X. G. Long, and R. J. Kurtz. Properties of helium defects in bcc and fcc metals investigated with density functional theory. *Physical Review B*, 80(5):054104, 2009. [2](#)
- [17] L. Ventelon, B. Wirth, and C. Domain. Helium-self-interstitial atom interaction in alpha-iron. *Journal of Nuclear Materials*, 351(1-3):119–132, 2006. [2](#)
- [18] D. Stewart, Y. Osetskiy, and R. Stoller. Atomistic studies of formation and diffusion of helium clusters and bubbles in bcc iron. *Journal of Nuclear Materials*, 417(1-3):1110–1114, 2011. [2](#)
- [19] E. Hayward and C. Deo. Synergistic effects in hydrogen-helium bubbles. *Journal of Physics-Condensed Matter*, 24(26):265402, 2012. [2](#)
- [20] Qian Li, C.M. Parish, K.A. Powers, and M.K. Miller. Helium solubility and bubble formation in a nanostructured ferritic alloy. *Journal of Nuclear Materials*, 445(13):165 – 174, 2014. [2](#)
- [21] P. L. Lane and P. J. Goodhew. Helium bubble nucleation at grain boundaries. *Philosophical Magazine A*, 48(6):965–986, 1983. [2](#)
- [22] V. Randle. Interactions between grain boundaries and helium bubbles in an austenitic steel during strain induced grain growth. *Acta Metallurgica et Materialia*, 39(4):481 – 492, 1991. [2](#)
- [23] R. Janisch and C. Elsasser. Segregated light elements at grain boundaries in niobium and molybdenum. *Physical Review B*, 67(22), 2003. [3](#)
- [24] M. Yamaguchi, Y. Nishiyama, and H. Kaburaki. Decohesion of iron grain boundaries by sulfur or phosphorous segregation: First-principles calculations. *Physical Review B*, 76(3), 2007. [3](#)

- [25] A. Kiejna and E. Wachowicz. Segregation of cr impurities at bcc iron surfaces: First-principles calculations. *Physical Review B*, 78(11), 2008. [3](#)
- [26] R. Janisch and C. Elsasser. Growth and mechanical properties of a moc precipitate at a mo grain boundary: An ab initio density functional theory study. *Physical Review B*, 77(9), 2008. [3](#)
- [27] T. Ossowski, E. Wachowicz, and A. Kiejna. Effect of iron additions on intergranular cohesion in chromium. *Journal of Physics-Condensed Matter*, 21(48), 2009. [3](#)
- [28] E. Wachowicz and A. Kiejna. Effect of impurities on structural, cohesive and magnetic properties of grain boundaries in alpha-fe. *Modelling and Simulation in Materials Science and Engineering*, 19(2), 2011. [3](#)
- [29] K. N. Solanki, M. A. Tschopp, M. A. Bhatia, and N. R. Rhodes. Atomistic investigation of the role of grain boundary structure on hydrogen segregation and embrittlement in alpha-fe. *Metallurgical and Materials Transactions a-Physical Metallurgy and Materials Science*, 44A(3):1365–1375, 2013. [3](#), [4](#)
- [30] N. R. Rhodes, M. A. Tschopp, and K. N. Solanki. Quantifying the energetics and length scales of carbon segregation to alpha-fe symmetric tilt grain boundaries using atomistic simulations. *Modelling and Simulation in Materials Science and Engineering*, 21(3):035009, 2013. [3](#), [4](#)
- [31] M. A. Tschopp, M. F. Horstemeyer, F. Gao, X. Sun, and M. Khaleel. Energetic driving force for preferential binding of self-interstitial atoms to fe grain boundaries over vacancies. *Scripta Materialia*, 64(9):908–911, 2011. [3](#), [4](#), [5](#), [6](#)
- [32] M. A. Tschopp, K. N. Solanki, F. Gao, X. Sun, M. A. Khaleel, and M. F. Horstemeyer. Probing grain boundary sink strength at the nanoscale: Energetics and length scales of vacancy and interstitial absorption by grain boundaries in alpha-fe. *Physical Review B*, 85(6):064108, 2012. [3](#), [4](#), [5](#), [6](#), [26](#)
- [33] R. J. Kurtz and H. L. Heinisch. The effects of grain boundary structure on binding of he in fe. *Journal of Nuclear Materials*, 329:1199–1203, 2004. [3](#)

