INTERACTION OF He_nV_m CLUSTERS WITH COHERENT AND SEMI-COHERENT Fe/Cu INTERFACES – R. J. Kurtz, H. L. Heinisch, and F. Gao (Pacific Northwest National Laboratory)*

OBJECTIVE

To use molecular dynamics computer simulations to compare the trapping of He_nV_m clusters at coherent and semi-coherent bcc Fe/bcc Cu interfaces. The semi-coherent interfaces contain an array of misfit dislocations.

SUMMARY

Previous computational modeling has shown that interstitial and substitutional He as well as He-divacancy clusters are strongly bound to extended defects in Fe such as dislocations, grain boundaries and particle-matrix interfaces. One aspect of the earlier work was the interaction of He with nanometer-scale, coherent particles embedded in an Fe matrix. Our earlier research also established that the core of an edge dislocation strongly traps He. Thus we hypothesized that a semi-coherent interface might be a stronger trap for He than a coherent interface due to the array of misfit dislocations needed to accommodate the lattice parameter mismatch between the particle and the matrix in the semi-coherent case. In the present study we employ atomisitic simulations to compare the binding of He_nV_m complexes to coherent and semi-coherent bcc Fe/ bcc Cu interfaces. The simulations show that the binding energy of He_nV_m complexes to a coherent Fe/Cu interface range from 0.35 eV for a single vacancy up to 0.70 eV for a He_1V_2 complex. A semi-coherent interface was found to be a much stronger trap for He near the core of a misfit dislocation. Binding energies varied from 0.86 eV for a substitutional He atom up to 2.38 eV for a He_1V_2 complex. These binding energies were found to be significantly larger than the values obtained for simple edge dislocations in Fe. The trend in binding energies can be rationalized in terms of the spatial dependence of excess atomic volume for each interface.

PROGRESS AND STATUS

Introduction

The work reported here is part of a comprehensive effort to develop a multi-scale model of He transport and fate in ferritic/martensitic alloys [1]. The model will be used to predict the performance of irradiated ferritic/martensitic steels, both conventional and oxide dispersion strengthened. In previous studies we employed atomistic simulations to explore the binding and migration of He at extended defects in Fe such as dislocations, grain boundaries (GB), and particle-matrix interfaces [2-5]. The results showed that interstitial He is strongly bound to both dislocations and GBs with maximum binding energies ranging from 0.55-2.66 eV. Substitutional He is also bound to dislocations and GBs, but much more weakly than for interstitial He, with maximum binding energies between 0.17-0.78 eV. Point defect complexes are also bound to coherent, positive misfit, 2 nm Cu particles embedded in an Fe matrix with binding energies ranging from 0.50-0.58 eV for single vacancies and substitutional He atoms. Divacancies and He/di-vacancy complexes are more strongly bound with binding energies of ~0.85 eV. Point defects are not as strongly bound to particles elastically softer than Fe when compared to particles elastically stiffer than Fe.

A key result from this research is that binding energies strongly correlate with defect excess volume. Consequently edge dislocations are stronger He traps than screw dislocations because of the much larger excess volume available in an edge dislocation compared with a screw dislocation. However, jogs on edge dislocations are even stronger traps for He. Helium trapping at GBs is somewhat greater to somewhat less than for dislocations depending on the type of GB. Coherent, positive misfit, Cu nanoparticles also efficiently trap He, but it is apparent that semi-coherent particles may be more efficient traps because of the excess volume associated with the array of misfit dislocations needed to accommodate the lattice parameter mismatch between the particle and matrix. Consequently our interest

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here is to compare the relative efficiency for trapping He_nV_m complexes at a coherent interface between bcc Fe and bcc Cu to a semi-coherent interface between the same two materials.

