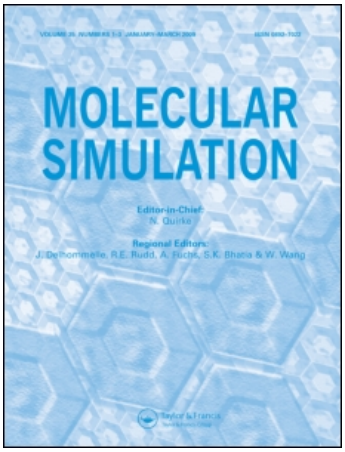

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MOLECULAR DYNAMICS OF RADIATION DAMAGE IN AMORPHOUS $Pd_{80}Si_{20}$ ALLOY USING N^+ IONS

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Irradiation experiments on amorphous $Pd_{80}Si_{20}$ alloy were carried out using 2.0 MeV N^+ ions. X-ray diffraction (XRD), small angle x-ray scattering (SAXS), and extended x-ray absorption fine structure (EXAFS) were measured before and after irradiation.

A molecular dynamics (MD) simulation (for a bigger system than in our previous work) was performed to simulate radiation damage of an amorphous $Pd_{80}Si_{20}$ alloy by an accelerated N^+ ion with several keV. Similarity of the experimental and the computational structural change was observed. A void, which had never been observed in the previous simulations with smaller acceleration energies of the N^+ ion, was clearly observed which might explain the increase of the experimental structure factor in a small angle region. Additionally, the process from the appearance of the void to its extinction was examined in detail.

KEY WORDS: Molecular dynamics, amorphous alloys, radiation damage.

1 INTRODUCTION

Computer simulation of radiation damage has been widely performed since the study of Gibson *et al.* [1] for Cu and Fe metals in 1960. In most cases, however, irradiated materials were crystals, not amorphous materials. MD simulation has shown remarkable results in many studies of noncrystalline materials such as liquids and amorphous solids, so that it was used in the present simulation for radiation damage of an amorphous alloy.

We have studied radiation effects of an amorphous $Pd_{80}Si_{20}$ alloy by an accelerated N^+ ion according to the MD technique [2, 3]. The following results have been obtained in these simulations.

(1) Threshold energy of atomic displacement in the simulated system is about 40 eV. This value is close to that of Pd metal, 34 eV [4].

(2) The environment near the primary knock-on atom (PKA) is actually in a liquid state.

(3) The triangular prism as shown in Figure 1(a), which is considered as a basic structure of short range in this system [5], seems to be partly destroyed by the irradiation.

(4) Some cascades were observed in the simulation with 1.0 keV N^+ ion.

The second and the third results listed above explain damping of scattering amplitude of $S(Q)$ estimated by XRD experiment. However, increase of $S(Q)$ in a small

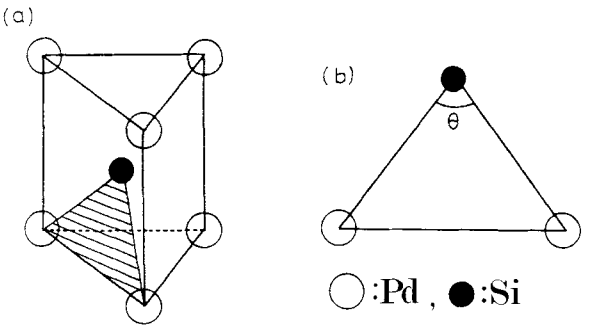

Figure 1 Model of short range structure of amorphous $Pd_{80}Si_{20}$ alloy.

angle region which had been observed by XRD experiment (equivalent to increase of SAXS intensity), was not represented in the previous simulations. A void had not been generated because of the low acceleration energy of an N^+ ion in the previous work. In order to make a void which is an assembly of vacancies and expected to be closely associated with SAXS intensity, a much higher acceleration energy of N^+ ion is required in the simulation. Since the acceleration energy is finally distributed to all atoms in the irradiated system, then to make MD simulation with high acceleration energy, a corresponding large system is required. Numbers of particles, acceleration energies, and other parameters in the previous simulations and in this work are summarized in Table 1.

