The influence of dynamical structural relaxation of point defect clusters on void formation in irradiated copper

Y. Shimomura *, I. Mukouda, K. Sugio

Applied Physics and Chemistry, Faculty of Engineering, Hiroshima University, 1-4-1 Kagamiyama, Higashi-Hiroshima 739, Japan

Abstract

In the neutron-irradiation experiment with a temperature controlled capsule at JMTR, residual-gas-free copper was irradiated at 200°C and 300°C together with as-received copper. The fluences were 5×10^{18} n/cm^2 (the low fluence) to 1×10^{20} n/cm^2 (the high fluence). TEM observation of the irradiated specimens showed that interstitial clusters form a colony at the low fluence which develops into a dislocation structure at the high fluence. Between the colonies only vacancy clusters in the form of voids and stacking fault tetrahedra (sft) were observed. There are no effects of residual gas atoms on the formation of voids at the low fluence although the effects become appreciable at the high fluence. The number of vacancies which are accumulated in a void is 350 times larger than that in a sft at the low fluence. The number density of voids decreased with increasing neutron fluence while the number density of sft increased. The voids form uniformly in copper irradiated to the low fluence while they were observed along dislocations at the high fluence. Computer simulations by molecular dynamics show that small interstitial clusters relax to a bundle of ⟨110⟩ crowdions and move long distances in response to small strain fields. Interstitial clusters move along a ⟨110⟩ direction and can switch to other ⟨110⟩ directions, and form groups of clusters. At high temperature, a dense colony of the clusters forms and develops into a dislocation structure. It is shown that small vacancy clusters relax to movable structures at high temperature. The structure consists of vacancies which are connected in a curved string shape. Along the vacancy strings, many relaxations of a tri-vacancy of Damask–Dienes–Weizer type (3v–sft) were observed. Such a relaxation to the 3v–sft type makes it difficult for a single vacancy evaporation. Small vacancy clusters move and coalesce into larger vacancy clusters. The linkage of the results of experiments and computer-simulations suggests that voids nucleate as a metastable defects at coalesced vacancy clusters at high temperature. The nucleation of voids is not affected by the influence of gas atoms dissolved in the material. Micro-voids migrate in the specimens after their nucleation. During their movement, gas atoms are trapped in the voids. The trapping of a larger number of gas atoms limits the movement of voids. This leads to a higher number density of voids in the as-received copper than in residual-gas-free specimens at the high fluence. Voids form uniformly in specimens at the low fluence and they migrate to dislocation lines. Dislocations are also trapped at voids during climbing by absorbing interstitial clusters. These finally lead to the preferential formation of voids along dislocation lines. © 1997 Elsevier Science B.V.

1. Introduction

In neutron irradiated metals, the same number of vacancies and interstitials is formed at the displacement damage cascades. Voids are observed in neutron-irradiated metals along dislocation lines [1–3], and it has been believed that this preferential formation of voids is due to the bias effect by which interstitial atoms are absorbed preferentially by dislocation lines leaving vacancies nearby [4,5]. Vacancies which are left along dislocations aggregate to form voids. The important effects of gas atoms on the formation of voids was recognized from the experimental observations that the number density of voids increases in the irradiated specimens in which gas atoms are pre-doped before the irradiation [6,7]. The helium atom is believed to be important to the nucleation of voids due to its small solubility in metals [8]. Many of the experimental results reported show that pre-doped helium atoms increase the number density

* Corresponding author. Tel.: +81-824 247 618; fax: +81-824 227 192, e-mail: shimo@ipc.hiroshima-u.ac.jp.

of voids formed in irradiated metals [9,10]. The present authors have studied the effect of hydrogen atoms on the nucleation of voids by computer simulation [11]. In copper, a triangular tri-vacancy 3v–60 relaxes to the Damask–Dienes–Weizer structure 3v–sft [12,13]. An atom which composes a tetrahedron with a triangular tri-vacancy 3v–60 moves to the center of the tetrahedron. This relaxation is a fundamental step for a vacancy cluster to grow into a stacking fault tetrahedron (sft). When a hydrogen atom is trapped at small vacancy clusters, it can prevent small vacancy clusters to relax to sft. Hydrogen atoms move on the surface of voids and suppress its relaxation of 3v–sft on a void surface. The present authors prepared the residual-gas-free copper by melting the material in a highly evacuated vacuum of 1×10^{-8} Torr. When both as-received copper and residual-gas-free copper were neutron-irradiated at 400°C to the fluence of 1×10^{20} n/cm^2, the number density of voids in residual-gas-free copper was one tenth of that which was observed in the as-received material [14]. In neutron-irradiated Cu–5 at.% Al which was irradiated at FFTF-MOTA to the fluence of 1×10^{22} n/cm^2, voids were not observed in residual gas free specimens while a large number of large voids were

observed in as-fabricated Cu–5 at.% Al [15]. In neutron-irradiated practical alloys of SUS316 at FFTF-MOTA, voids were not observed in residual-gas-free specimens while a large number of voids was observed in as-received ones [16]. There was no appreciable difference between the void formation in neutron-irradiated residual-gas-free and as-received specimens of nickel and Cu–5% Ni [16].

