THE EFFECTS OF GRAIN BOUNDARY STRUCTURE ON BINDING OF He IN Fe—R. J Kurtz and H. L. Heinisch, Jr. (Pacific Northwest National Laboratory)*

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EXTENDED ABSTRACT

Atomistic computer simulations were used to explore the effect of grain boundary (GB) structure on the binding energy of He in Fe. Symmetrical tilt GBs spanning a range of GB energies and excess volumes were examined. While symmetrical tilt GBs represent only a small fraction of the GB character distribution in actual materials, the present results span a wide range of GB properties, and therefore are likely relevant to more complex GB structures.

Most of the details pertaining to the methodology used in the calculations of the atomic arrangements of GBs have been described in detail elsewhere [1, 2]. The model consists of a two part computational cell, rectangular in shape. One part, Region I, contains movable atoms embedded in a semi-rigid part, Region II. The GB approximately bisects the model as shown in Figure 1. Equilibrium, ~0 K, structures are obtained via relaxation using molecular dynamics with an energy quench. The two grains are free to move and undergo homogenous displacement in all three directions and this movement occurs during the relaxation via a viscous drag algorithm. Periodic border conditions are employed in the *x* and *z* directions. Four symmetric tilt GBs were studied in this work, all a common <101> tilt axis. The four GBs were $\Sigma 3$ {112} Θ = 70.53°, $\Sigma 11$ {323} Θ = 50.48°, $\Sigma 9$ {114} Θ = 38.94°, and $\Sigma 3$ {111} Θ = 70.53°. The interatomic potential used in this research has been described in detail previously [3].

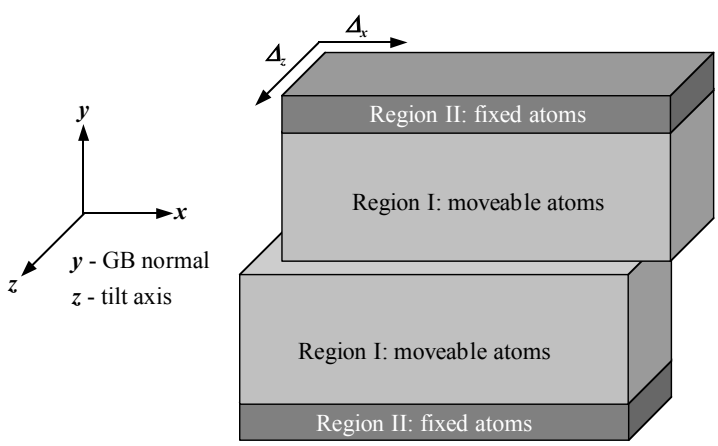

Figure 1. Model geometry used in GB simulations. Models are periodic in the *x* and *z* directions. Δ_x and Δ_z are translation vectors parallel to the grain boundary plane.

An energy distribution function was generated for each boundary by dividing the GB into a large number of slices and computing the excess potential energy E_{xs}/A for each slice, which is

$$\frac{E_{xs}}{A} = \frac{\Sigma\left(E_{gb} - E_p\right)}{L_z w} \qquad (1)$$

where E_{gb} is the potential energy of an atom in the GB model, E_p is the potential energy of an atom in a perfect crystal, L_z is the thickness of the model parallel to the tilt axis and *w* is the slice width. The

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summation is performed over all atoms in a slice. The GB energy per unit area, γ_{gb}, can be determined by integrating the energy distribution function over several repeat periods. Table 1 lists γ_{gb} for the four boundaries examined here. The GB energies are generally quite large relative to free surface energies. For the Fe potential employed here the free surface energies γ_{100}, γ_{110} and γ_{111} are 1.81, 1.58 and 2.00 J/m^2, respectively. It should be noted that the calculated free surface energies are slightly low relative to experimentally measured values for Fe, which are typically in the neighborhood of 1.6 – 2.3 J/m^2.

Table 1. Grain boundary energy and excess volume for the four symmetric tilt boundaries considered in this study. The tilt axis is <101>.

Σ	GB Plane	γ_{gb}, J/m^2	V_{gb}/A, nm
3	{112}	0.30	0.007
11	{323}	1.00	0.022
9	{114}	1.40	0.036
3	{111}	1.51	0.041

Another important property is the volume expansion normal to the GB plane. This quantity is determined by calculating the excess volume per unit area of GB. Excess atomic volumes were determined from the relation

$$\Omega_{xs} = \Omega_v - \Omega_p \qquad (2)$$

where Ω_v is the Voronoi volume of an atom in the GB model and Ω_p is the atomic volume of an Fe atom in a perfect, unstrained lattice. The Voronoi volume is the volume of a polyhedron whose faces are perpendicular bisectors of the lines connecting an atom to its nearest neighbors. The atomic volume for Fe in this study is 0.01178 nm^3. The excess volume, V_{gb}, in a rectangular patch of GB of area, A, is computed from

$$\frac{V_{gb}}{A} = \frac{\sum \Omega_{xs}}{L_x L_z} \qquad (3)$$

where L_x is the length of the GB perpendicular to the tilt axis. In order to properly compute V_{gb}/A a sufficiently large volume of material must be chosen to account for excess volume variation in the GB plane and normal to it. In this work we computed values of Ω_{xs} for atom planes parallel to the GB until it was essentially zero. Furthermore, values of L_x and L_z were selected to include several repeat periods in those directions so that an accurate estimate of the GB excess volume could be obtained. Table 1 gives V_{gb}/A for the GBs investigated in this study. Note there is good correlation between the GB energy and excess volume.