Computational Methods

Details of the computational methods for studying the interaction of He_nV_m complexes with various defects in an Fe matrix have been described previously [5]. Here we present only the salient features of the calculations pertaining to the question of He trapping at coherent versus semi-coherent interfaces. The model consists of a two-part rectangular computational cell, periodic in x and z. One part, Region 1, contains movable atoms embedded in a semi-rigid part, Region 2. The interface approximately bisects the model as shown in Figure 1. Equilibrium structures at T ~ 0K are obtained via relaxation using a conjugate gradient scheme. The two crystals on either side of the interface are free to move and undergo homogenous strain in all three directions. This movement occurs during the relaxation via a viscous drag algorithm, i.e., the velocities and strain rates associated with such motions are proportional to the net forces acting on each of the two crystals within Region 1.

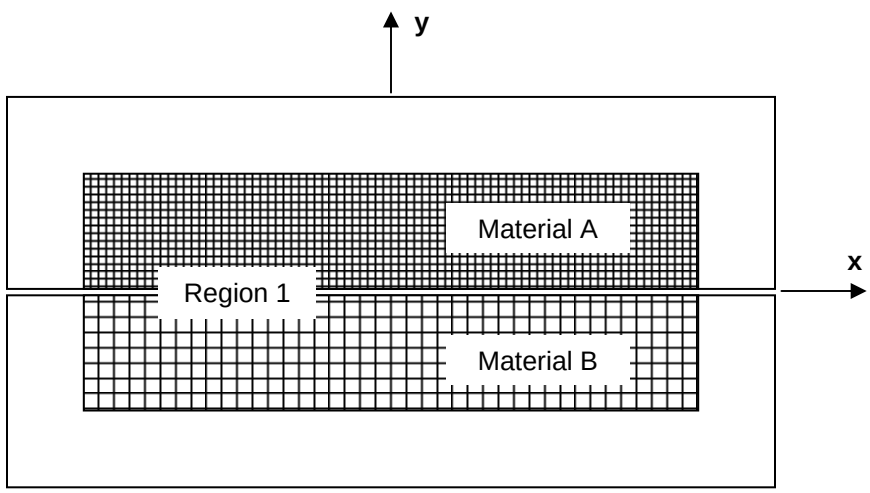

Figure 1. Schematic of the model. The interface is parallel to the x-z plane.

Coherent Interface

A cube-on-cube oriented Fe/Cu interface was studied with the interface parallel to (010). This interface was selected for investigation so that the results could be compared to a previous study of coherent Cu nanoparticles in Fe [5]. With the Fe and Cu interatomic potentials employed here [5] the lattice parameter for Fe is 0.28665 nm and for bcc Cu is 0.29607 nm, which corresponds to a mismatch of ~3.2%. Completely coherent interfaces in thick Fe/Cu bilayers likely never occur because they are energetically unfavorable compared to semi-coherent interfaces, but it is instructive to examine a coherent system because it is the favored configuration for thin layers and for nano-scale particles constrained by the crystal structure of the matrix phase. In order to construct a coherent interface that is in mechanical equilibrium the procedure described by Hoagland et al. [6] was followed. Triaxial strains were applied to each layer so that the Fe layer was in a state of biaxial tension and the Cu layer biaxial compression. The computational cell was then relaxed. To determine defect formation energies, various He_nV_m (n=0,1; m=1,2) complexes were placed at specific locations within the relaxed computational cell and the atoms in the cell were relaxed again. The binding energy of the He_nV_m complex to the coherent interface is the difference between the formation energy of the He_nV_m complex in the interface model and its formation energy in either a perfect crystal of bcc Fe or bcc Cu depending on which side of the interface the defect was located.

Semi-coherent Interface

Misfit dislocations are spontaneously created when two semi-infinite perfect crystals with different lattice parameters are joined together. The long-range elastic portion of the dislocation is not present in Region 2, and consequently Region 1 contains an image field. However, the stress and displacement fields of a periodic array of such dislocations with spacing, d, have relatively short range, vanishing with increasing distance from the interface. Thus, in bilayers where the misfit spacing is less than the height of the model, it is not necessary to adjust the positions of the atoms in Region 2. Near the interface, between misfit dislocations, coherency stresses are high. Binding energies of He_nV_m complexes were determined in the same manner as for the coherent interface. The structure of the coherent Fe/Cu interface compared to the semi-coherent Fe/Cu interface is illustrated in Figure 2. Note only one layer of atoms normal to the page is shown in Figure 2.