We carried out the neutron-irradiation experiment of copper with the temperature controlled capsule at JMTR (Japanese Materials Testing Reactor) [17]; the temperature was controlled at 200°C and 300°C. The experimental results force us to modify the understanding on the void formation in neutron-irradiated metals described above. Following the neutron-irradiation to the low fluence of 5×10^{18} n/cm^2, there was no difference in the number density of voids in copper of as-received and residual-gas-free type. Voids form uniformly in the specimens at low fluence. Voids form independent of the existence of dislocation lines. The number density of voids decreases with increasing neutron fluence while the size of voids increases with increasing fluence. Interstitials are collected in groups of interstitial clusters. Between the groups of interstitial clusters, only vacancy clusters are left. The
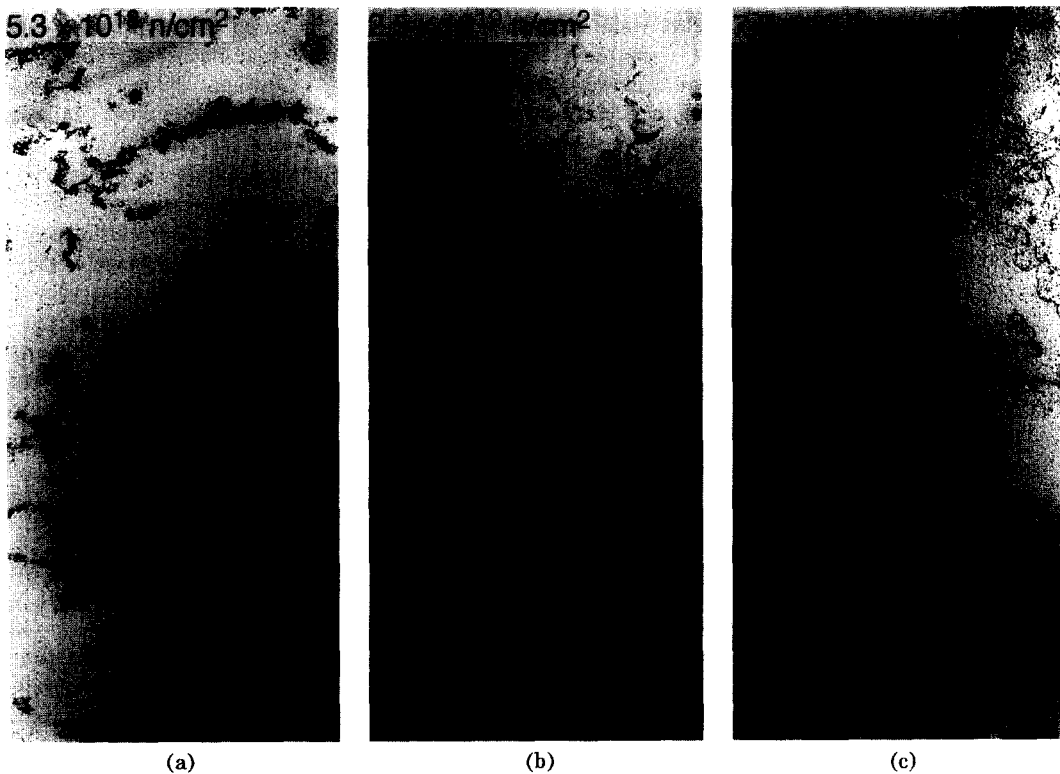

Fig. 1. The evolution of dislocation structure in neutron-irradiated copper. (a) The interstitial clusters form groups which develop into a dense colony and finally develop dislocations, (b) an intermediate stage of development of dislocation structure and (c) the whole region is covered by dislocations.

densely collected groups of interstitial clusters, which is referred to as a colony, evolve to form a dislocation structure. The computer simulation by molecular dynamics shows that interstitial clusters relax to a bundle of $\langle 110 \rangle$ crowdions and can move with a small activation energy. The movement of interstitial clusters responds to the strain field. This makes it possible for interstitial clusters to be collected into colonies. Vacancy clusters at small size relax into a structure which is mobile. By their movement, vacancy clusters coalesce to form large clusters. The coalesced vacancy clusters grow into micro-voids as a metastable structure which is activated thermally at high temperature. The nucleation of micro-voids by this process occurs without the inclusion of gas atoms. The micro-voids thus formed move as a cluster. During the movement of voids, gas atoms are trapped by voids. If a large number of

gas atoms are trapped, the movement of voids is degraded. In the present paper, the experimental results are shown in Section 2 and the results of computer simulation are shown in Section 3.