Estimation of ionic flux is difficult in our simulated system. However, the experimental structural change with increase of ionic flux was not drastic, but gradual, *i.e.*, qualitative structural change may not depend on flux, so that similarity of structural change after the experimental and the computational irradiation may allow the interpretation of the experimental change using computation.

2 EXPERIMENTAL

The irradiation experiment was carried out by the van de Graaff accelerator in Tokyo Institute of Technology. The dimension of the samples used was thin ribbon of 3.0 mm width and 60 μm thickness. These were irradiated by 2.0 MeV N^+ ion. Irradiation flux was 4.3×10^{20} ions/m^2. The samples were cooled by thermal conduction of copper using liquid nitrogen during the irradiation experiment in order to avoid annealing of damage.

Table 1 Previous and present MD simulation.

basic cell	*number*	*energy*	*step width*
cube	1000	300 eV	0.2 fsec
cube	4096	500 eV	0.20 fsec
sphere	7686	2 keV	0.10 fsec
*sphere	35449	5 keV	0.05 fsec

*in this work.

The measurements of XRD, SAXS, and EXAFS were carried out before and after the irradiation.

3 COMPUTER SIMULATION

The pair potential used in this work was the form as follow,

$$u_{ij}(r) = \frac{z_i z_j e^2}{r} \exp(-\lambda r) + b \exp\left\{\frac{(r_i + r_j) - r}{\sigma}\right\}$$

where z_i, r_i, λ, and σ are adjustable parameters. This formula is considered to be a combination of screened coulomb potential by conduction electron, namely the Yukawa potential and repulsive potential of the Born-Mayer type. Parameters are listed in Table 2. These values were chosen to ensure good agreement between the structure factor $S(Q)$ and radial distribution function $G(r)$ obtained by XRD measurement and by MD simulation [2, 3].

The employed cell is not a cube, but a sphere with a radius of 50.0 Å which consists of 35449 atoms (Pd: 28376, Si: 7072). The cell with an N^+ ion initially located at the center was annealed at 3000 K by the isothermal MD simulation [6]. After which the temperature of the system was gradually depressed to 77 K (liquid nitrogen), an N^+ ion was accelerated with 5.0 keV, then an isobaric MD simulation, which is described in [2], was carried out. The system was set at 0 K, that is, all atoms are at rest before the irradiation, this procedure was successfully employed by King *et al.* [7] to investigate radiation damage of copper by the MD simulation. At initial steps, all interactions between particles in the cell were not calculated but restricted within an inner sphere of the system with a radius of 15.0 Å, in which there were 959 particles including the N^+ ion. The size of the inner sphere was extended from 15.0 Å to 20.0 Å as the propagation of energy to outside: the criterion of the extension is that kinetic energies of atoms in the periphery of the sphere exceeds (3/2)kT (T = 300 K). Interactions between atoms inside and outside the inner cell were also calculated, but the forces for the outside atoms were ignored before the extension of the cell. Such a procedure was repeated after that up to 50.0 Å in radius by 5.0 Å. The value of 5.0 Å corresponds to the cut off distance of the pair potential. In order to perform the isobaric MD simulation, the system was uniformly expanded to keep a constant pressure. The expansion of the cell was finally 3.0%. Surface effects which arise from the periodic boundary conditions, were reduced by the large system size, *i.e.*, the structure factor of this system is almost same as that in the system with the periodic boundary condition [2]. The calculation was terminated after 150.0 fsec, when the

Table 2 Parameters used in the pair potential.

parameters	*Pd*	*Si*	*N*
number	28376	7072	1
r_i/A	1.42	1.00	0.70
z_i	−0.8	+4.0	+1.0
b/J	0.338×10^{-19}		
λ/A^{-1}	0.70		
σ/A	0.10		

propagation of the energy originated from an N^+ ion reached the outside of the cell (50.0 Å). There are no knock-on atoms having kinetic energy more than 1.0 eV at the end of the simulation.

The utilizations of above technique and a supercomputer with vector processors made it possible to carry out the MD simulation for a large system. The time of 150 fsec is reasonable for radiation damage process to finish [8].

4 RESULTS AND DISCUSSION

4.1 *XRD and SAXS*

Figure 2(a) and (b) show structure factors $S(Q)$ obtained by XRD and SAXS before and after the irradiation. The following Debye scattering equation was applied to the calculation of $S(Q)$ using the positional data at each time step, to trace structural changes during the simulation.