- [34] F. Gao, H. Heinisch, and R. J. Kurtz. Diffusion of he interstitials in grain boundaries in alpha-fe. *Journal of Nuclear Materials*, 351(1-3):133–140, 2006. [3](#)
- [35] R. J. Kurtz, H. L. Heinisch, and F. Gao. Modeling of he-defect interactions in ferritic alloys for fusion. *Journal of Nuclear Materials*, 382(2-3):134–142, 2008. [3](#)
- [36] F. Gao, H. L. Heinisch, and R. J. Kurtz. Migration of vacancies, he interstitials and he-vacancy clusters at grain boundaries in alpha-fe. *Journal of Nuclear Materials*, 386-88:390–394, 2009. [3](#)
- [37] D. Terentyev and X. He. Dimensionality of interstitial he migration in $\langle 110 \rangle$ tilt grain boundaries in alpha-fe. *Computational Materials Science*, 49(4):858–864, 2010. [3](#)
- [38] L. Zhang, X. L. Shu, S. O. Jin, Y. Zhang, and G. H. Lu. First-principles study of he effects in a bcc fe grain boundary: site preference, segregation and theoretical tensile strength. *Journal of Physics-Condensed Matter*, 22(37):375401, 2010. [3](#)
- [39] L. Zhang, Y. Zhang, W. T. Geng, and G. H. Lu. Towards theoretical connection between tensile strength of a grain boundary and segregated impurity concentration: Helium in iron as an example. *EPL*, 98(1):17001, 2012. [3](#)
- [40] D. Terentyev and X. He. Effect of cr precipitates and he bubbles on the strength of $\langle 110 \rangle$ tilt grain boundaries in bcc fe: An atomistic study. *Computational Materials Science*, 50(3):925–933, 2011. [3](#)
- [41] L. Zhang, C. C. Fu, and G. H. Lu. Energetic landscape and diffusion of he in alpha-fe grain boundaries from first principles. *Physical Review B*, 87(13):134107, 2013. [3](#), [5](#)
- [42] L. Zhang, Y. Zhang, and G. H. Lu. Structure and stability of he and he-vacancy clusters at a sigma 5(310)/[001] grain boundary in bcc fe from first-principles. *Journal of Physics-Condensed Matter*, 25(9):095001, 2013. [3](#)
- [43] M.A. Tschopp, F. Gao, L. Yang, and K.N. Solanki. Binding energetics of substitutional and interstitial helium and di-helium defects with grain boundary structure in α -fe. *Journal of Applied Physics*, 115:033503, 2014. [3](#), [4](#), [5](#), [6](#), [7](#), [19](#), [26](#)

- [44] M. A. Tschopp, F. Gao, and K. N. Solanki. Binding of he_nv clusters to α -Fe grain boundaries. *Journal of Applied Physics*, 115(23):233501, 2014. [3](#), [4](#), [5](#), [6](#), [7](#), [14](#), [15](#), [19](#), [26](#), [30](#)
- [45] L. Yang, F. Gao, R.J. Kurtz, and X.T. Zu. Atomistic simulations of helium clustering and grain boundary reconstruction in alpha-iron. *Acta Materialia*, 82(0):275 – 286, 2015. [3](#)
- [46] Lei Zhang, Chu-Chun Fu, Erin Hayward, and Guang-Hong Lu. Properties of he clustering in α -fe grain boundaries. *Journal of Nuclear Materials*, in press, 2015. [3](#)
- [47] C. P. Xu, X. Y. Liu, F. Gao, Y. H. Li, and Y. Q. Wang. Modeling radiation damage near grain boundary in helium-doped alpha-iron. *Nuclear Instruments & Methods in Physics Research Section B-Beam Interactions with Materials and Atoms*, 332:426–431, 2014. [3](#)
- [48] K. Morishita, R. Sugano, B. D. Wirth, and T. D. de la Rubia. Thermal stability of helium-vacancy clusters in iron. *Nuclear Instruments & Methods in Physics Research Section B-Beam Interactions with Materials and Atoms*, 202:76–81, 2003. [3](#)
- [49] M. I. Baskes and V. Vitek. Trapping of hydrogen and helium at grain-boundaries in nickel - an atomistic study. *Metallurgical Transactions a-Physical Metallurgy and Materials Science*, 16(9):1625–1631, 1985. [3](#)
- [50] K. Refson. Moldy: a portable molecular dynamics simulation program for serial and parallel computers. *Computer Physics Communications*, 126(3):310–329, 2000. [5](#)
- [51] G. J. Ackland, K. D’Mellow, S. L. Daraszewicz, D. J. Hepburn, M. Uhrin, and K. Stratford. The moldy short-range molecular dynamics package. *Computer Physics Communications*, 182(12):2587–2604, 2011. [5](#)
- [52] F. Gao, D. J. Bacon, P. E. J. Flewitt, and T. A. Lewis. A molecular dynamics study of temperature effects on defect production by displacement cascades in alpha-iron. *Journal of Nuclear Materials*, 249(1):77–86, 1997. [5](#)
- [53] G. J. Ackland, M. I. Mendelev, D. J. Srolovitz, S. Han, and A. V. Barashev. Development of an interatomic potential for phosphorus impurities in alpha-iron. *Journal of Physics-Condensed Matter*, 16(27):S2629–S2642, 2004. [5](#)

