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A molecular dynamics simulation study of small cluster formation and migration in metals

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Abstract

Molecular dynamics (MD) simulations were performed to investigate the kinetics and energetics of self-interstitial atom (SIA) clusters in vanadium, tantalum and copper. The formation energies of the SIA clusters in all the metals are well represented by a power function with a 0.75 exponent of the cluster size. The cluster diffusivities strongly depend on their structure. In vanadium and tantalum, all the SIA pairs in clusters are located along the $\langle 111 \rangle$ direction rather than the $\langle 110 \rangle$ direction. The clusters can migrate one-dimensionally in the $\langle 111 \rangle$ direction with a small activation energy of around 0.1 eV. In copper, the collective orientation preference of the SIA pairs is not observed indicating that rotation of several pairs in the cluster is required for the cluster to migrate. The activation energy for the rotation is not so high as the cluster migration energy itself. The difference in the SIA cluster migration behavior between bcc and fcc metals is discussed. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

The first wall and divertor materials of nuclear fusion reactors are exposed to D–T neutron bombardment leading to the displacement atoms, which may cause various changes in the microstructures and mechanical properties, that are, in many cases, undesirable for the integrity of the reactor. Although a knowledge of the properties of point defects and their clusters is essential for understanding and predicting the effects of radiation damage in materials, even the defect migration is complicated. Recent studies showed that small self-interstitial atom (SIA) clusters migrate rapidly in metals [1–4]. The rapid diffusion of the clusters is one of the important aspects of the theoretical work on the impact of defect production by displacement cascades on microstructural changes in materials under irradiation, which

is called ‘production bias model (PBM)’ [5,6]. The rapid diffusion is considered to promote the removal of SIA clusters into defect sinks producing asymmetry in the production of single vacancies and interstitials. However, a quantitative description of the cluster migration is not sufficient at present. In the present study, we performed molecular dynamics (MD) simulations to elucidate the behavior of point defects and their clusters in vanadium, tantalum and copper, which are important candidates for use in nuclear fusion reactors.

2. Molecular dynamics model

MD simulations were carried out to investigate the formation and migration energies, and the stable structure of SIA clusters in bcc vanadium and tantalum, and fcc copper. All the simulations presented here were performed with the MD simulation code, MDCASK [7]. The interatomic potential employed for copper was the EAM potential modified by Pronnecke et al. [8]. As for vanadium and tantalum, we chose the Finnis–Sinclair (FS) many-body potentials [9], which are widely

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accepted for use in atomistic computer simulations of metals. Following the approach by Pronnecke et al. [8], the repulsive part of the potentials was modified to connect the universal potential of Biersack, Littmark and Ziegler [10], which gives a good representation of interaction between two atoms at close separation. The cohesive term of the FS potential was also modified to smoothly approach a constant value for interaction distances smaller than the nearest neighbor distance of atoms. This truncation made the potential effectively transformed to a two-body interaction in the higher energy range. An appropriate choice of the knot of the different potential functions can reproduce the zero temperature and pressure equation of Rose et al. [11]. The number of atoms in the simulation box ranged from several hundreds to a few thousands depending on the size of the defect cluster in question. A periodic boundary condition was employed with a constant simulation volume.

3. Point defect and cluster energies

The simulation volume containing SIA dumbbells, the number of which ranged up to several tens, was first well equilibrated at a given temperature around 1000 K to allow sufficient diffusion and relaxation. Then the simulated annealing was applied, where the temperature was gradually decreased. After it was completed, the velocity of each atom was forced to be zero. Thus, the volume was quenched to 0 K.

The formation energies of defects are obtained by calculating the potential energies of a system of atoms including the defects, and subtracting that of a perfect system containing the same number of atoms. It is found that the calculated formation energies of SIAs and their clusters in vanadium, tantalum and copper are well represented by power law functions with a 0.75 exponent, which are $3.313n^{0.75}$, $7.267n^{0.75}$ and $3.259n^{0.75}$ in eV, respectively. Here n is the number of SIAs in the cluster. The size dependence is slightly greater than that for iron [12], where the exponent value is $2/3$ rather than 0.75. In all the metals, the formation energies of vacancies and their clusters are always smaller than those of SIA clusters, and they are also represented by a power function, i.e., $2.078n^{0.75}$, $3.295n^{0.75}$ and $1.555n^{0.75}$ in eV in vanadium, tantalum and copper, respectively.