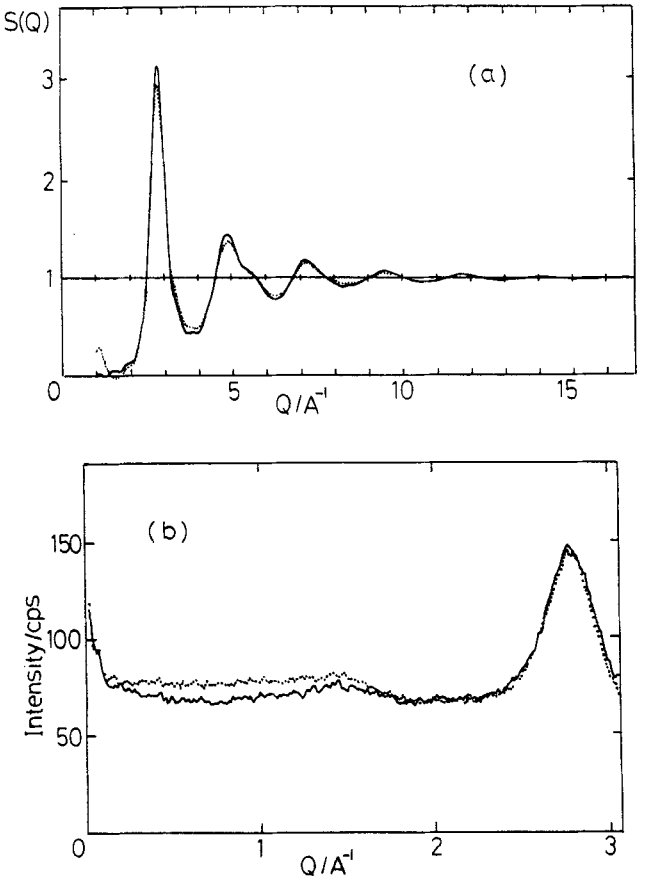

Figure 2 (a) Structure factors $S(Q)$ by XRD and (b) SAXS intensity, —— before irradiation; - - - after irradiation.

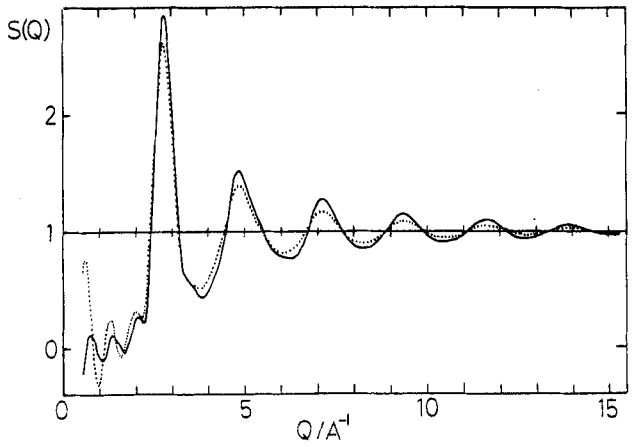

Figure 3 Structure factors $S(Q)$ by MD simulation, —— before irradiation; - - - after irradiation.

$$S(Q) = 1 + \frac{\sum_i \sum_j' f_i(Q) f_i(Q) \dfrac{\sin(Qr_{ij})}{Qr_{ij}}}{\sum_i f_i^2(Q)}$$

where $f_i(Q)$ is the atomic scattering factor of the atom i and r_{ij} is the interatomic distance between the atoms i and j.

Damping of scattering amplitude and increase of SAXS after the irradiation were observed as well as the previous measurements. The functions $S(Q)$ from the MD simulation, which are based on the positional data before the acceleration of N^+ ion and after 150 fsec, are shown in Figure 3. The damping of the amplitude and the increase of the SAXS are introduced by the irradiation simultaneously, while in the previous simulations, the former alone was observed.