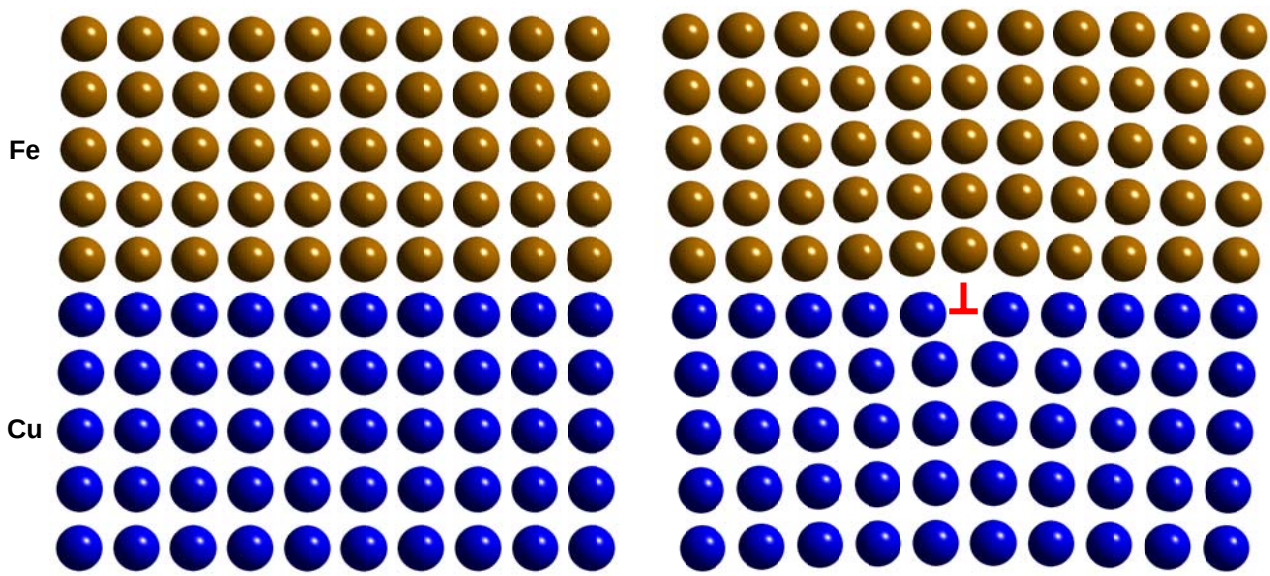

Figure 2. Structure of a coherent Fe/Cu interface on left and a semi-coherent Fe/Cu interface on right. Only one layer of atoms normal to the page is shown.

Results

Coherent Interface

Excess volume within and near interfaces strongly influences the disposition of He in crystalline materials. The atomic volume is defined as the locus of all points in space surrounding an atom that are closer to that atom than to any other atom. Excess volume at a location near an interface is defined in terms of the deviation of the atomic volume at that location from the atomic volume at a similar location in a perfect lattice. Here we calculate excess atomic volume centered on lattice sites. The distribution of excess atomic volume for the coherent Fe/Cu interface is shown in Figure 3. Note there is positive excess atomic volume everywhere in the Fe layer, and negative excess volume everywhere in the Cu layer. This is because the Fe layer is dilated relative to a perfect Fe lattice and the Cu layer is compressed relative to a perfect bcc Cu lattice. Near the interface in the first two layers of Fe and Cu the excess volume is either larger or smaller than the values far from the interface.