The stable configuration of single SIAs in metals depends on the lattice structure; single SIAs form dumbbells oriented along the $\langle 110 \rangle$ direction in the bcc metals, and along the $\langle 100 \rangle$ direction in copper. The separation distances between two atoms of the dumbbells are 0.228 nm, $(0.751a_0)$, 0.249 nm $(0.752a_0)$ and 0.214 nm $(0.595a_0)$ for vanadium, tantalum and copper, respectively, where a_0 is the zero temperature lattice parameter. In all the metals, the most stable structures

of SIA clusters are collapsed configurations on close-packed planes. Therefore, they are represented by the direction of SIA pairs in the clusters, which depend on the size of the clusters. The size dependence also depends on the metal. The most stable structure of di-interstitial atoms in the bcc metals is two $[110]$ dumbbells parallel to each other with the nearest neighbor distance separation along the $[1\bar{1}1]$ direction, or the equivalent configuration. For copper, the most stable configuration is two $\langle 100 \rangle$ dumbbells perpendicular to each other with the nearest neighbor distance separation. For a greater size, it is more complicated. In the bcc metals, when the SIA number in the cluster increases, all the SIA pairs gradually rotate to locate along the same $\langle 111 \rangle$ direction rather than $\langle 110 \rangle$. All the SIA pairs in clusters are finally oriented along $\langle 111 \rangle$, and form perfect loops with Burgers vector, $b = (a_0/2)\langle 111 \rangle$, showing a good agreement with the case for iron [3,12]. The size dependence of the orientation preference of the SIA pairs in clusters, again, strongly depends on the metals. At least five SIAs are required to complete the directional change in vanadium, while four SIAs are enough for it in tantalum. In copper, on the other hand, the orientation preference is not so simple. Every SIA pair is not located along the same direction, which is associated with the fact that the interstitial loop in fcc metals usually forms a faulted configuration. It is emphasized here that the collective orientation of the SIA pairs in clusters to the same direction is energetically more difficult in the fcc metal than in the bcc metals. This fact is considered to have an impact on the difference in the cluster migration behavior in metals between fcc and bcc lattices, as discussed below.

4. Point defect and cluster diffusivities

MD simulations have the advantage of calculating the absolute values of defect diffusivities by following the spatial trajectories of the defects as a function of time. The diffusion coefficient can be calculated with the equation $D_d = R^2/zt$, where the term R^2 is the mean value of the squared displacements of the defect center-of-mass, t is the elapsed time, and the factor z takes 6 and 2 for three- and one-dimensional migrations, respectively. In the simulations, we typically simulate diffusion for 5–10 ns during which the defects can typically make more than several hundred hops depending on the cluster size, temperature and the metal in question. Fig. 1 shows the Arrhenius plot of the diffusion coefficients of the single SIAs and their clusters in the metals. As a reference, the diffusion coefficients of the vacancies and their clusters only for vanadium are also indicated. The parameters for the exponential functions fitted to these diffusivities are listed in Table 1.

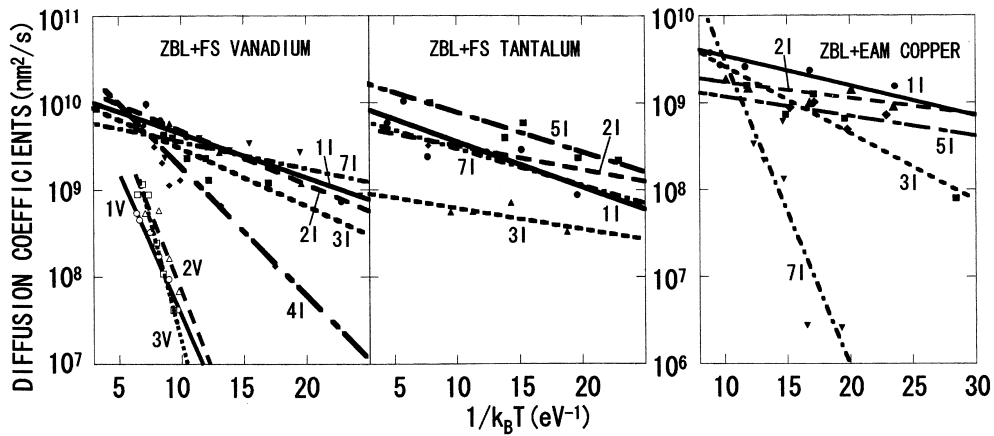


Fig. 1. Arrhenius plot of the calculated diffusion coefficients of the point defects and their clusters in vanadium, tantalum and copper. In the plot, 1I, 2I, 1V, 2V etc. indicate single SIA, di-SIAs, single vacancy, di-vacancies, etc., respectively. Cluster migration strongly depends on the cluster structure.

