Abstract: Molecular dynamics and molecular statics of computer-simulations of structural relaxation of small vacancy clusters in pure copper are carried out to study the atomistics of void formation in neutron-irradiated metals. The code that is utilized in the present work implements the potential of embedded atom method (EAM) of many body nature. A tri-vacancy relaxes to a Dama-Bilmes type of stacking fault tetrahedron (sft)\([111]\), in which an atom in a tetrahedron of 4 vacancy shows harmonics oscillation with appreciable magnitude of amplitude. The movement of this kind makes an important role on the relaxation of vacancy clusters of either small or larger size. A stable hexa-vacancy fluctuates in the structure between a sft and a void. The structure of seven-vacancy clusters fluctuates also between a sft and a void. Vacancy clusters whose size is more than eight generally relax to a sft or a collapsed platelet. When hydrogen atoms are trapped to either 6\(\times\)void or 7\(\times\)void, these atoms stay in voids for appreciable times and prevent the relaxation of vacancy clusters to sft. This kind of gas-atom-trapped void grows to large voids by the further absorption of vacancies. In neutron-irradiated copper, vacancy clusters which have a void structure and whose size is larger than eight could be formed directly in the displacement damage cascades. Only by the trap of gas atoms such as hydrogen atoms and helium atoms, these can grow to large voids without relaxing to collapsed structures.

Keywords: Void, Nucleation, MD simulation, Atomistics, EAM potential, Vacancy clusters, Stacking fault tetrahedra, Structural fluctuation, Hydrogen, Helium

1. INTRODUCTION

When metals are neutron-irradiated in appropriate temperatures to high fluences, voids generally form. Many voids form along dislocations while some form in isolated crystal grain without connecting to dislocations. Stoller and Oddett\([2,3]\) experimentally and theoretically explored that these voids form under the influence of helium of nuclear-transmutation products. In Stoller’s model, micro-bubbles in which large number of helium are trapped are thought to be the nucleus of voids. The atomistic of void formation is still unsolved problem. Recently the present authors found that the residual gas which dissolves in metals plays an important role on void formation\([4]\). Therefore it is undoubtedly that voids are formed under the influence of dissolved gas atoms. Neutron-irradiation experiments of highly out-gassed metals are in progress by the present authors at KOR-II reactor and at LANL irradiation facility.

In the present computer-simulation work, the relaxation of small vacancy clusters to a stable structure is studied with the simulation of molecular dynamics (MD) and molecular statics (MS). The dynamical structural fluctuation of small vacancy cluster during MD runs is also examined. During a MD run for 10 picosec at 500 K, the structural change of which activation energy is less than 0.2 eV can be visualised. The thermal relaxation whose activation energy is larger than 0.3 eV have to be calculated by the molecular statics calculation. A hydrogen atom is included in the present computer-simulation. The EAM potential of hydrogen atom in copper is due to D 되 and Banks who made parameterization of potential by fitting to the result of quantum mechanical calculations by
2. COMPUTER-SIMULATION

Computer-simulations were carried out with the code DYNABO that was developed by Daw, Foiles and Baskes in Sandia National Laboratory in Livermore[6]. The EAM potential of copper that is utilized in the present simulation was parametrized by T. Diaz de la Rubia with the Foiles' procedures[7]. The size of vacancy clusters which are covered in the present simulation is below 13. The crystal in which vacancy clusters are included is composed by 1372 atoms (7 x 7 x 7 a_o, a_o = lattice constant). Periodic boundary condition is applied to crystal surface. The temperature of crystal was set either 300 K or 500 K. Molecular dynamics simulation was carried out for 10 psec with 2 psec step. At every 2 psec step, the atom configuration was energy-minimized to 0 K configuration. Intermediate stage of structural relaxation during MD runs were filed at each 0.04 psec interval. Traces of atom movement during 2 psec MD run are figured out on a graph. The migration energy of vacancy is calculated by forcing a moving atom to the saddle point in 0 K static crystal. Atoms which locate on the nearest position of the moving atom were forced to be constrained on the saddle point plane.

3. RESULTS

3.1 Vacancy Clustering Processes

Characteristic physical constants of single-, di- and tri-vacancy are listed on Table 1. The migration energy of single vacancy is 0.62 eV which seems to be in reasonable range to the values obtained experimentally. The migration energies of di- and tri-vacancy as shown in Table 1 are rather low which have to be examined experimentally in future. The relaxation volume of single-, di- and tri-vacancy is not so large that these vacancies do not show remarkable collapsing. It is noted that tri-vacancy of 3V-60° tends to relax to Damask-Dienes type of tri-vacancy[9]. This is referred to as a 3v-sft. The binding energies of di- and tri-vacancy are also listed on the Table 1. The binding energy of di-vacancy is calculated to be 0.15 eV and is in the range of so-called low binding energy.

Table 1 Characteristic Physical Constants of 1V, 2V, and 3V.