2. Temperature-controlled neutron-irradiation of pure copper at 200°C and 300°C

In this experiment, both the as-received copper and residual-gas-free copper were irradiated together. The neutron irradiation was carried out in the temperature-controlled capsule at JMTR [18,19]. The neutron fluences were 5×10^{18}, 2×10^{19} and 1×10^{20} n/cm^2 which are referred to as the low fluence, the intermediate fluence and the high fluence, respectively. The specimens were irradi-
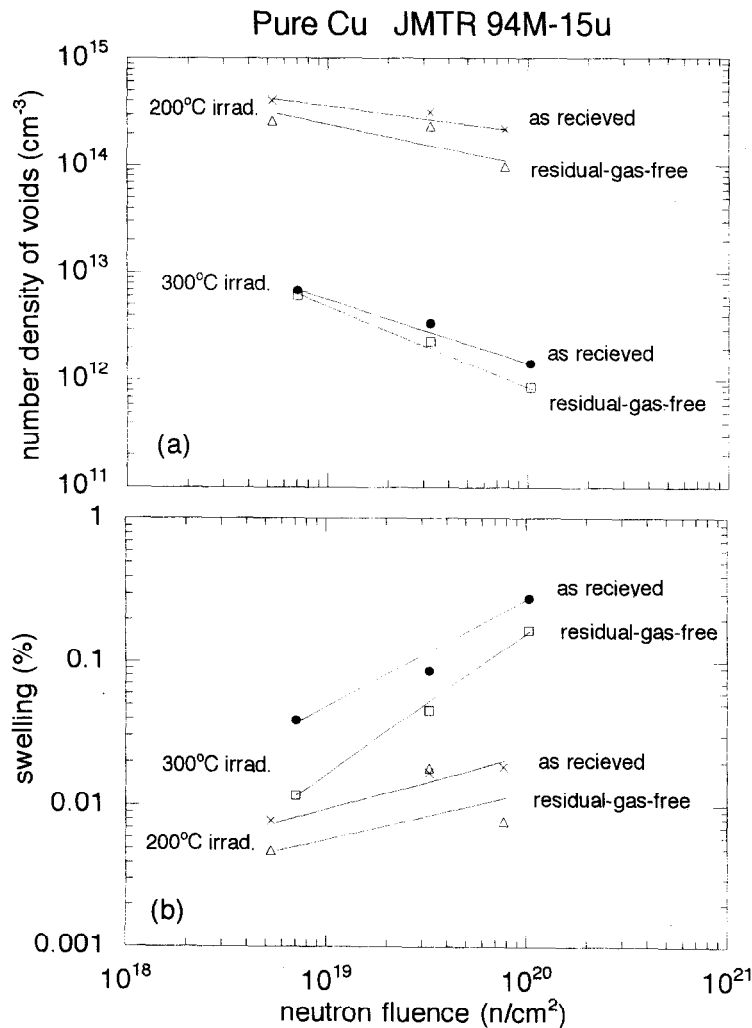
Fig. 2. The variation of the number density and swelling in neutron-irradiated copper versus the neutron fluence. (a) The number density of voids and (b) the swelling due to the void formation.
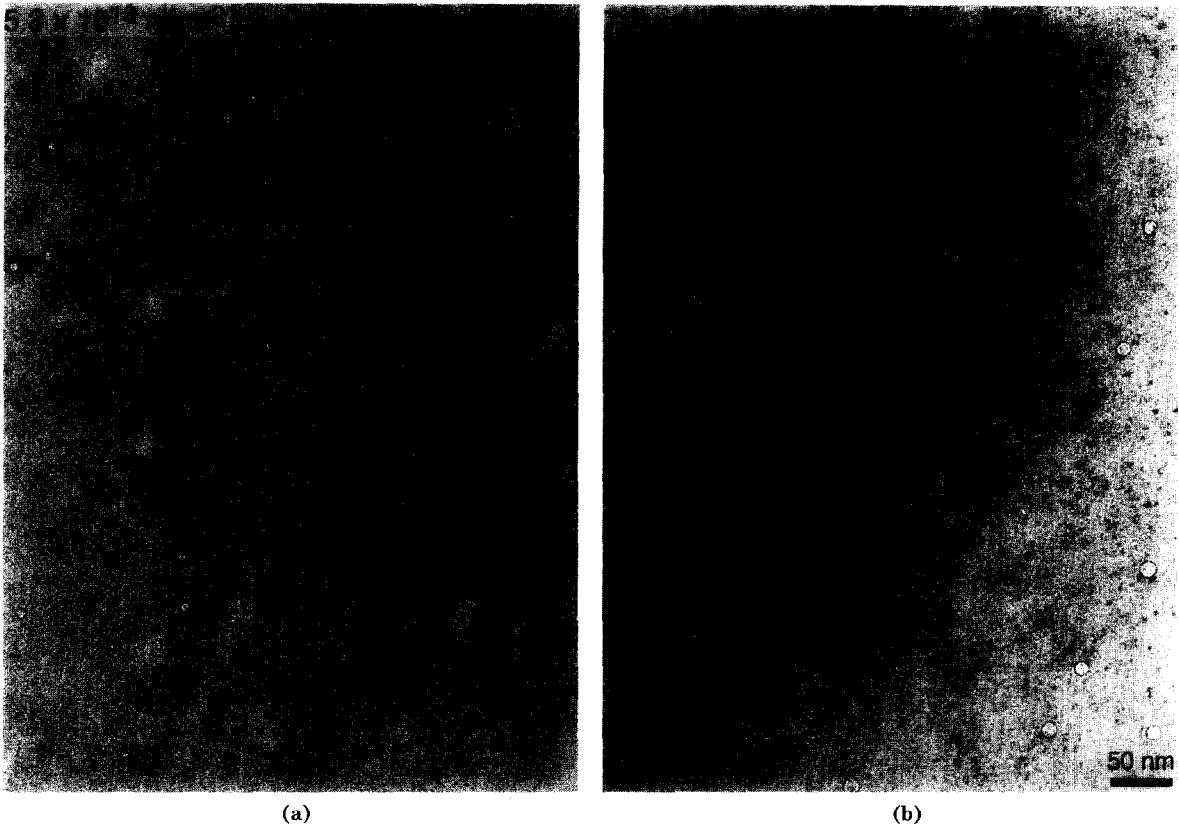
Cu JMTR 94M-15u 200°C

(a)   (b)

Fig. 3. Voids which were observed in neutron-irradiated copper at 200°C. (a) With 5.3×10^{18} n/cm^2, (b) 7.7×10^{19} n/cm^2. The number density of voids is larger in (a) than that in (b).

ated at 200°C and 300°C. Fig. 1(a) shows the formation of an interstitial cluster colony at the low fluence, Fig. 1(b) the evolution of the colony into dislocations at the intermediate fluence and Fig. 1(c) the development to dislocation structure which covers the whole crystal at the high fluence. In the region between colonies in irradiated copper, only vacancy clusters of both sft and void type were observed. Fig. 2(a) shows the number density of voids versus the neutron fluence which was observed in the specimens irradiated at 200°C and 300°C. The number density of voids at the low fluence was the same in both the as-received copper and residual-gas-free copper. The number density of voids decreased with increasing neutron fluence. The difference in the number density of voids between the two types of specimens becomes significant with increasing neutron fluence. The number density of voids in residual-gas-free specimens is lower than that in as-received copper. Fig. 2(b) shows the void swelling versus the neutron fluence in the specimens irradiated at 200°C and 300°C. The average size of voids increases with the neutron fluence. Fig. 3(a) and (b) show sft and voids

Fig. 4. The relaxed structure of interstitial clusters. The cluster is composed of parallel ⟨110⟩ crowdions. An interstitial is shown by two large balls. A small ball indicates the atom position at which the atom was located before an interstitial is introduced.

which were observed in specimens irradiated at 200°C to the low fluence and the high fluence, respectively. It can be seen that the number density of voids decreases with increasing neutron fluence while the size of voids increases with the fluence. It should be noted here that the number of vacancies which aggregate in the average void is 350 times larger than that in the average sft in the specimens irradiated to the low fluence. The average sizes of void and sft were 7.2 and 2.7 nm respectively in the low fluence neutron irradiated copper at 200°C. Voids form uniformly in irradiated specimens at the low fluence while voids were observed along dislocation lines at the high fluence. It is not clear whether voids migrate to dislocation lines or dislocation lines move to voids by climb motion and are trapped. It seems that both processes are operating. At the medium fluence of irradiation, voids are observed

on a straight dislocation line. At high fluence, a bundle of dislocation lines are observed to be trapped at a void [15].