In vanadium and tantalum, di-interstitial atoms can diffuse very rapidly comparable to the diffusion of single SIAs. Especially for tantalum, the diffusivities for the di-interstitials are greater than that for the single SIAs at temperatures below 1200 K. With increasing the size of the SIA clusters more, the size dependence of the diffusivities becomes very complicated. The larger clusters, typically with seven SIAs, can migrate one-dimensionally with very low migration energies along the same direction of the SIA pairs in the cluster. Their diffusion coefficients are comparable to or greater than that of single SIAs. The geometry of the centers of the dumbbells in the seven-SIA cluster takes three-dimensional

rather than one-dimensional. In copper, on the other hand, the seven-SIA cluster migrates slower than those of smaller clusters at the temperatures investigated here.

Fig. 2 shows the Arrhenius plot of the rotation frequencies of the SIA pairs in clusters in metals as a function of the cluster size. In all the metals, the rotation of the SIA cluster direction becomes less frequent with increasing cluster size. Moreover, it is emphasized that the clusters, which have seven SIAs in vanadium and five and seven SIAs in tantalum, did not rotate at all during the present simulation period. However, in copper, the activation energy for the rotation of SIA pairs in clusters is not so high, even for the seven-SIA cluster.

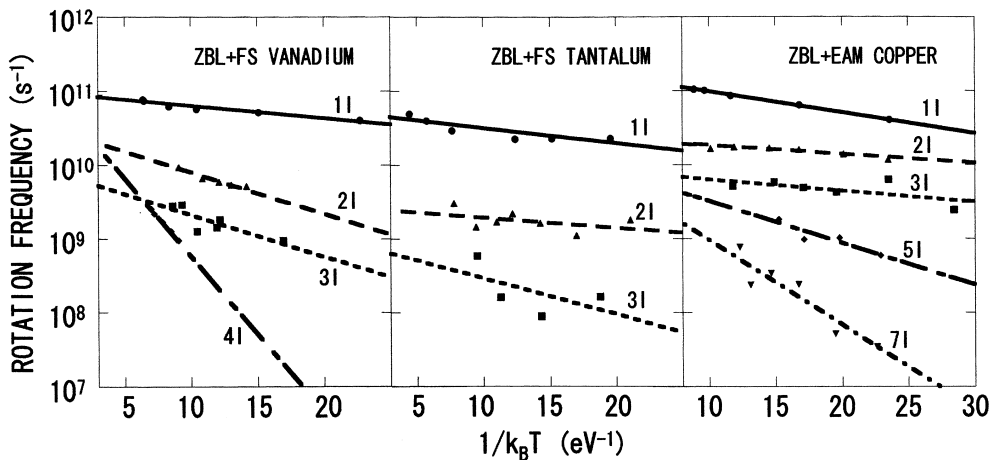


Fig. 2. Arrhenius plot of the direction change of SIAs and their clusters. The cluster direction is defined as the direction along which all SIA pairs in the cluster are located. The collective orientation of all the SIA pairs is energetically stable in the relatively larger cluster in bcc metals, but it is not in fcc metals. It is noted that the seven-SIA cluster in vanadium and the five- and seven-SIA clusters in tantalum did not change the direction at all during the present simulation period.

