

FINDING POSSIBLE TRANSITION STATES OF DEFECTS IN SILICON-CARBIDE AND ALPHA-IRON USING THE DIMER METHOD – F. Gao, W. J. Weber and L. R. Corrales (Pacific Northwest National Laboratory)* G. Henkelman and H. Jónsson (University of Washington)

EXTENDED ABSTRACT

This is an extended abstract of a paper submitted for publication in the proceedings of the 6th COSIRES Conference, June 23-27, 2002, Dresden, Germany, to be published in Nucl. Inst. and Methods B.

The 'dimer' method was employed to search for possible transition states and their saddle point energies for interstitials and small interstitial clusters in SiC and α -Fe. The dimer method is a technique for finding saddle points in the potential energy surface within a solid, without knowledge of the final state of transition, and without the use of second derivatives of the potential, has been recently developed by Henkelman and Jónsson [1]. In addition to the calculation of activation energies of point defect and cluster migration along the $\langle 111 \rangle$ direction in α -Fe, the activation energies for the directional change of interstitial clusters is investigated.

The dimer method, described in detail elsewhere [1], involves two atomic images of the system, separated by a very small 3N-dimensional unit vector. The energy of this dimer and the force on the midpoint, as well as the curvature of the potential at the dimer, can be calculated from the forces acting on the two images. The net force on the dimer is minimized by rotation of the dimer, and the dimer is translated so as to move up the potential surface. Saddle points are located through a series of rotations and translations of the dimer. Upon finding a saddle point, the dimer is returned to the starting configuration, and it is randomly assigned a new orientation as a starting configuration for another saddle point search. In principle, all saddle points surrounding the initial configuration can be found. In practice, the same saddle point or symmetrically equivalent saddle points are often found, and occasionally no saddle points are located after a reasonable expenditure of computer time. Once the saddle point is found, the minimum energy path to the next energy basin can be determined, and the changes in atom positions during the transition can be followed.

Silicon Carbide

The transition states and mechanisms for migration of interstitials in SiC are studied in a cubic box of 125 unit cells consisting of 1000 atoms with periodic boundary conditions. The lowest energy configuration for the C interstitial, based on the potentials used here, is the $C^+-C\langle 100 \rangle$ dumbbell at a C site, with a formation energy of 3.04 eV. This minimum state is used as the initial configuration for the saddle point searches. The dimer run consisted of 800 randomly chosen initial dimer orientations about this minimum. In SiC, the potential migration pathways for the C interstitial are found to consist of the first neighbor jump via a Si site, having an activation energy of 0.81 eV, or second neighbor jumps from a C site directly to another C site with activation energies on the order of 1.5 eV. The results for SiC are somewhat difficult to interpret, because the dimer method finds multiple shallow saddle points along a single transition path. The interatomic potential used for SiC in these calculations was developed by Gao and Weber [2] based on the Brenner formalism [3]. Tersoff potentials lead to similar behavior. Perhaps better potentials for SiC need to be developed.

Interstitials in α -Fe

For interstitials and interstitial clusters in α -Fe, supercells containing from 2000 to 8192 atoms are employed to ensure that the effects of interactions of a cluster with its periodic images are negligible. For single interstitials the $\langle 110 \rangle$ dumbbell is used as an initial configuration for saddle point searches. Of 500 dimer searches, 425 converge to saddle points with an energy of 0.16 eV, which corresponds to the

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configuration change from a $\langle 110 \rangle$ dumbbell to a $\langle 111 \rangle$ crowdion. Fifteen searches converge to other saddle points, but they are not associated with the originally minimum configuration. Sixty searches fail to find saddle points within 500 iterations. Continuing searches starting from the final configuration of the previous run (i.e. $\langle 111 \rangle$ crowdion) result in two significant saddle points, one representing the directional change from the $\langle 111 \rangle$ crowdion to a $\langle 110 \rangle$ dumbbell and another one corresponding to an energy barrier for migration along the $\langle 111 \rangle$ direction. The energy path for a single interstitial is shown in Figure 1, where the relative coordination is used such that the distance from the $\langle 110 \rangle$ dumbbell to the final $\langle 111 \rangle$ configuration is one unit. It can be seen that the migration of a single interstitial consists of two mechanisms. One involves rotation from the stable $\langle 110 \rangle$ dumbbell to a metastable $\langle 111 \rangle$ crowdion with an energy of 0.163 eV, and the other is the migration of a crowdion along the $\langle 111 \rangle$ direction with the activation energy of 0.0022 eV. These mechanisms are similar to those observed in the MD simulations of defect diffusion [4,5].