4.2 *Atomic Arrangements*

Cross sectional figures of atomic arrangements near the center of the spherical cell after 50.0 and 100.0 fsec are drawn in Figure 4. A void is clearly observed after 50.0 fsec. While a depleted zone had been seen in the previous simulation, such a clear void was never detected. This void became indistinct by penetration of the surrounding atoms after 100.0 fsec. This penetration may be a reason why an amorphous alloy is tough for radiation damage, because it had never seen in the simulation of Cu crystal [6]. The initial state, however, does not turn back completely and a much larger depleted zone than those observed previously was left after 150.0 fsec. Number density within a radius of 20.0 Å after 150 fsec was 0.0619/Å^3 as compared with 0.0677/Å^3 before the irradiation. This value corresponds to the expansion of the cell and the existence of the depleted zone, and is very close to that in a liquid state of the system, 0.0621/Å^3 [9]. Increase of the SAXS seems to be mainly assigned to this depleted zone, because there is a considerable discrepancy of density between center and outer of the cell.

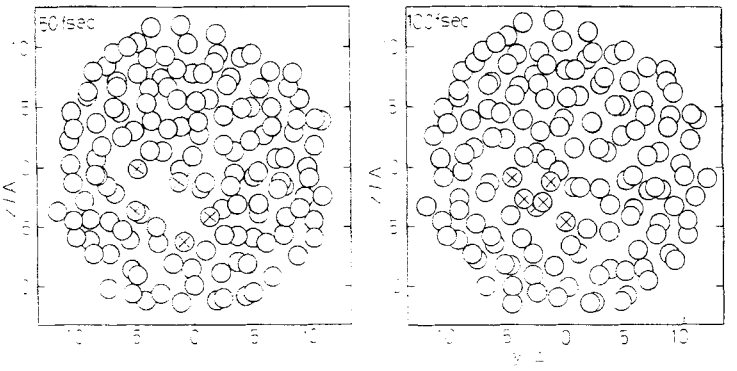

Figure 4 Atomic arrangements in y–x slab of thickness 5.0 Å near the center of basic cell (Particle marked as cross is penetrative atom.).

4.3 *Statistical Analysis*

Two kinds of statistical analyses, the Voronoi polyhedron analysis [10] and calculation of angular distribution of nearest Pd–Si–Pd, were performed using the positional data from the MD simulation. The Voronoi polyhedron analysis is effective to investigate a local environment, and the angular distribution is closely associated with short range order (SRO).

Frequency distribution of appearance of each polygon on polyhedron before the irradiation (open rectangular) and after 150.0 fsec (shaded rectangular) are compared in Figure 5. Before the irradiation, the frequency of pentagon is much higher than others. It is a characteristic of amorphous material, that is, a plane cannot be filled completely with pentagons. The frequency of pentagons after 150.0 fsec decreases, and others increase. This does not indicate crystallization, because if a crystallization occurs in this system, only the frequency of the characteristic polygon corresponding

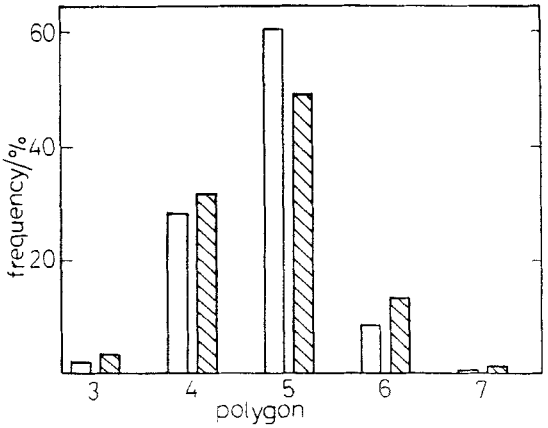

Figure 5 Distribution of polygon at initial step (open rectangular) and after 150 fsec (shaded rectangular).

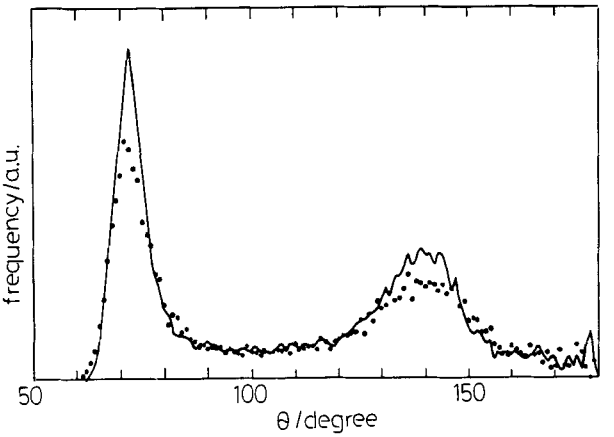

Figure 6 Distribution of angle of two nearest neighbor Pd atoms from a central Si atom, —— before irradiation; - - - after irradiation.

to the crystal is expected to increase. However, all polygons except pentagon increase, which can be seen in a liquid state [11]. It suggests that the depleted zone is actually in a liquid state.