Table 1
Arrhenius plot fitting parameters of migration and rotation of point defects and their clusters in vanadium, tantalum and copper. The diffusion coefficients and rotation frequencies are both represented by $A \exp(-B/k_B T)$, where k_B and T are the Boltzmann constant and temperature, respectively

Number of defects in cluster	Vanadium			Tantalum			Copper		
	Migration		Rotation	Migration		Rotation	Migration		Rotation
	A (10^{10} nm ² /s)	B (eV)	A (10^{10} s ⁻¹)	A (10^{10} nm ² /s)	B (eV)	A (10^{10} s ⁻¹)	A (10^{10} nm ² /s)	B (eV)	A (10^{10} s ⁻¹)
1 SIA	1.423	0.116	9.185	0.037	0.102	5.038	0.049	0.078	18.66
2 SIA	1.856	0.139	2.537	0.117	0.062	0.270	0.032	0.042	2.373
3 SIA	1.399	0.156	0.730	0.124	0.053	0.089	0.113	0.177	0.904
4 SIA	5.070	0.335	6.475	0.465	—	—	—	—	—
5 SIA	—	—	—	—	0.105	0.000	N/A	0.050	1.127
7 SIA	0.719 ^a	0.069	0.000	N/A	0.097	0.000	N/A	0.823	1.320
1 vacancy	8.191	0.763	—	—	—	—	—	—	—
2 vacancies	26.45	0.818	—	—	—	—	—	—	—
3 vacancies	462.1	1.227	—	—	—	—	—	—	—

^aOne-dimensional migration.

5. Discussion

When the SIA number in the cluster increases, all the SIA pairs gradually rotate and locate along one of the close-packed directions in the lattice. The minimum SIA numbers required for all the SIA pairs to rotate in the close-packed direction are five and four in vanadium and tantalum, respectively. More than seven SIAs are required in copper. The MD simulations using the model potential show that unrelaxed stacking-fault energies are 2.68, 3.82 and 0.00143 J/m² for vanadium, tantalum and copper, respectively. It may indicate that the clusters in the metal with higher stacking-fault energy show collective rotation of the SIA pairs occurred at smaller number of SIAs. The material dependence of the rotation behavior would be associated with the unfaulting characteristics in the metals. Again, the collective rotation of the SIA pairs in the cluster take place at the smaller number of the SIA pairs in the metals with higher stacking-fault energy resulting in transformation into highly glissile cluster.

The correlation factor for defect diffusion is defined as the fraction of the tracer diffusion coefficient (D_t) to the defect diffusion coefficient (D_d) [12]. For vacancy diffusion in vanadium, the correlation factor is 0.714 well consistent with the theoretical correlation factor 0.727 for bcc metals. As for SIA diffusion, the correlation factors are 0.389 and 0.263 for vanadium and tantalum, respectively, which are comparable to the iron case [12]. However, the factor calculated here for the fcc copper is 0.662, which is obviously greater than those for the bcc metals. It would indicate that the one-dimensional random walk occurs more frequently in bcc metals than in copper, since a zero correlation factor corresponds to complete one-dimensional diffusion.

It is now clarified that the diffusivities of SIA clusters in metals are profoundly associated with the structure of the cluster. When the SIA number in the cluster in bcc metals increases, all the SIA pairs locate along the close-packed direction, and then, with considerably higher diffusivities, the cluster can easily migrate one-dimensionally along this direction. Such larger clusters cannot change their diffusion direction any more. On the other hand, in fcc metals, all SIA pairs in clusters do not locate along the same direction. This difference appears to be associated with the stacking-fault characteristics of metals, as discussed above. The rotation of the SIA pairs to the close-packed direction in the fcc lattice is required for the cluster to migrate along this direction. This is the difference in the migration behavior of SIA clusters in metals between fcc and bcc lattices.

6. Conclusion

The energetics and kinetics of single SIAs and their clusters in metals were investigated using MD tech-

niques with the reliable many-body interatomic potentials. The following are the conclusions of this work.

1. SIA cluster formation energies in metals can be represented by a power law function of the cluster size. With increasing the number of SIAs in the cluster, the SIA pairs rotate to locate along the close-packed direction $\langle 111 \rangle$ in bcc metals. On the other hand, in fcc metals, the direction of the SIA pairs in clusters is complicated. It is a reflection of the very small stacking-fault energy.
2. In bcc metals, even the larger SIA clusters can easily migrate along $\langle 111 \rangle$, along which the SIA pairs are oriented, but it is very difficult for the clusters to change their migration direction. On the other hand, in fcc metals, the direction of the SIA pairs in the cluster should turn to the same direction for the cluster to migrate. However, the clusters can easily rotate their migration direction with activation energies less than a few tenths of eV.

Acknowledgements

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