Dynamical Study of Spatio-Temporal Structural Fluctuations in the Intermetallic Compound Nickel–Titanium during Radiation-Induced Crystalline-to-Amorphous Transformation

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We have studied nanostructural fluctuations during electron irradiation in the ordered intermetallic compound NiTi by performing irradiation experiments with a high-resolution high-voltage electron microscope (HVEM) and molecular dynamics (MD) simulations. It was observed that atom clusters formed and disappeared repeatedly during irradiation, which results in the structural fluctuation. Comparing the experimental results with the MD simulations, we conclude that such spatio-temporal structural fluctuations under irradiation can be accounted for the evolution of metastable nanoclusters. The present study demonstrates the usefulness of high-resolution HVEM for in situ studies of dynamic, nanoscale fluctuation phenomena.

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1. Introduction

Although amorphization of intermetallic compounds by energetic-particle irradiation has long been studied,1–5 only recently is high-resolution high-voltage electron microscopy (HVEM) becoming a potential technique for investigating the dynamical changes in atomic order that occur during the crystalline-to-amorphous transition. We have indeed used this technique to evaluate temporal fluctuations in the microstructure and the lifetime of corresponding metastable, nanoscale clusters that form and disappear rapidly. When the number of atoms involved in the system is small, one would expect that spatial and temporal stochastic fluctuations (i.e., the so-called statistical fluctuations), might play a key role in the local structural characterization. In this paper, we report on the irradiation-dose dependence of the fluctuations observed in irradiation experiment and molecular dynamics (MD) simulation.

2. Experimental Procedure

2.1 HVEM experiment

NiTi TEM samples (Ti–51 at%Ni, B2 ordered structure) were prepared from 3 mm disks which were pre-annealed at 1273 K (1 h), followed by electrochemical polishing. They were then irradiated with 1.25-MeV electrons (dose rate: 1.0 × 10^{24} e/m^2 s) in a high-resolution high-voltage electron microscope (HVEM) (JEM-ARM1300) at Hokkaido University. The point-to-point resolution of this microscope is 0.12 nm. During electron irradiation, high-resolution images taken nearly in Scherzer defocus condition (approximately, −57 nm) were video-recorded by means of a charge-coupled device camera. The minimum time interval for acquiring the images was 1/30 s. Fast Fourier transform (FFT) image analysis was performed to elucidate the amorphizing transition process.

2.2 Evaluation of “local amorphization parameter”

To evaluate the structural disorder, we obtained local amorphization parameters, P, by measuring the intensity ratio of the diffuse-halo region (excluding the fundamental spots) to the fundamental spots on an FFT pattern.6) A measure of the extent of amorphization at time t is the quantity

\[ I(t) = I_{H}(t)/I_{F}(t), \]  

(1)

where \( I_{H}(t) \) and \( I_{F}(t) \) are the integrated intensities (over a 10-pixel width in 256 × 256 images) at an arbitrary point on the diffuse halo and at the [110] fundamental spot in the FFT pattern, respectively (see Fig. 1). Since the halo contains the [110] spot, one has \( I_{H}(t) = I_{F}(t) \) when the sample is completely amorphous, and \( I_{H}(t) = 0 \) for the completely-crystalline state. Hence, \( I(t) \) varies from 0 (for the completely-crystalline state) to 1 (for the completely-amorphous state). However, to minimize the effect of background noise, especially artifacts introduced by the FFT, we use the normalized local amorphization parameter, \( P(t) \), defined as

\[ P(t) = (I(t) - I(0))/(1 - I(0)). \]  

(2)

Like \( I(t) \), \( P(t) \) varies from 0 to 1 as the sample goes from the fully-crystalline to the completely-amorphous state.

2.3 Molecular dynamics simulation

MD simulation and statistical analysis of structural changes in the irradiated compound were performed using the interatomic potentials derived by Sabochick and Lam7) employing the embedded-atom method. A system containing

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2000 atoms (1000 atoms for each component, a supercell size: approximately 27 nm$^3$), subjected to periodic-boundary and constant-pressure conditions was used in the present study. One Frenkel pair was randomly created in the crystal every $10.0\Delta t$ ($\Delta t$ is a MD timestep, corresponding to 0.002 ps) for up to $2 \times 10^4 \Delta t$. The total number of Frenkel-pair insertions corresponds to an irradiation dose of 1.0 displacement per atom (dpa). Prior to the statistical analyses the systems were equilibrated for $10^4 \Delta t$, and several physical properties, including the system volume and the system’s potential and kinetic energies, were then evaluated during an additional $10^4 \Delta t$. The further details on the present MD simulation method are given in the Refs. 5) and 7).