<table>
<thead>
<tr>
<th>Vacancies</th>
<th>E_v (eV)</th>
<th>V_rel (at-vol/vacancy)</th>
<th>E_b (eV)</th>
<th>R_b (eV)</th>
<th>Path of migration</th>
</tr>
</thead>
<tbody>
<tr>
<td>1V</td>
<td>1.249</td>
<td>0.290</td>
<td>---</td>
<td>0.63</td>
<td></td>
</tr>
<tr>
<td>2V</td>
<td>2.346</td>
<td>0.20</td>
<td>0.15</td>
<td>0.33</td>
<td></td>
</tr>
<tr>
<td>3V (60°)</td>
<td>3.311</td>
<td>0.294</td>
<td>0.286</td>
<td>0.64</td>
<td>(3V-60 - 1V + 2V)</td>
</tr>
<tr>
<td>3V (90°)</td>
<td>3.414</td>
<td>0.336</td>
<td>0.183</td>
<td>0.35</td>
<td>(3V-90 - 3V-60)</td>
</tr>
<tr>
<td>3V (120°)</td>
<td>3.462</td>
<td>0.310</td>
<td>0.135</td>
<td>0.29</td>
<td>(3V-120 - 3V-60)</td>
</tr>
<tr>
<td>3V (180°)</td>
<td>3.414</td>
<td>0.338</td>
<td>0.183</td>
<td>---</td>
<td>(3V-180 - 3V-120 - 3V-90)</td>
</tr>
</tbody>
</table>
four atoms moves slightly towards the apex of tetrahedron, a 6v-sft changes to a 6v-void. The similar structural relaxation between sft and void occurs in a 7-vacancy. The structure of 7-vacancy is the combination of 6v-sft and 3v-sft attached on one of edges as reported previously[8]. The structure of 6v-sft in 7v fluctuates between sft and void. On the stage of vacancy clustering by further absorption of vacancies, vacancy clusters which have void structures as shown in Figs. 6(a) and (b) can be formed. Although these micro-voids are stable, it seems to be difficult to grow to a large void by further absorption of vacancies. This is due to the relaxation of component 3v in the clusters. An additional vacancy have to come to the exact position in order to grow void as void. The structure relaxes towards to either sft or collapsed platelet when a vacancy comes to some of the nearest neighbor positions. This is due to easy relaxation of 3v to 3v-sft as shown in Fig. 5(c). The details of atomistics of growth of vacancy clusters and their dynamics will be reported elsewhere by the present authors.

3.2 An Inclusion of Hydrogen Atom in Vacancy Clustering

When a hydrogen atom comes to the nearby position of vacancy clusters, it can be trapped...
Figure 4 The relaxation of (a) stable 4v-diamond plus single-vacancy to (b) octahedral 5v (5v-octahedron). In 5v-octahedron, an atom exists in octahedral 6v.

Figure 5 Trace of atom movement in 6v-sft. (a) Four atoms in 10 vacancy tetrahedron (6v in balance) move with large amplitude. (b) Static 6v-sft configuration. (c) Static 6v-void configuration.

Figure 6 Stable micro-void of (a) 7v and (b) 9v. It seems to be difficult that these micro-voids grow to large voids by absorbing vacancy due to easy relaxation of 3v to 3v-sft. (c) 3v-sft formation at 7v-void by addition of single vacancy.
Figure 7 Escaping of a hydrogen atom introduced in the nearest neighbor position of vacancies.

Figure 8 Movement of a hydrogen atom and Cu atoms in 6v-void. (a) without a hydrogen atom and (b) with a hydrogen atom. One of hydrogen atom shown at the same position is in starting position.
at vacancies by their mutual interaction. In the present computer-simulation, it was found that such a trapping of a hydrogen atom is not significant for vacancy clusters whose size is below five. A hydrogen atom escaped from these vacancies immediately during MD runs. Such escapes of hydrogen atoms are shown in Fig. 7. Figures 8(a) and (b) show the trace of movement of hydrogen and Cu atoms in 6v-void. The traces of movement of hydrogen atoms are projected on the triangular planes of 10 vacancy tetrahedron as in Fig. 5 and shown in Fig. 8. The movements of four atoms in 10 vacancy tetrahedron are also shown in Fig. 6. It can be seen in Fig. 8 that a hydrogen atom is trapped in void and the movement of four atoms with large magnitude of amplitude is perfectly suppressed when a hydrogen is included in a tetrahedron. Hydrogen atoms which is trapped in voids stop the fluctuation of 6v between 6v-sft and 6v-void. Structure of 6v can be kept as void by trapping of hydrogen. The simulation of growth of hydrogen-trapped void by absorbing a vacancy is now in progress. Followings have to study to understand more details of atomistics of void formation in neutron-irradiated metals.

1. It must carry out the calculation to clarify the role of helium atoms on the formation of voids.
2. The thermal stability of micro-void which trap gas-atoms needs to be studied by the computer-simulation.
3. It must be clarified how many number of gas-atoms as helium are necessary to be trapped in micro-voids to grow to a large void in neutron-irradiated metals.

Many voids form along dislocations. The preferential formation of voids on dislocations is due partly to the trapping of gas atoms along dislocations. Hexa-vacancies need to be formed along dislocations to nucleate voids. More works both theoretically and experimentally are needed to clarify the atomistics of void formation along dislocations.

4. SUMMARY

Computer-simulations of molecular dynamics and molecular statics are carried out to study the atomistics of void formation in copper. We understand that the atomistic and dynamics of vacancy clustering processes in copper. It was found that relaxed tri-vacancy and tetra-vacancy make important role on the formation of large vacancy clusters, stacking fault tetrahedra. It is concluded that large voids can not be formed by the clustering of vacancy. Gas atoms, either hydrogen or helium, are needed to stabilize void structure. The atomistic role of hydrogen on the void nucleation and growth is shown in the present work. In hexa-vacancy, for example, the four atoms which locate in 10 vacancy tetrahedron shows vibration of low frequency with large amplitude. Trapped hydrogen atoms in a micro-void suppress the vibration. Suppression of large amplitude of vibration in a component 3v-sft in large vacancy clusters occurs when hydrogen atoms are included in the clusters. Vacancy clusters which trap a hydrogen atom can keep the void structure and grow to a large void. It is not clear at present how many hydrogen atoms are needed to grow a micro-void to a large void. The role of helium atom on the formation of voids in neutron-irradiated metals is under investigation in the continuation of the present work.

REFERENCES