3. Dynamical structural relaxation of point defect clusters studied by computer simulation

Computer simulation of molecular dynamics and molecular statics was carried with the DYNAMO ver. 8.5 code which was developed by Daw et al. [20]. The embedded atom method (EAM) potential due to Daw and Baskes [21] was implemented in the code. The EAM potential utilized in the present work was parametrized by de la Rubia [22] following the Foiles procedure [23]. In the present simulation a crystal which is constituted of 4000 atoms $(10a_0 \times 10a_0 \times 10a_0$ where a_0 is the lattice con-
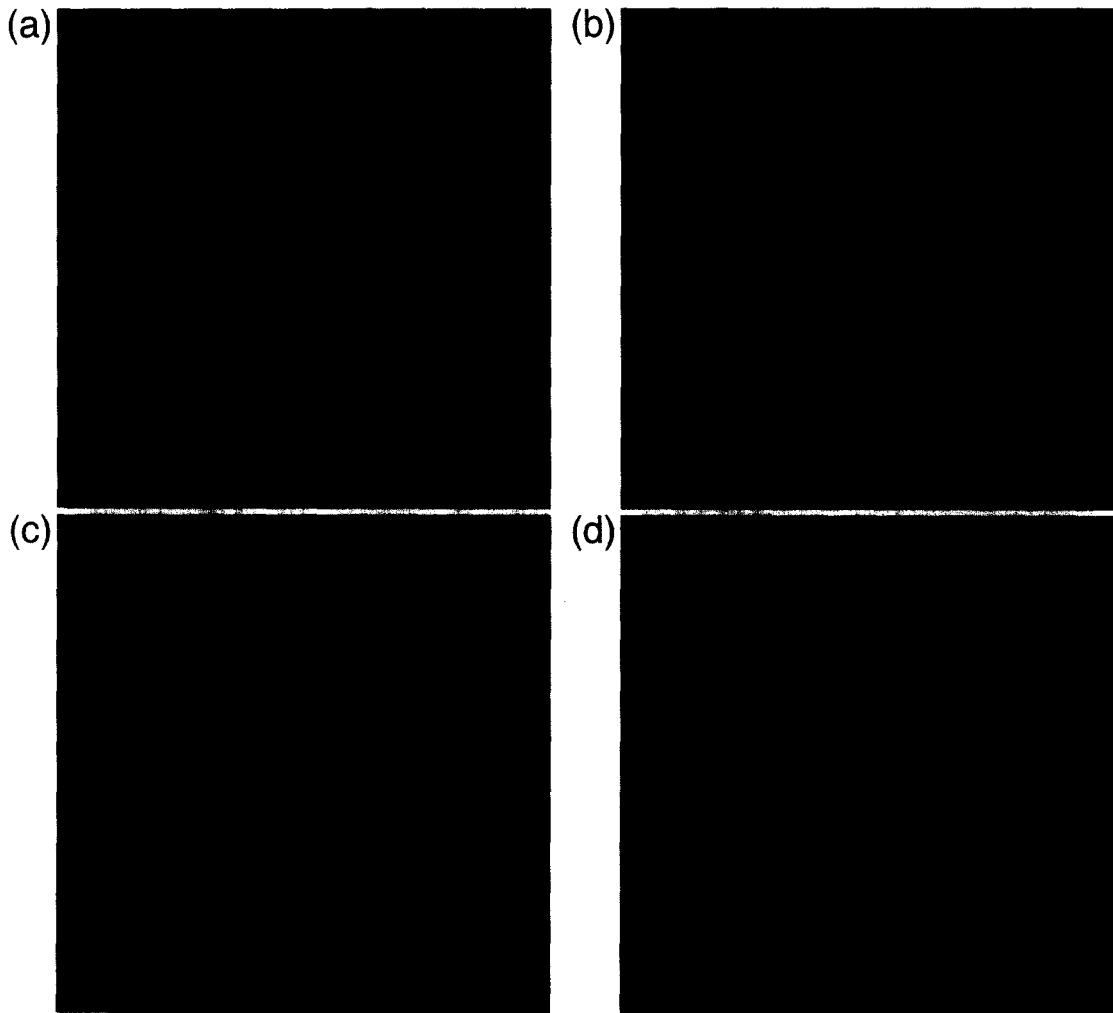