Frequency distribution of Pd–Si–Pd angle in triangular prism (indicated in Figure 1(b)) were calculated and shown in Figure 6. Since distances of the nearest Pd–Si and Pd–Pd pairs were 2.36 and 2.84 Å evaluated by XRD and EXAFS, this angle is estimated to be 74 degrees due to the Gaskell model [5]. A sharp peak is detected at 72 degrees and seems to correspond to the Pd–Si–Pd angle in the prism. Considerable decrease of this peak is detected after 150.0 fsec, which shows that the triangular prism was partly destroyed by the irradiation, in other words, that some SRO in this system was broken.

These results are almost the same as those performed previously [2, 3].

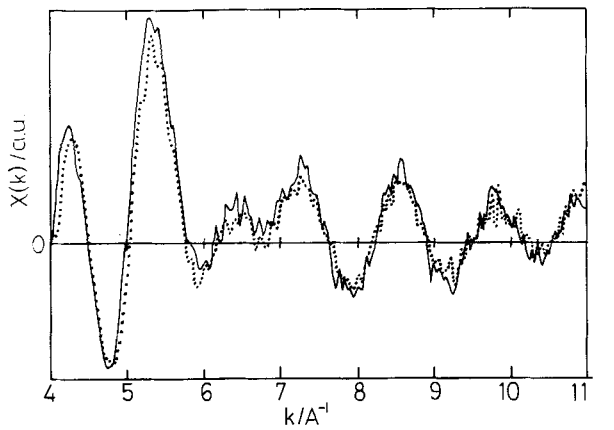

Figure 7 Observed EXAFS signals $X(k)$ by experiment, —— before irradiation, - - - after irradiation.

4.4 *EXAFS*

Since EXAFS is intended for studies of local structure, it is one of the most suitable methods to evaluate changes of the SRO. Observed EXAFS signals $\chi(k)$ after k-absorption edge of Pd are shown in Figure 7 before and after the irradiation. Radial structure functions $|F(r)|$ are obtained by the fourier transformation of $\chi(k)$,

$$F(r) = (2\pi)^{-1/2} \int_{k_{min}}^{k_{max}} k^3 \chi(k) \exp(-2\pi i k r)\, dk$$

and shown in Figure 8. Decrease and broadening of the first peak is detected after the irradiation. EXAFS signals $\chi_{1st}(k)$ from the first peak can be calculated by the reciprocal fourier transformation. Also from the MD simulation, the signals χ_{1st} can be synthesized using the following equation [12],

$$\chi(k) = \sum_j \frac{N_j f_j(k)}{k r_j^2} \sin(2kr_j + \phi_{ij}(k))$$

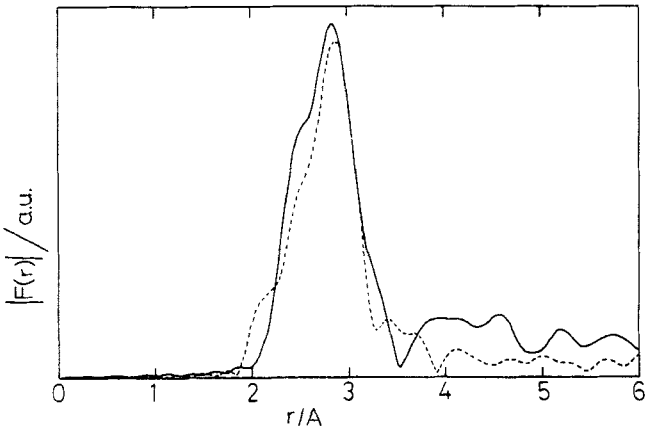

Figure 8 Radial structure functions $|F(r)|$, —— before irradiation, - - - after irradiation.

