STRONGLY NON-ARRHENIUS INTERSTITIAL DIFFUSION IN VANADIUM – S. Han, R. Car, and D. J. Srolovitz (Princeton University), L. A. Zepeda-Ruiz (LLNL),

OBJECTIVE

Self-interstitial atoms (SIA), produced in the irradiation of metals, are key components of the micro-structural evolution of the material. The microstructural evolution of the irradiated material is largely determined by the migration, clustering, and annihilation of the SIAs. The objective of this research is to study self-diffusion via SIA migration in pure vanadium through a multiscale computational study.

SUMMARY

We perform molecular dynamics simulation to study the diffusion of SIAs in vanadium. The interatomic potentials employed were developed by fitting to first-principle, quantum mechanical results on SIA structure and energetics. The present results demonstrate that the SIA in vanadium exists in a <111>-dumbbell configuration and migrates along <111> directions, in agreement with first-principles calculations. At low and intermediate T, the diffusion is one-dimensional, but at higher temperatures, the dumbbell can rotate into other <111> directions, resulting in three-dimensional at high T. The apparent activation energy for migration increases with temperature as a result of a complex correlation effect even at temperatures before significant dumbbell reorientation occurs.

INTRODUCTION

Vanadium alloys are important candidate materials for future fusion reactors. Although it is the evolution of point defect distribution that determine the ultimate lifetime of these materials, there have been very few reliable experimental or theoretical studies of the fundamental point defect properties in vanadium. Earlier experiments have shown that SIA diffusion occurs down to temperatures as low as~4K with a migration energy of less than 0.01 eV. Extensive computer simulation studies of radiation damage in other metals have been performed. For example, simulations of bcc Fe have shown that SIAs and SIA clusters (small, perfect dislocation loops) are created along close-packed directions and tend to migrate along specific crystallographic directions. In these materials, the SIAs lie in <110> directions but rotate into the <111> in order to migrate. The resulting diffusion occurs via migration in a <111> direction, relaxation into a stable <110> orientation and then rotation into another <111> directions; this yields a 3D random walk diffusional trajectory with an Arrhenius temperature dependence with a very low activation energy, usually ~0.1 eV. Simulation studies of SIA migration have also been performed for V. These show that SIA migration in V is very similar to that in Fe. Unfortunately, these are not consistent with our own first principles calculations, which clearly demonstrate that the stable SIA structure in V is a <111> oriented dumbbell, rather than the <110> oriented dumbbell in Fe. Given this fundamental discrepancy, we are forced to conclude that SIA migration in Fe and V are fundamentally different and SIA diffusion in V is poorly understtod. Therefore, we have undertaken a study of SIA migration in V using our new interatomic potential, which is designed to ensure consistency with the first principles calculations.

COMPUTATIONAL METHOD

The diffusion of individual SIAs in vanadium was investigated using the molecular dynamics (MD) simulation code MDCASK using a new parameterization of a Finnis-Sinclair/EAM potential for vanadium. The reparameterization was performed in order to ensure that the point defect properties were consistent with the predictions of our first-principles calculations that suggest that the most stable SIA is a <111>-dumbbell, which is nearly degenerate with the crowdion configuration. The resultant potential has been extensively tested and successfully used to calculate static point-defect properties in vanadium.

All simulations were performed with a cubic system of 16000 + 1 mobile atoms ($20a_0$x$20a_0$x$20a_0$ computational cell; a_0=3.03Å), with periodic boundary conditions. Simulations were run at temperatures between 100 and 1600 K. The SIA was introduced in the form of a stable <111>-dumbbell followed by a

10 ps equilibration run using a constant temperature ensemble (N,V,T). The simulation was then switched to a microcanonical ensemble (N, V,E) in order to study the SIA migration dynamics. Because of the highly correlated nature of interstitial diffusion, long runs (1 ns) were required to ensure that the reliable diffusivites could be extracted. numerical convergence.

In order to calculate diffusivities, we followed the procedure employed by Guinan *et al*. The total run time is partitioned in *m* intervals of equal duration time τ, and within each the average interstitial positions and orientations determined at intervals $\Delta\tau$. The latter is chosen to ensure that the individual measurements were uncorrelated. This procedure allows us to calculate *D* as the average of all D_i calculated in each segment as

$$D = \frac{1}{m}\sum_{i=1}^{m} D_i$$

$$= \frac{1}{m}\sum_{i=1}^{m} \frac{\langle R^2 \rangle}{2d\tau_i}$$

where $\langle R^2 \rangle$ is the mean squared distance from beginning to end of a trajectory over the time period τ and *d* is the dimensionality of the diffusion path (1D or 3D). In order to assure consistency of the procedure, τ was varied from 5 to 100 ps with $\Delta\tau$ = 1ps. The activation energy and pre-exponential for the diffusivity were obtained via least square fits to the logarithm of the diffusivity vs. 1/*T*.