Fig. 5. The coalescence of two interstitial clusters whose size is 5 and 11 interstitials during MD simulation at 1100 K. The time is the elapsed time of the unit of ps. Both interstitial clusters move during the MD run.
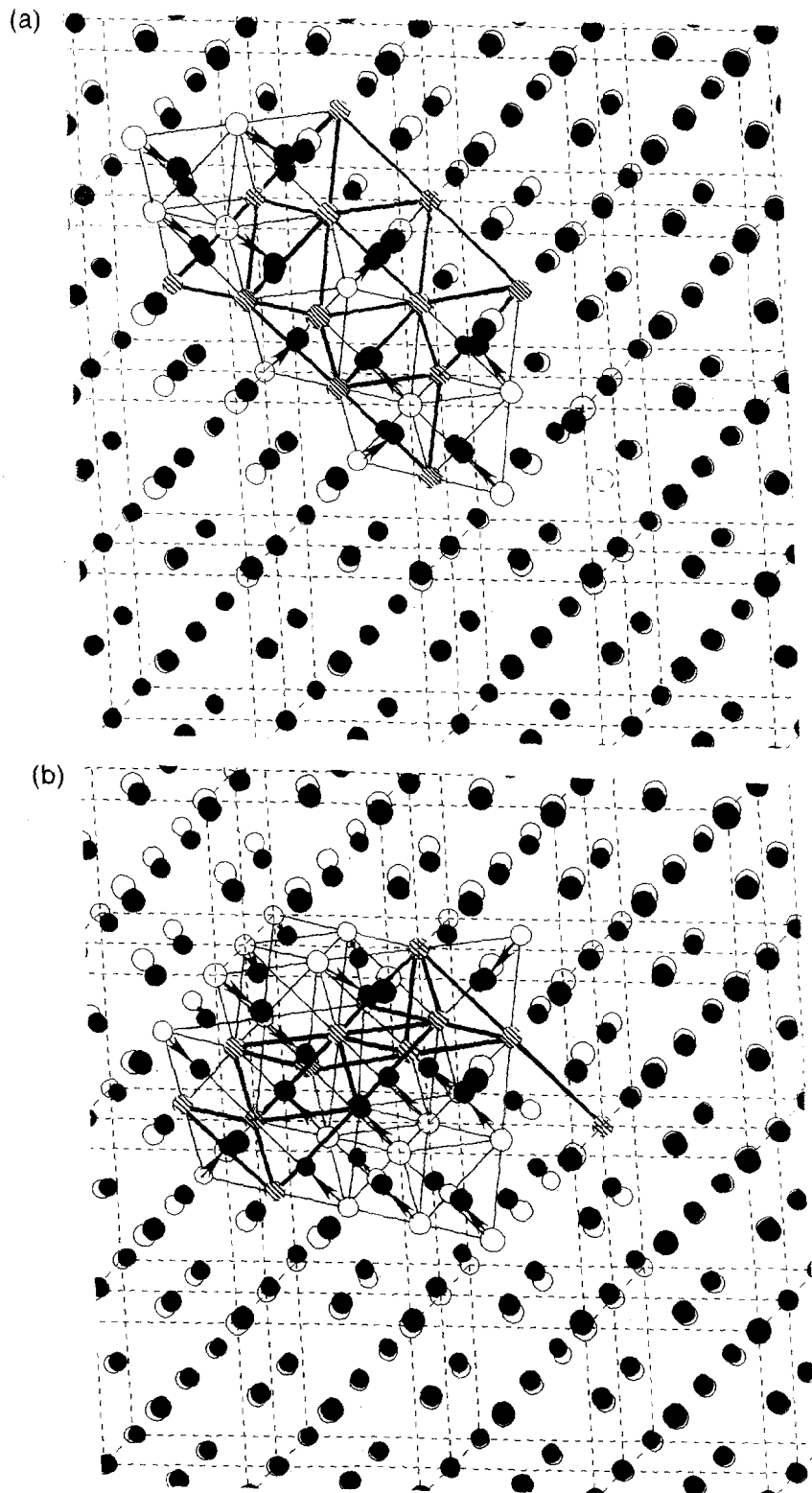
Fig. 6. The relaxed structure of vacancy clusters during MD run at 600 K. A vacancy cluster relaxes to a structure in which vacancies are connected as a string. Along the string, many of Damask–Dienes–Weizer type of relaxations occur as seen in figures. (a) A 10v-void, (b) a 15v-platelet