The binding energies of various He_nV_m complexes to a coherent Fe/Cu interface are presented in Figure 4. Single vacancies and substitutional He atoms are bound to the coherent interface on the Fe side of the bilayer with maximum binding energies of 0.35 and 0.41 eV, respectively. Divacancies and a He_1V_2 complex, with maximum binding energies of 0.66 and 0.70 eV, respectively, are more strongly bound to

the Fe side of the bilayer than are single vacancies or substitutional He atoms. The Cu layer adjacent to the interface is a relatively unfavorable site for substitutional He and the He_1V_2 complex. However, the same layer was not observed to be unfavorable for either vacancy-type defect. From these results we can conclude that the trend of binding energies to the interface for point defects containing He follows the distribution of excess atomic volume given in Figure 3.

Semi-coherent Interface

The distribution of excess atomic volume for the semi-coherent Fe/Cu interface is illustrated in Figure 5. The plot shows the excess volume for only the first two layers or rows of Fe atoms adjacent to the interface as a function of distance from the origin of the misfit dislocation. Midway between misfit dislocations the interface is coherent, so the excess volume should correspond to the value found for a purely coherent interface. From Figure 3 the excess volume for the first and second Fe layers is about 0.4 and 0.2 $Å^3$, respectively. Approximately the same values for excess volume are found in the semi-coherent model at distances far from the origin of the misfit dislocation. From Figure 5 the excess volume at ~40 Å from the misfit dislocation is 0.41 and 0.22 $Å^3$ for the first and second Fe layers, respectively. Consequently we would expect that the binding of point defects remote from misfit dislocations in the semi-coherent model will exhibit behavior similar to that found for the purely coherent case. Near the misfit dislocation there is a sharp increase in excess volume in the first Fe layer. The increase in excess volume dies away quickly with distance from the misfit dislocation and is almost the same as the purely coherent case excess volume at 6 Å away. In contrast, there is a sharp decrease in excess volume for atoms in the second Fe layer near the misfit origin. This is not surprising since the extra half plane of atoms associated with the misfit dislocation resides on the Fe side of the interface so a local state of compression exists in this region.

Figure 6 shows the dependence of binding energies for single vacancies or substitutional He atoms located in either the first or second layer of Fe atoms adjacent to the interface as a function of distance from the misfit dislocation origin. The largest binding energies for these point defect types occur in the first layer of Fe atoms where the peak positive excess volume is found. Single vacancies are bound somewhat more strongly (0.95 eV) to the misfit dislocation than substitutional He atoms (0.85 eV). The binding energy of substitutional He to the misfit dislocation is larger than the value found for the same point defect to an edge dislocation in pure Fe (0.51 eV) [3]. This may be due to the dilated state of the Fe in the Fe/Cu interface relative to an edge dislocation in pure Fe, although the calculated excess volume for the edge dislocation was about 1.2 $Å^3$ [3] compared to an excess volume for the misfit dislocation of 0.75 $Å^3$. In the second Fe layer we find single vacancies are bound to the misfit dislocation core with an energy of about 0.32 eV. This is expected since the compressive stress field of the misfit is a region where vacancies should segregate. On the other hand, substitutional He atoms are not attracted to this region due to an unfavorable excess volume. The situation for binding of divacancies and a He_1V_2 complex to the semi-coherent interface is shown in Figure 7. In the first Fe layer these defects are very strongly bound to the misfit dislocation with the binding energy for a divacancy of 1.47 eV and for the He_1V_2 complex 2.38 eV. We have also investigated the binding of a He_1V_2 complex to an edge dislocation in pure Fe and determined the binding energy to be 1.26 eV. Clearly the He_1V_2 complex is much more strongly bound to the misfit dislocation than it is to a simple edge dislocation in pure Fe. For the second Fe layer both divacancies and the He_1V_2 complex are less strongly bound to the misfit dislocation than for the first Fe layer. The divacancy is the most strongly bound in this region (0.64 eV) compared to the He_1V_2 complex (0.42 eV). Evidently, segregation of divacancies to the compressive side of the misfit dislocation should facilitate binding of He-vacancy clusters in this region.