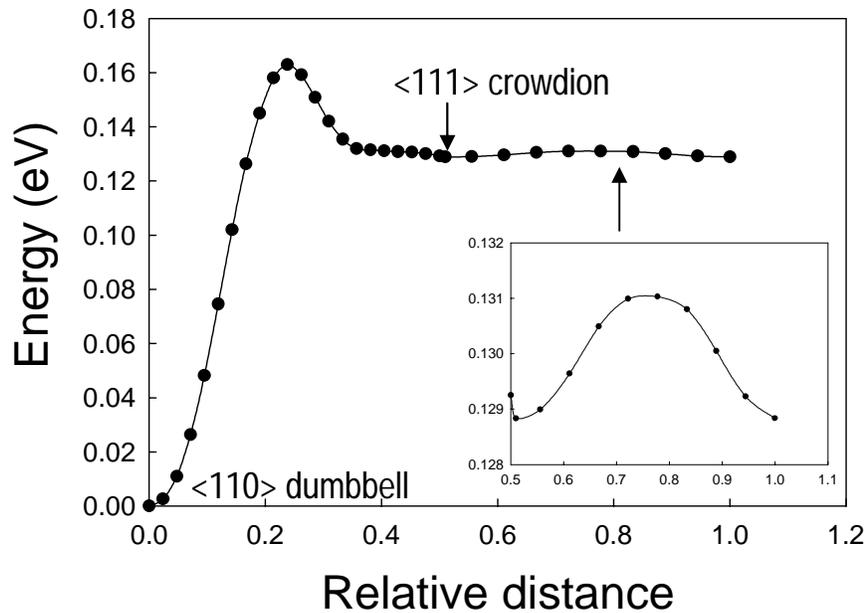


Figure 1. The minimum path traced out as the interstitial changes its direction from the initial $\langle 110 \rangle$ dumbbell to a $\langle 111 \rangle$ crowdion and migration along the $\langle 111 \rangle$ direction.

Interstitial Clusters in α -Fe

One of the important applications of the dimer method in this paper is to search for the transition states of interstitial clusters. Cluster sizes containing up to 10 SIAs are studied, and all initial states are set as compact $\langle 111 \rangle$ crowdion cluster configurations. The minimum paths associated with the saddle points, which relate to the migration along $\langle 111 \rangle$ direction and the directional change of clusters, have been traced out for interstitial clusters. It is found that the activation energies for migration along the $\langle 111 \rangle$ direction vary with cluster size and range from 0.0022 to 0.039 eV, in reasonable agreement with previous studies using MD simulations [6].

The minimum energy paths corresponding to saddle points for directional changes are shown in Figure 2, where the reaction coordinate is scaled so that the distance between two minima is unity. The paths that do not terminate back at zero energy correspond to configuration changes from a $\langle 110 \rangle$ dumbbell to a $\langle 111 \rangle$ crowdion for a single interstitial and from $\langle 111 \rangle$ crowdions to $\langle 110 \rangle$ dumbbells for di- and tri-interstitial clusters. The energy barriers for these processes, which represent the energy for directional

change, E_{dc} , from the $\langle 111 \rangle$ direction to another, are plotted in Figure 3, together with the binding energy per defect in a cluster for comparison. As shown, the energy for directional change is very high in comparison with the migration energy along $\langle 111 \rangle$ direction and generally increases with increasing cluster size. The value for E_{dc} is 0.163 eV, 0.133 eV and 0.342 eV for $N=1, 2$ and 3 , respectively, which are smaller than the migration energy of a single vacancy (0.78 eV for the potential used). These clusters can easily change their direction by activation at room temperature. The energy of the directional change for a cluster of size 4 and 5 is about 1 eV, and these clusters may change their direction at high temperatures. When the cluster size is larger than 5, E_{dc} is in excess of 2 eV, so that the directional