which relaxes to a sft structure. In this figure, a solid circle shows the atom position and an open circle is atom site in perfect copper. A striped circle is vacancy position.
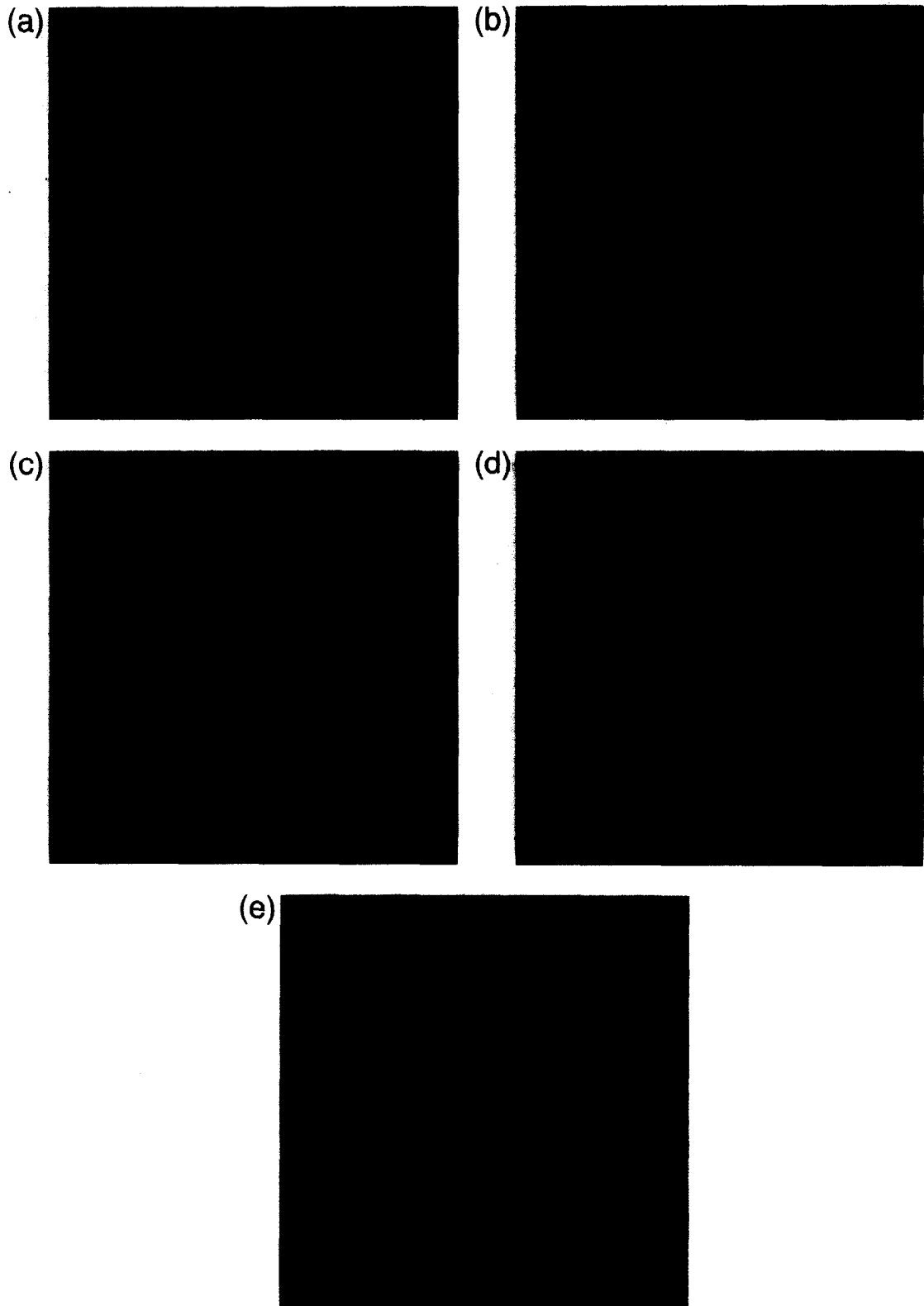
Fig. 7. The movement and coalescence of seven 10v-voids during MD simulation at 1100 K. The time indicates the elapsed time in ps during MD.
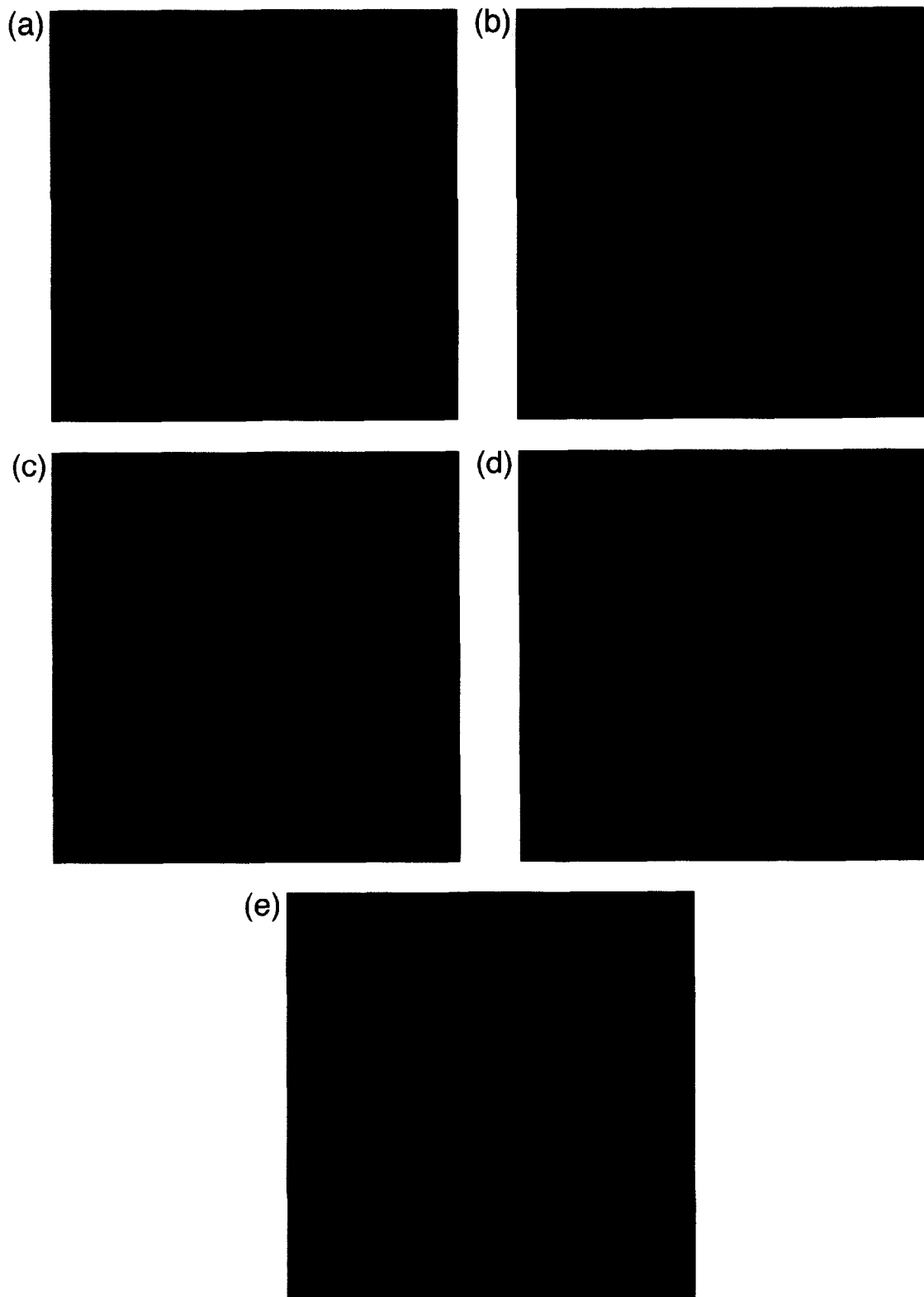
Fig. 8. The movement and coalescence of seven 15v–vacancy platelets during MD at 1100 K. The time indicates the elapsed time in ps during MD.