- [54] F. Gao, H. Q. Deng, H. L. Heinisch, and R. J. Kurtz. A new fe-he interatomic potential based on ab initio calculations in alpha-fe. *Journal of Nuclear Materials*, 418(1-3):115–120, 2011. [5](#), [8](#)
- [55] P. H. Chen, X. C. Lai, K. Z. Liu, X. L. Wang, B. Bai, B. Y. Ao, and Y. Long. Development of a pair potential for fe-he by lattice inversion. *Journal of Nuclear Materials*, 405(2):156–159, 2010. [8](#)
- [56] D. M. Stewart, Y. N. Osetsky, R. E. Stoller, S. I. Golubov, T. Seletskaya, and P. J. Kamenski. Atomistic studies of helium defect properties in bcc iron: Comparison of he-fe potentials. *Philosophical Magazine*, 90(7-8):935–944, 2010. [8](#)

Appendix

5.1. Formation/Binding Energies of Interstitial He and He_nV Clusters

Quantifying the binding energy of an interstitial He atom to an existing He_nV cluster within the grain boundary and how this is affected by the grain boundary environment requires formation and binding energies of these individual He configurations with the different grain boundaries from the present study. This information has been calculated in Tschopp et al. [32, 43, 44] and is displayed in Figures A1 and A2. Figure A1 displays the grain boundary structure and the spatial distribution of binding energies for interstitial He and di-interstitial He atoms for the ten $\langle 100 \rangle$ (top rows) and $\langle 110 \rangle$ (bottom rows) symmetric tilt grain boundaries examined within. The grain boundaries in this figure are arranged in order of increasing misorientation angle (top to bottom) for each symmetric tilt grain boundary system. First, the dichromatic grain boundary structure images indicate the relative atomic positions into the page (i.e., in the tilt direction) by coloring atoms either white or black for different $\{100\}$ or $\{110\}$ planes (i.e., the planes perpendicular to the tilt direction). For the binding energy calculations for interstitial He, each site corresponds to 20 simulations performed with different starting locations for interstitial He. Subsequently, the statistics of the binding energy for each site can be computed and plotted as a function of spatial position with respect to the (nearest) Fe atom site. Figure A1 displays the maximum binding energy (i.e., minimum formation energy) and the mean binding energy for the ten grain boundaries. The sites are colored by the binding energy, which is scaled between zero and the maximum binding energy over all sites and GBs for that particular interstitial He defect (i.e., the maximum over the entire column); in a similar manner, this plot can be viewed in terms of formation energies, which are scaled between the bulk formation energy (white) to the minimum formation energy (red). The maximum binding energy indicates the relative strength of attraction for each site, since it includes the most favorable interstitial location from a number of potential interstitial He/ He_2 locations surrounding each Fe atom. The mean binding energy indicates that, although some interstitial He/ He_2 locations at a particular Fe site may have high maximum binding energies, as the distance from the GB center increases there is a higher probability that a number of interstitial locations also have much lower binding energies, which resemble the formation/binding energies in the single crystal lattice. In agreement with previous findings [43, 44], the $\Sigma 3(112)$ twin boundary displays binding behavior with He that differs from the other nine grain boundaries in this study – in this sense, the $\Sigma 3(112)$ GB can be considered

a ‘special’ boundary while all others can be considered more representative of general high angle grain boundaries.

Figure A2 displays the spatial distribution of binding energies for He_nV clusters for the ten $\langle 100 \rangle$ (top rows) and $\langle 110 \rangle$ (bottom rows) symmetric tilt grain boundaries. Many of the characteristics of these plots are similar to Figure A1: the boundaries are ordered similarly in terms of misorientation angle (from top to bottom) and tilt systems ($\langle 100 \rangle$, $\langle 110 \rangle$); He_2V to He_8V are the maximum binding energies from 20 starting configurations for each site; and the colorbar is scaled for each defect based on the maximum binding energy over all GBs (i.e., the entire column [exact maximum binding energies are 0.699, 1.617, 2.430, 2.981, 4.029, 4.801, 5.851, and 6.780 eV for $n=1-8$ atoms in He_nV]). First, there are general trends for all grain boundaries and structures. The most noticeable trend is that the binding energy for the He_nV clusters increases as the sites are located closer to the grain boundary center. In general, the largest binding energies are along the center of the grain boundary plane or along the 1st layer from the GB plane. There is also a noticeable symmetry to the binding energies about the grain boundary plane due to the symmetric nature of these grain boundary structures. Second, for a specific He_nV cluster, each column shows how the grain boundary structure affects the binding energy of that particular He configuration. Again, the most noticeable trend is that the $\Sigma 3(112)$ twin boundary has a behavior different from the other nine grain boundaries, irrespective of the number of He atoms in the monovacancy. Last, for a specific grain boundary, moving from left to right within each row increases the number of He atoms in the monovacancy. The most noticeable trend is that the binding behavior becomes more uniform at the grain boundary. That is, the binding energy of a He_1V cluster is likely more influenced by the local (first-nearest-neighbor) grain boundary environment than the binding energy of a He_8V cluster, which is perhaps expected based on a larger dilational strain induced by a larger He cluster. Hence, for much larger clusters, the binding behavior may be more strongly influenced by the thermodynamic reduction in the overall grain boundary energy.