RESULTS

In order to investigate the migration mechanism of SIA in V, we first analyzed the interstitial trajectories as a function of temperature. Representative trajectories of the SIA center of mass are shown in Figure 1.
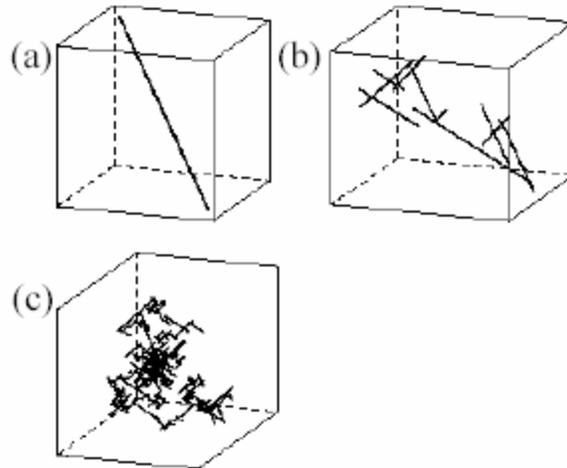

Figure 1: Typical trajectories of migrating SIAs at three different temperatures: (a) T = 100K, (b) T = 700K, and (c) T = 1300K.

We analyzed each trajectory to determine the migration mechanism and type of interstitial. For each temperature, more than 1000 jumps were observed. The interstitial migration mechanism was found to be temperature dependent. For low and intermediate temperatures (100-600 K) the SIA executes an essentially 1D random walk along a <111>-direction, as shown in Fig. 1(a). As temperature increases to T~700K, the SIA begins to make infrequent rotations from one <111>- to a different <111>-direction (passing through a <110>-dumbbell configuration). This results in a 3D trajectory that consists of long 1D

random walk segments with abrupt reorientations, as seen in Fig. 1(b). At very high temperatures, the rotation events become very frequent, such that the SIA is performing a truly 3D random walk (as shown in Fig. 1(c)). Although these results are similar to those reported for other bcc metals (i.e., Fe and Mo), it is fundamentally different. This difference is associated with the stable form of the interstitial - <111>-dumbbell in V and <110>-dumbbell in Fe and Mo. In the Fe and Mo cases, the reorientation or rotation events were associated with the relaxation of the dumbbells from their migration orientations <111> into their stable orientations <110>. Such relaxation events do not occur in the present V case, since the <111>-dumbbell is both the stable and migration form of the SIA. In fact, the <110>-dumbbell orientation corresponds to the saddle point in the V SIA rotation from one <111> orientation to another.

To obtain a more detailed understanding of SIA migration, we monitored the frequency for rotation from one <111>- to any other <111>-direction. Figure 2 shows the rotation frequency vs. $1/k_BT$ for temperatures between 700 and 1600 K (for T < 600K, no rotations were observed).
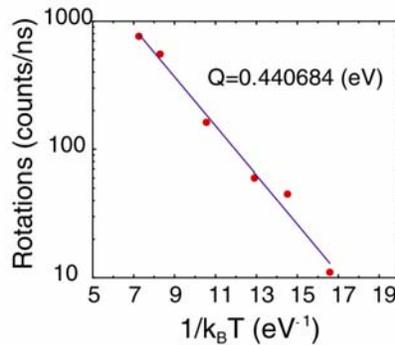

Fig. 2: Arrhenius plot of the SIA rotation frequency.

The logarithm of the rotation frequency is a linear function of the inverse temperature. This suggests that rotation is a thermally activated (Arrhenius) process. The activation energy obtained from Fig. 2, E_m=0.42eV, is consistent with first principles calculations and static calculations using the new interatomic potential which predict a rotational barrier for SIAs in V of 0.35 and 0.4 eV, respectively. The pre-exponential factor obtained from the fit was D_0=1.67x10^{13} rotations/s.
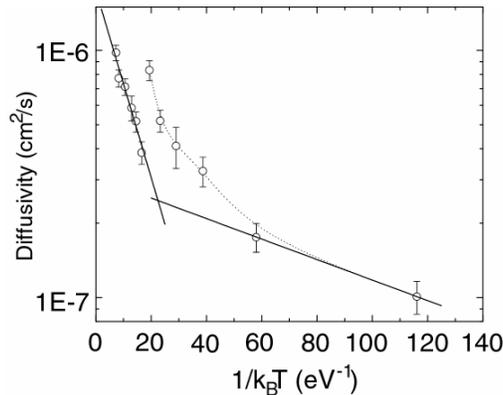