Diffraction patterns and high-resolution TEM images were then independently calculated by using the multislice method in conjunction with the MD-generated atomic configurations. We assumed the following values, typical for the HVEM conditions in our experiment: 15 nm for the sample thickness, 1.25 MV for the accelerating voltage, and 2.65 mm for the spherical aberration parameter. 8)

3. Results and Discussion

3.1 Atomic structural changes during irradiation

Figures 1(a) and (b) show the experimental and simulated high-resolution HVEM images, respectively, at various dose levels during irradiation at 300 K. The film orientation was $\langle 111 \rangle$, as is the electron incidence direction. During the amorphization process, nanosized atom clusters were seen to repeatedly form and annihilate in the images (indicated by the circles). Correspondingly, extra spots appeared and disappeared in the diffraction patterns. The response of the compound to irradiation in the MD simulation can be summarized as follows: chemical disordering occurs progressively after a short irradiation time, and then topological disordering begins and proceeds until amorphization is completed. The corresponding ranges of irradiation doses are 0–0.15 dpa for chemical disordering and 0.15–0.25 dpa for topological disordering leading to amorphization. To study chemical disordering, we monitored the disappearance of $\{100\}$ long-range-order spots in the MD diffraction patterns, viewing from the $\langle 110 \rangle$ direction. The $\{100\}$ spots disappeared at 0.16 dpa in the present study.

3.2 Nanostructural fluctuations during the amorphization process

Figures 2(a) and (b) illustrate the dose-dependent fluctuations of the normalized local amorphization parameter, $P$, obtained from the FFT patterns and the diffraction patterns shown in Figs. 1(a) and (b). It can be seen that the onset of amorphization occurs near 0.15 dpa and the fluctuation amplitudes become larger in the topological-disordering stage, between 0.15 and 0.25 dpa in the MD simulation (Fig. 2(b)). The fluctuation continues even after amorphization has been completed. This fluctuation behavior was observed both in the HVEM experiment and in the MD simulation. The values of $P$ in Fig. 2(b) exceed 1.0 (for complete amorphization) from time to time, the reason being that the intensities of the initially-chosen fundamental spots became weaker than those formed in other portions of the diffuse halo. At higher temperatures, the experimental fluctuations show longer periods because they are influenced not only by spontaneous defect recombination but also by radiation-induced diffusional processes. The duration of fluctuation in the HVEM experimental results is longer than that of the MD simulation. The reason is probably that the present MD simulation does not take into account factors such as thermal diffusion, channelling effect, and surface effects associated with the actual thin-foil specimens.

Figure 3(a) illustrates the fluctuations in the potential energy per atom ($\Delta E: \text{potential energy change}, N: \text{atomic number}$). Fluctuations between 0.2 and 0.4 dpa are enlarged in...
Fig. 2 (a) Dose-dependent fluctuations in the normalized local amorphization parameter, $P$, during in situ irradiation at 300 K. (b) Dose-dependent fluctuations in the normalized local amorphization parameter, $P$, observed in MD simulation at 300 K.

Fig. 3 (a) Simulated temporal fluctuations in the potential energy, $\Delta E/N$. (b) Enlarged fluctuations between 0.2 and 0.4 dpa.

4. Concluding Remarks

Dynamical observations of the radiation-induced amorphization process in NiTi were carried out using high-resolution HVEM and MD simulations. Nanometer-sized clusters were found to appear and disappear in the irradiated region. Spatio-temporal fluctuations during irradiation were manifested through the dose-dependent local amorphization parameter and in the calculated potential energy. The random formation and annihilation of nanocrystalline clusters are responsible for these fluctuations, which might be related to transitions between the ideal glass state and a metastable, unrelaxed state in an energy-dissipative system under irradiation. The observed fluctuations obey a power law, based on the analysis of the data shown in Figs. 2 and 3. The detail on the power-law will be discussed elsewhere. The structural fluctuation behavior suggests that the irradiation field in an HVEM can provide a means to explore nonequilibrium open systems. Various aspects of transient atomic clusters and their structure have not been clarified in the present study but are the subject of our ongoing work.

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REFERENCES