stant) was utilized. The periodic boundary condition is applied on the surface.

3.1. Stress sensitive movement of interstitial clusters with a low activation energy

Computer simulations show that interstitial clusters whose size is larger than three relax to the structure of a bundle of parallel $\langle 110 \rangle$ crowdions [24]. These clusters of parallel crowdions migrate with the very small activation energy of migration [24,25]. In Cu, Ag and Au, a single interstitial relaxes to a $\langle 100 \rangle$ dumbbell and makes a zigzag movement along $\langle 100 \rangle$ directions. The activation energy of a single interstitial in Cu is in the range of 0.1 eV. A di-interstitial in Cu and Ag relaxes to parallel $\langle 100 \rangle$ dumbbells which migrate with a zigzag movement towards $\langle 100 \rangle$ directions. In Au, a di-interstitial relaxes to parallel $\langle 110 \rangle$ crowdions which migrate with the activation energy of 1×10^{-4} eV [24]. This is the reason why the stage I annealing is not observed in an electron-irradiated gold at 2 K [26].

Fig. 4 shows the structure of a cluster of 20 interstitials whose structure is relaxed by running an MD simulation at 600 K. All interstitials align to $\langle 110 \rangle$ crowdions and the center positions of the $\langle 110 \rangle$ crowdions are not on the same plane as seen in Fig. 4. When an interstitial cluster relaxes to a bundle of $\langle 110 \rangle$ crowdions, the cluster moves with the activation energy as small as 1×10^{-4} eV. This kind of movement was observed in gold which was D–T neutron-irradiated at low temperature [27]. The movement of an interstitial cluster of parallel $\langle 110 \rangle$ crowdions is sensitive to the local strain field. One of the origins of the sensitivity is due to the small migration energy of interstitial clusters. The change of migration energy in strain field is small so that the significant attraction to the strain center occurs only in the case of a small migration energy which could be modified appreciably by the strain effects. Another origin of the sensitivity is the wide range of extension of displacement along a $\langle 110 \rangle$ direction in a crowdion. Fig. 5(a)–(d) show results of sequential movements of interstitial clusters in Cu whose sizes are 5 interstitials and 11 interstitials. The simulation was carried out at 600 K. It should be noted that an interstitial cluster of larger size moves frequently rather than the movement of smaller interstitial clusters. An interstitial cluster of $\langle 110 \rangle$ crowdions switches the moving direction from one $\langle 110 \rangle$ to another $\langle 110 \rangle$ direction and finally approaches the strain center. The formation of group of interstitial clusters was observed in D–T neutron-irradiated fcc metals at low temperature [29]. In copper which was neutron-irradiated at 200°C, the group gets much denser and finally develops into dislocations as shown in Fig. 1.

3.2. The movement of vacancy clusters as a cluster at high temperature

The way in which a vacancy cluster relaxes at high temperature was examined by computer simulation.

Molecular dynamics simulation was carried out with a crystal of 4000 atoms in which several vacancy clusters were introduced. At high temperature, a vacancy cluster relaxes to a string structure in which vacancies are connected with each other to a shape of curved string. Fig. 6(a) and (b) show the relaxed structure of 14v-void and 15v-platelet observed in Cu respectively, for which MD simulation was carried out at 600 K. Along such a string of vacancies many relaxations of the 3v–sft type were observed. The 3v–sft relaxation occurs not only at a 3v–60 vacancy but also includes newly created vacancies at the 3v–sft relaxation. Due to this 3v–sft relaxation, a vacancy cluster moves as a cluster rather than by the evaporation of vacancies from the clusters. The movement of vacancy clusters in the string structure proceeds with the combined steps of the 3v–sft and 3v–90 configurations. Fig. 7(a)–(e) show the movement of seven vacancy clusters of 10v-void type in 4000 Cu atoms at 1000 K. The vacancy clusters finally aggregate into a single vacancy cluster as shown in Fig. 7(e). Fig. 8(a) to (e) show the rearrangement of seven triangular 15v vacancy platelets. A triangular 15v-platelet relaxes at first to the 15v–sft structure and subsequently relaxes to the mobile structure. These clusters formed a single vacancy cluster as shown in Fig. 8(e). Vacancy clusters of small size, both of voids and sft, move to aggregate and form a single cluster.

It should be noted that the movement of vacancy clusters occurs with a smaller activation energy than that which is needed to evaporate a single vacancy. In the thin-foil annealing experiment by TEM [17], it was found that voids move much easier than does a sft. Actually, the frequent movement of sft was not observed. The shrinkage of sft was not detected during annealing at 400°C of the neutron-irradiated copper [17].

4. Discussion

4.1. Atomistic process of void formation in neutron-irradiated fcc metals at high temperature

It is generally accepted that voids nucleate with the trapping of gas atoms at small vacancy clusters in neutron-irradiated fcc metals at high temperature [8]. In the neutron irradiation experiment with the capsule which was temperature-controlled at 200°C and 300°C in JMTR, we could not observe a significant difference between the number density of voids in neutron-irradiated as-received copper and residual-gas-free copper. This indicates that gas atoms which are dissolved in copper are not responsible for the nucleation of voids at these temperatures although a remarkable difference was observed after 1×10^{20} n/cm^2 irradiation at 400°C between these two types of copper as reported previously [14]. The number of vacancies which is contained in a void is 350 times larger than that in a sft in copper which was irradiated at 200°C to the low flu-

ence. The number density of voids decreased with increasing neutron fluence while the number density of sft increased with increasing neutron fluence in the irradiation at 200°C.

Combining the results of computer simulations with these experimental results, we arrive at the conclusion that voids nucleate by the coalescence of moving vacancy clusters. When two vacancy clusters of the string structure coalesce, the vacancy cluster stays in a string structure which is in a metastable state at high temperature. Microvoids of the string structure move with the small activation energy below that of the migration of divacancies. Therefore the movement of voids is affected remarkably by the local strain field. The number density of voids in copper neutron-irradiated at 200°C decreased with increasing neutron fluence while the number density of sft increased with increasing the fluence. These results are due to the increment of dislocation density which is formed by the grouping of interstitial clusters. Zinkle et al. [28] reported that the formation of voids was not observed when copper was irradiated below 180°C. This is due to the difficulty of the relaxation to the string structure below 180°C. The mechanism of the movement of voids under the strain field is through the configuration path of 3v–sft and 3v–90 in the string structure of the vacancy clusters. Voids move almost as a void after relaxing to the string structure.