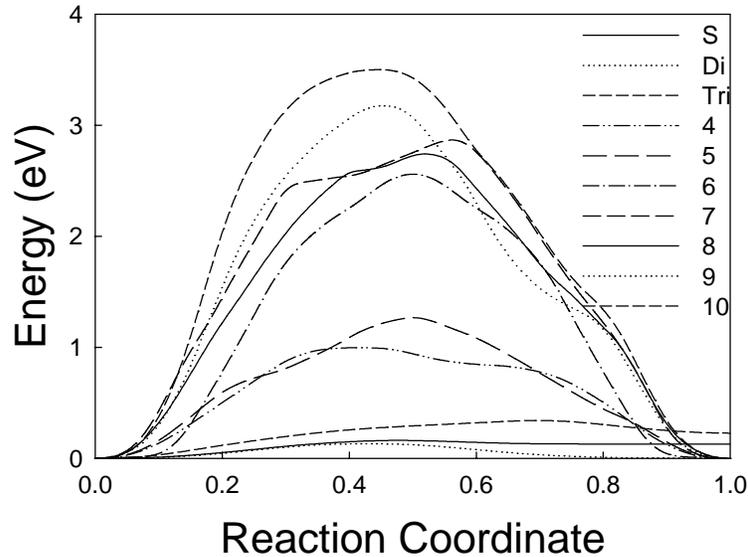


Figure 2. The minimum paths for the directional change for a cluster size up to 10 SIAs, where the reaction coordinate has been scaled so that 0 represents the initial minimum and 1 indicates the final state.

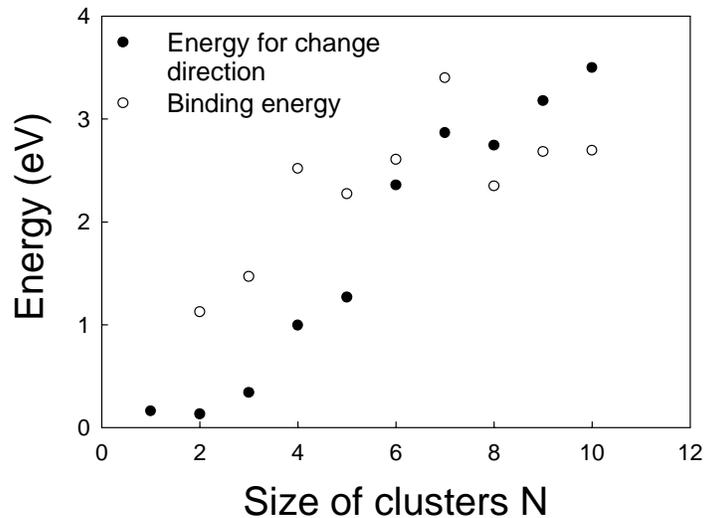


Figure 3. The energy barriers of the directional change for interstitial clusters in α -Fe, together with the binding energy per defect in a cluster for comparison.

change by thermally activated process becomes impossible, even at very high temperatures. It is interesting to note that the binding energy is larger than E_{dc} for cluster sizes up to seven, above which it is smaller than E_{dc} . This may suggest that any cluster size larger than seven may not change its direction before they dissociate into small clusters. Detailed analysis shows that single interstitial, di- and tri-interstitial clusters change their direction via $\langle 110 \rangle$ configurations. When the size of a cluster is larger than three, the situation becomes more complicated, and the mechanism for directional change is completely different from that for small clusters. It is found that the directional change for clusters larger than three is a two-step process, consisting of translation along the $\langle 100 \rangle$ direction and rotation into an equivalent $\langle 111 \rangle$ configuration [7].

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