Figure A1: The grain boundary structure for $\langle 100 \rangle$ and $\langle 110 \rangle$ STGBs (upper and lower rows) where black and white atoms denote atoms lying on different $\{100\}$ and $\{110\}$ planes, respectively. The maximum and mean binding energies of interstitial He (HeInt) in various sites is also shown. The atoms are colored by the binding energy, which is scaled between zero and the maximum binding energy over all GBs and GB sites for each interstitial He defect.

Figure A2: The minimum binding energies of the eight different He_nV defects in various sites for all ten high angle grain boundaries (upper rows – $\langle 100 \rangle$ GBs, lower rows – $\langle 110 \rangle$ GBs). The atoms are colored by the binding energy, which is scaled between zero and the maximum binding energy over all GBs and GB sites for each He_nV cluster.

5.2. Model example and parameter interpretation

As an example of the fit of Eq. 2 to atomistic energies, Figure A3 fits the aforementioned equation to the binding energies of He_8V clusters to the grain boundary for all grain boundaries except for the $\Sigma 3\{112\}$ GB. The constant c_3 is both set to 2 in one instance (solid black line) and is allowed to vary in another (dotted black line) to test whether c_3 is required to best capture the atomistic results. Both model fits capture the general trend of the binding energies as a function of distance – if the variability about the mean binding energies is important, an approach similar to that applied in Tschopp et al. [44] can be used to capture this. A few other features are accentuated in this plot for the $c_3 = 2$ model fit to better understand the meaning of the constants c_1 , c_2 , and c_3 in Equation 2. First, the constant c_1 (yellow star) indicates the (mean) binding energy of the He_8V cluster at a grain boundary distance of zero. Second, the constant c_2 , which has units

Figure A3: Evolution of He_8V binding energy as a function of distance for all grain boundaries except the $\Sigma 3\{112\}$ GB. The line is the least-squares fit of the model (Eq. 2) to the atomistic data both using both $c_3 = 2$ ($c_1 = 6.4$ eV, $c_2 = 5.1$ Å) and allowing c_3 to vary ($c_1 = 5.7$ eV, $c_2 = 5.3$ Å, $c_3 = 4.2$).

of distance ($\text{\AA}$), is identified on both sides of the grain boundary (yellow diamond); since $-(x/c_2)^{c_3} = -1$ in Eq. 2, this length scale constant always intersects the curve at $0.3679c_1$, regardless of the value of the constant c_3 , i.e., both models pass through this point. Since the model form is similar to a normal distribution (Gaussian), as shown here, it is apparent that the c_1 term describes the height of the normal distribution (i.e., the maximum binding energy or minimum formation energy) while the c_2 term describes the width of the distribution. Third, the constant c_3 controls the slope of the transition region, which may be important in certain cases. The solid line represents the model with $c_3 = 2$, which reverts Eq. 2 to the form of a normal distribution. Allowing c_3 to vary within the model altered the shape of the curve, causing both c_1 and c_2 to change. As c_3 increases far beyond 2, the curve gradually transforms towards a step function. Last, as a length scale metric that is a function of the constants c_1 , c_2 , and c_3 , the full width half maximum (FWHM) distance is used herein. For example, FWHM changes with the slope of the transition region c_3 (compare FWHM in Table 2), unlike the length scale constant c_2 . It can be easily shown that this value is calculated by:

$$\text{FWHM} = 2c_2 [\ln(2)]^{1/c_3}. \quad (4)$$

The two models (with $c_3 = 2$ and with varying c_3) can be compared in terms of their fit to the atomistic data. First, when c_3 is included as a model fitting parameter, $c_3 > 2$ and the R^2 of the model fit is improved by only a slight amount (average of 2%) with the best improvement obtained for larger He-V clusters (up to 3.5% improvement). The parameter c_1 is decreased slightly and c_2 is increased slightly in the model with varying c_3 , resulting in FWHM values that can differ by over 1 $\text{\AA}$ in some cases. The minor difference caused by varying c_3 resulted in using the prior Gaussian-based model with $c_3 = 2$ throughout the present work.