Fig. 3: Arrhenius plot of the SIA diffusion

The diffusivities, D, were obtained as described above over a range of temperatures. The results are shown in Fig. 3. Since we observe no rotations below 700K, we assume that the d=1 below 700K and d=3 above 700K. This switch in the value of d used in the determination of D is responsible for the abrupt

drop in D at 700K observed in Fig. 3. The data clearly show that the diffusivity is an Arrhenius function of temperature at high T and at low T, with a continuous transition from a low activation energy at low T to a higher activation energy at elevated T. For low temperatures we obtain D_0=3.0594x10^{-7} cm^2/s and E_m=0.0095 eV. This is in agreement with experimental data that shows that interstitial diffusion in V occurs even at 4 K with a migration energy < 0.01 eV. For high temperatures, we obtained D_0=1.7504x10^{-6} cm^2/s and E_m=0.0872 eV. We observe that at intermediate temperatures (200K < T < 600 K), D increases with T. This is interesting because the SIA undergo **NO** rotations during the course of this simulation until T is raised to 700K or above.

DISCUSSION AND CONCLUSION

The presence of a nonlinear regime in the Arrhenius diagram for temperatures between 200 and 600 K is surprising. As discussed above, previous studies of SIA migration in bcc metals showed that SIA migration is a multiple step process that involves not only translation of <111>-oriented dumbbells along a <111>-direction, but also rotations from the stable <110>- to <111>-oriented dumbbells. One could argue that the non-linearity observed in Fig. 3 is a result of the competition (over a certain temperature regime) of these thermally activated processes. But this is clearly not the situation in the case of V. As shown in Fig. 2 no changes in <111>-dumbbell orientation were observed for T< 700 K, *i.e.* SIA migration was purely 1D. Furthermore, analysis of atomic coordinates showed that in this temperature regime, the SIA exists only in a <111>-oriented dumbbell with only small angular deviations (these can be substantial at T~600 K. These deviations are consistent with first-principles results which show that the <111>-dumbbell configuration is stable relative to other dumbbell orientations, but the dumbbell energy varies slowly with misorientation around the <111>-orientation.

Since we have demonstrated that the transition from 1D to 3D diffusion is not responsible for the change in the apparent activation energy for SIA diffusion in V, we must look for another explanation. This can be found in the correlation factor for diffusion. Detailed examination of the SIA trajectories in V shows that SIA hops are correlated. At low temperature, the SIA has a higher probability of jumping back in the direction from whence it came, rather than forward along the same trajectory. We quantified this observation by measuring a correlation factor for SIA diffusion ψ, defined as

$$\psi = \frac{1}{m}\sum_{i=1}^{m}\sigma_i\sigma_{i+1}$$

where σ_i=1 if the SIA moves to the "left" and σ_i=-1 if the SIA moves in towards the "right". In this way, a value of ψ=1 would mean that the SIA executed m jumps all in the same direction, a value of ψ=-1 would mean that the SIA jumps in the opposite direction than its previous jump, and a value of ψ=0 implies an uncorrelated random walk. A plot of ψ as a function of temperature is shown in Fig. 4.
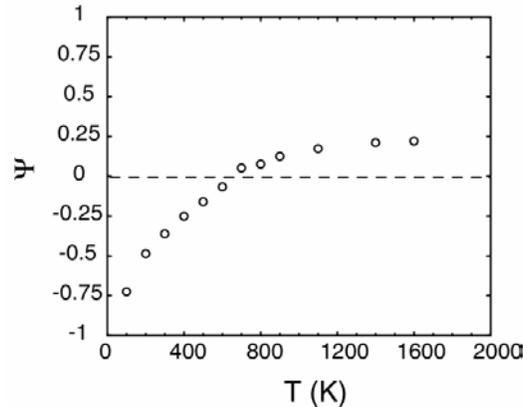

Fig. 4: Correlation factor versus temperature.

From this, we observe that at low T the SIA tends to jump back in the direction from whence it came, while at high T the random walk is more nearly perfect. At high T, there is a slight tendency for the hops to continue in the same direction (e.g.,, a small number of multiple site hops). At low T the SIA has very little thermal energy and hence tends to "bounce off" the next atom and return to its previous position while at high T the higher thermal energy gives rise to a 1D collision cascade. Thus, the non-Arrhenius behavior is not from competing thermally activated events as reported in Fe or Mo, but rather from a temperature-dependent correlation factor.