4.2. The role of gas atom on the formation of voids

After the nucleation of voids, voids move as a void itself. By coalescence with other migrating voids, it grows to a larger size. During the movement of voids, gas atoms are trapped at voids. The helium atoms stay in the center part of voids. The hydrogen atoms move along the surface of voids. Both kinds of gas atoms suppress the relaxation of the 3v–sft type which appears on the surface of voids. This causes the mobility of gas-atom-trapped voids to be reduced with increasing numbers of trapped gas atoms. In the present experiments, the number density of voids which were observed in as-received copper remained higher than in residual-gas-free specimens.

5. Summary

It was believed previously that voids nucleate at gas-atom trapped vacancy clusters. Gas atoms in vacancy clusters prevent collapse to the relaxed structure. The neutron irradiation with pure copper in the temperature controlled capsule at JMTR suggests that this is not the case. The linkage of experimental results and computer simulations suggests that small vacancy clusters can migrate and coalesce to grow into large voids at high temperature. The vacancy clusters can relax to the metastable void structure by the thermal activation. This relaxation to voids does not occur at room temperature. Due to this

relaxation, voids nucleate without requiring gas atoms in vacancy clusters at high temperature. Voids grow to a large size by coalescing with another migrating voids. While growing into large voids, gas atoms are trapped by the voids which degrade their movement. This prevents further coalescence and causes the number density of voids to remain higher in specimens which contain the residual gas atoms.

Acknowledgements

References

[1] C.A. English, B.L. Eyre, J.W. Muncie, Philos. Mag. A56 (1987) 453.
[2] H.R. Brager, J. Nucl. Mater. 141–143 (1986) 163.
[3] B.N. Singh, A. Horsewell, D.S. Gelles, F.A. Garner, J. Nucl. Mater. 191–194 (1992) 1172.
[4] L.K. Mansur, Nucl. Technol. 40 (1978) 5.
[5] A.D. Brailsford, R. Bullough, J. Nucl. Mater. 44 (1972) 121.
[6] L.D. Glowinski, C. Fiche, J. Nucl. Mater. 61 (1976) 29.
[7] J.M. Lanore, G.L. Glowinski, A. Risbet, P. Regnier, J. L. Flament, V.L. Levy, Y. Adda, in: Fundamental Aspects of Radiation Damage in Metals, vol. 2, USERDA, CONF-751006, Gatlinburg, TN, 1976, eds. M.T. Robinson, F.W. Young Jr., p. 1169.
[8] R.E. Stoller, G.R. Odette, Radiation-induced changes in microstructure, in: 13th Int. Symp. (part I), ASTM STP 955, eds. F.A. Garner, N.H. Packan and A.S. Kumar (American Society for Testing and Materials, Philadelphia, PA, 1987) p. 358.
[9] R.E. Stoller, J. Nucl. Mater. 174 (1990) 289.
[10] L.K. Mansur, W.A. Coghlan, J. Nucl. Mater. 119 (1983) 1.
[11] Y. Shimomura, M.W. Guinan, T.D. de la Rubia, J. Nucl. Mater 205 (1993) 374.
[12] A.C. Damask, G.J. Dienes, V.G. Weizer, Phys. Rev. 113 (1959) 781.
[13] Y. Shimomura, R. Nishiguchi, T.D. de la Rubia, M.W. Guinan, Radiat. Eff. Def. Solids 129 (1994) 81.
[14] K. Yamakawa, I. Mukouda, Y. Shimomura, J. Nucl. Mater. 191–194 (1992) 374.
[15] Y. Shimomura, I. Mukouda, F.A. Garner, FFTF/MOTA Ann. Prog. Rep. fusion year 1993 (1995) 249–256.
[16] Y. Shimomura, I. Mukouda, M. Kiritani, S. Kojima, F.A. Garner, J. Nucl. Mater. 212–215 (1994) 352.
[17] I. Mukouda, Y. Shimomura, J. Nucl. Mater., submitted.
[18] M. Narui, T. Segawa, Y. Endoh, T. Uramota, T. Shikama, H. Kayano, M. Kiritani, J. Nucl. Mater. 212–215 (1994) 1645.
[19] M. Narui, H. Kurishita, H. Kayano, T. Sagawa, N. Yoshida, M. Kiritani, J. Nucl. Mater. 212–215 (1994) 1665.

[20] M.S. Daw, S.M. Foiles, M.I. Baskes, Dynamo code version 8.5, Sandia National Laboratory, 1986.

[21] M.S. Daw, M.I. Baskes, Phys. Rev. B29 (1984) 6443.

[22] T.D. de la Rubia, unpublished work.

[23] S.M. Foiles, M.I. Baskes, M.S. Daw, Phys. Rev. B37 (1988) 10387.

[24] Y. Shimomura, K. Sugio, P. Zhao, J. Phys. Soc. Jpn., submitted.

[25] P. Zhao, Y. Shimomura, to be published.

[26] P.S. Gwotze, J.S. Koehler, Phys. Rev. B8 (1973) 3616.

[27] Y. Shimomura, R. Nishiguch, T.D. de la Rubia, M.W. Guinan, Radiat. Eff. Def. Solids 130&131 (1994) 483.

[28] S.J. Zinkle, L.E. Seitzman, W.G. Wolfer, Philos. Mag. A55 (1987) 111.

[29] Y. Shimomura, M.W. Guinan, M. Kiritani, J. Nucl. Mater. 133&134 (1985) 415.