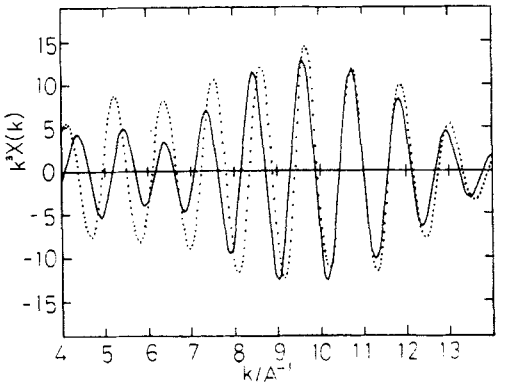

Figure 9 EXAFS signals $k^3\chi(k)$ from the first shell, —— experimental; - - - MD simulation.

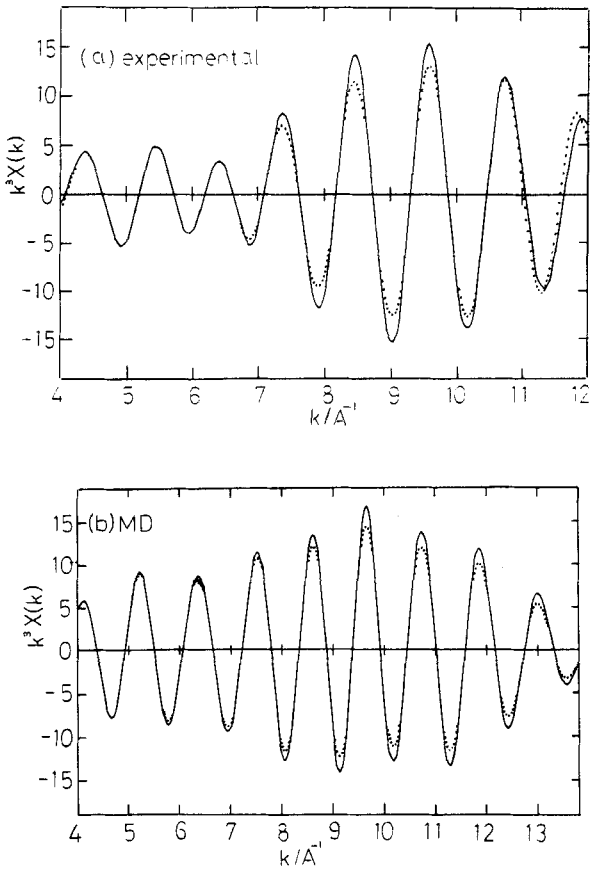

Figure 10 EXAFS signals $k^3\chi(k)$ from the first shell of (a) experiment and (b) MD simulation, —— before irradiation, – – – after irradiation.

where $f_j(k)$ is the backscattering amplitude of atomic species j, N_j is the coordination number of atom j around atom i, and ϕ_{ij} is the total phase shift [12]. The functions $k^3\chi_{1st}(k)$ obtained in the experiment and synthesized from the MD simulation are compared in Figure 9. The experimental features are reproduced by the simulation, but an agreement between the two curves is not satisfactory, especially on the low k side. The values of $k^3\chi_{1st}(k)$ before and after the irradiation by the experiment and the simulation are shown in Figures 10(a) and (b), respectively. Damping of amplitude, which was similar to that in structure factor by XRD, is detected by the EXAFS, and it is reproduced by the simulation.

5 CONCLUSIONS

MD simulation for radiation damage of amorphous $Pd_{80}Si_{20}$ alloy by N^+ ion with energy of 5 keV was performed in a large system, and the following conclusions were obtained.

(1) A void was clearly observed, but it became finally a large depleted zone through penetration of the surrounding atoms. It seems to be one of the reasons why amorphous alloy is tough for radiation damage.

(2) Increase of SAXS intensity was reproduced by the MD simulation, and seems to be closely associated with the large depleted zone.

(3) Results of statistical analyses, the Voronoi polyhedron analysis and angular distribution of the nearest Pd–Si–Pd, were essentially unchanged between the previous simulations with less acceleration energies and this work.

(4) EXAFS experiment was performed and synthesized from the data of the MD simulation.

Acknowledgements

The calculations were performed by supercomputer ETA[10] in the computer center at Tokyo Institute of Technology.

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