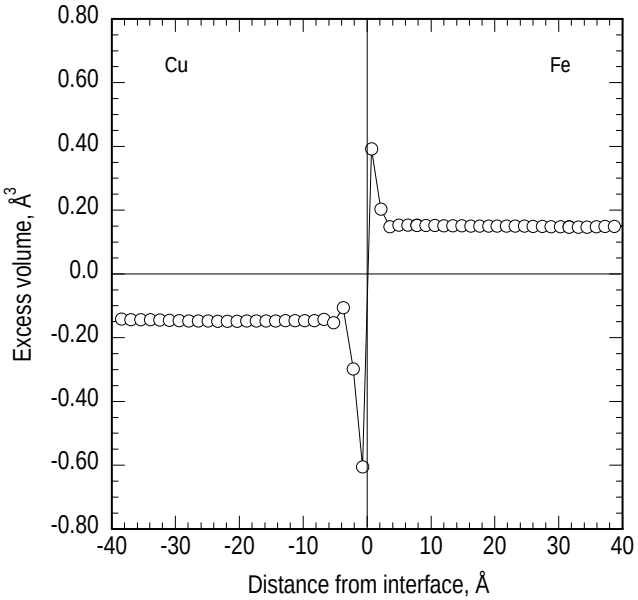

Figure 3. Distribution of excess atomic volume in a coherent Fe/Cu interface.

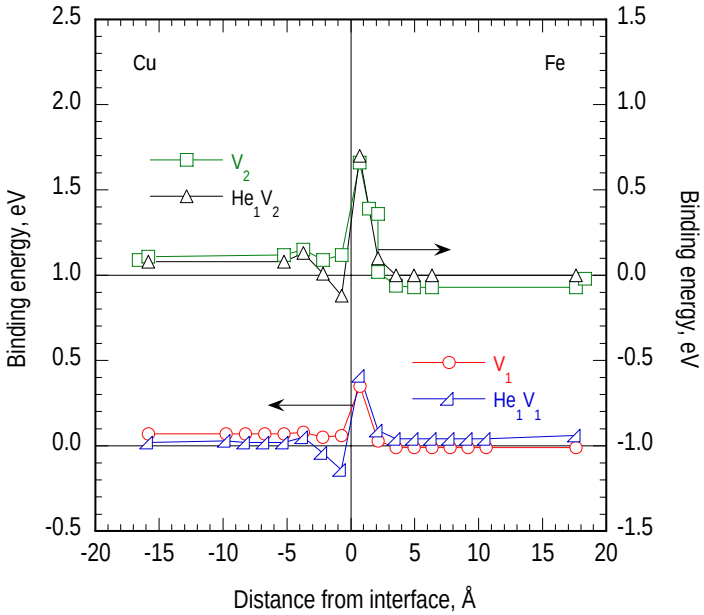

Figure 4. Binding energy of vacancies and He_nV_m complexes to a coherent Fe/Cu interface.

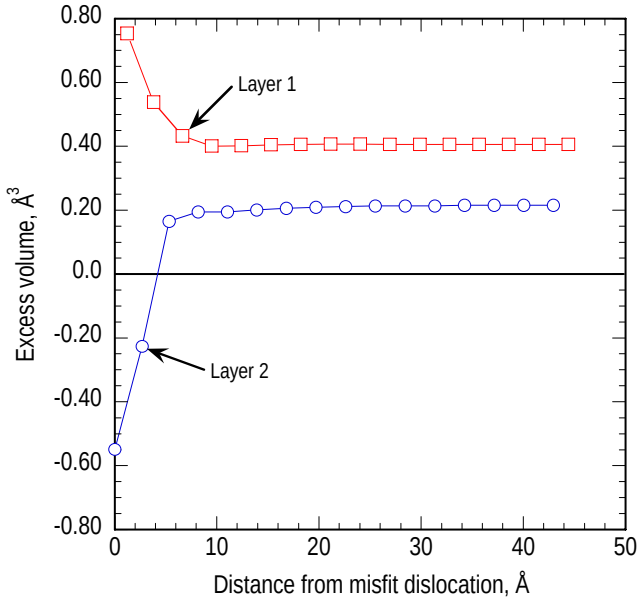

Figure 5. Dependence of excess atomic volume parallel to a semi-coherent Fe/Cu interface for the first two layers of Fe atoms adjacent to the interface as a function of distance from a misfit dislocation.