Binding of He to GBs was explored by insertion of a single He atom in either a substitutional or interstitial location, and then relaxing the simulation block. Both atomic displacements of Region I atoms and rigid-body translations of the two grains were allowed during the relaxation. Since the excess volume varies significantly in the GB core a large number of different starting positions for the He atom were examined. Binding energies at a particular site α (either substitutional or interstitial) in and near the GB core were determined from the equation

$$E_B^{\alpha} = E_{gb}^{\alpha} - E_{gb} - E_f^{\alpha} \qquad (4)$$

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. In Figure 2 the substitutional or interstitial He binding energy is plotted as a function of distance from the Σ3 {111} GB. Also shown in Figure 2 is the distance dependence of the excess volume normal to the GB plane. Three observations may be made from this plot. First, the binding energy of substitutional He is considerably smaller than interstitial He, indicating that interstitial He will be strongly trapped by vacancies in the GB. Relative to the bulk, interstitial He is very strongly bound to the GB, a result similar to the findings of Baskes and Vitek in Ni [4]. Second, the binding energy for both substitutional and interstitial He atoms approaches zero at a

distance of about 0.7 nm from the GB. Similar results were obtained for the other GBs investigated in this study. This "capture radius" depended on GB properties. The Σ3 {112} GB, with the lowest GB energy and V_{gb}/A, gave a capture radius of only ~0.3 nm. Third, the He binding energy is highly non-uniform in the GB core. There appears to be a rough correspondence between the distance dependence of the He binding energies and the excess volume, but this is certainly not unequivocal. As shown in the plot in Figure 3, there is an excellent correlation between the maximum binding energy for both substitutional and interstitial He and the GB excess volume.

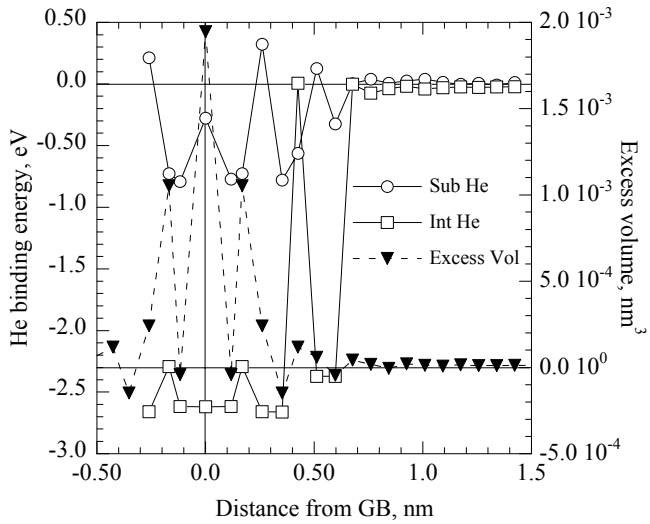

Figure 2. Dependence of excess volume and He binding energy on distance from the GB plane.

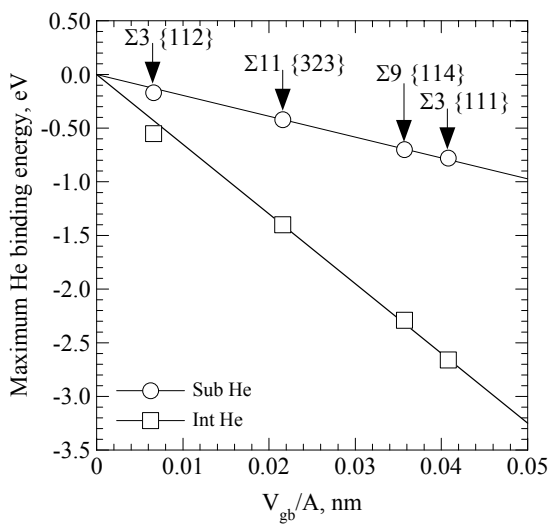

Figure 3. Dependence of the maximum He binding energy on GB excess volume.

Conclusions

The results show that both substitutional and interstitial He atoms are bound to all of the GBs studied. Interstitial He is more strongly bound (E^{i}_{gb} ~0.5 to 2.7 eV) to the GB core than substitutional He (E^{s}_{gb} ~0.2 to 0.8 eV). The maximum binding energy of He was found to increase linearly with GB excess volume. The capture radius for a He atom varied from ~0.3 to 0.7 nm and also depended on GB

properties. Lastly, the He binding energy varied significantly within the GB core and approximately corresponded to the variation in atomic excess volume normal to the GB plane. Further work is needed to investigate the effect of multiple He atoms and vacancies on binding to GBs. In addition, migration of He along the GB is an important transport mechanism that will be the subject of a future atomistic study.

References

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