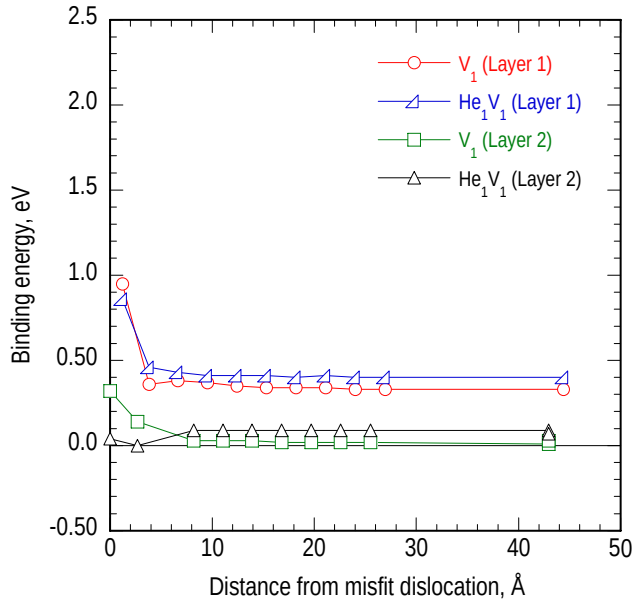

Figure 6. Binding energies of single vacancies and substitutional He atoms to semi-coherent Fe/Cu interface for the first two layers of Fe atoms adjacent to the interface.

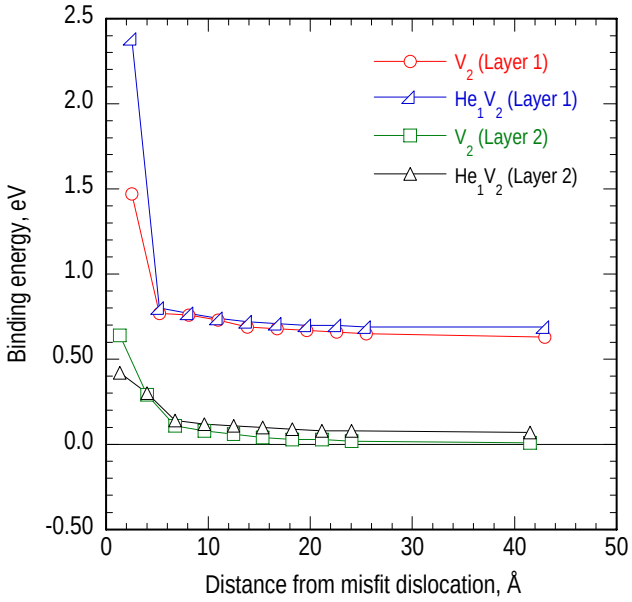

Figure 7. Binding energies of divacancies and He_1V_2 complexes to a semi-coherent Fe/Cu interface for the first two layers of Fe atoms adjacent to the interface.

Summary

He_nV_m complexes are bound to a coherent bcc Fe/bcc Cu interface with binding energies ranging from 0.35 eV for a single vacancy up to 0.70 eV for a He_1V_2 complex. He_nV_m complexes are more strongly bound to a semi-coherent Fe/Cu interface in the vicinity of the misfit dislocation with maximum binding energies ranging from 0.86 eV for a substitutional He atom up to 2.38 eV for a He_1V_2 complex. The binding energy trend for point defects containing He atoms follows the spatial dependence of excess atomic volume for each interface.

References

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