Molecular Dynamics Analysis of Nucleation in Structural Transformation[†]

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The characteristics of the microstructure produced by a solid/solid transformation greatly depend on the nucleation process of the product phase. The objective of this study is to obtain a definite image of the atomistic nucleation process of structural transformation, which accompanies a change in atomic density, by clarifying (a) the spatial change with time, and (b) the role of dislocations in the nucleation process in computer-modeled metallic crystals. We employed a NPT ensemble attained by the constraint method proposed by Evans and Morriss. To model a fcc/bcc transformation: (a) relaxation of the initial configuration of perfect and defected fcc lattice is done by using the Finnis-Sinclair potential that stabilizes the fcc structure, and then (b) the system is set to be transformed by applying a bcc potential to all atoms at once. Using Voronoi polyhedra analysis, the crystal structure is distinguished on an atomic scale.

Changes in crystal structure are found to occur in the system modeled by the NTP ensemble and the potential-change procedure employed in the present study. In a perfect crystal, the change in the number of bcc constituent atoms saturates at about 40% in all atoms in the system and consequently the structural transformation does not proceed further. It is thought that this is the state of fluctuation. In a crystal containing a dislocation, structural transformation starts around the dislocation and it is observed that the crystallographic orientation of formed crystals is restricted. The number of bcc constituent atoms increases steadily. Whether nucleation of structural transformation occurs or not is clearly distinguished by the initial state of the crystal.

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I. Introduction

The characteristics of the microstructure produced by a solid/solid transformation greatly depend on the nucleation process of the product phase. The distribution and selection of the crystallographic orientation of the product phase are determined at the stage of nucleation. Observing the nucleation process has been a long-cherished goal in the Materials Science field, however, atomic phenomena of this kind are hard to observe experimentally. If we consider the structural transformation that accompanies a change in atomic density, analytical evaluation is also difficult because the process relates to many-body problem in a wide sense. Generally, considerations of energetics concern only equilibrium states and do not give us information on the process. Classical nucleation theory provides a concept of the critical size of a nucleus, however it does not offer information on the realistic situation of atomic and dynamic phenomena. Consequently, we need an atomistic approach to understand the process of nucleation.

Recently, in cases where simple inter-atomic potential is supposed, molecular dynamics (MD) calculations can be executed at a practical speed. Using this method properly, a clear image of the nucleation process may be

obtained by observing the movements of atoms and the necessary conditions of the nucleation site can be discussed definitely by changing the initial conditions without experimental limitations.

The reason for which the structural transformation occurs is still far from being understood. Therefore the application of MD calculations using complex potentials to the study of this field is thought to be less effective at present. We selected the MD method using simple inter-atomic potentials to make clear not "why" but "how" the transformation occurs.

The objective of this study is to obtain a definite image of the atomistic nucleation process of structural transformation by clarifying (a) the spatial change with time, and (b) the role of dislocations in the nucleation process in computer-modeled metallic crystals.

II. Procedures

1. Molecular dynamics method

In using the MD method, modeling and conditions are the most important factors. It is known that the Parrinello-Rahman method⁽¹⁾, which permits the change of the shape of the calculating cell, is very useful for studying the relationship between crystal structure and inter-atomic potential. However, to investigate the process of structural transformation, this method is not appropriate because the dynamic process during transformation in this method is simply a calculating process and

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does not have a physical meaning. Firstly we need to check whether structural change can occur in more constrained situations, which is thought to be more realistic.

The NPT (number of atoms, pressure and temperature in a system is kept constant) ensemble we employed is attained by the constraint method proposed by Evans and Morriss⁽²⁾⁽³⁾. In this method, the movement of atoms and the volume of the calculating cell are controlled by the following equations:

$$\begin{aligned}\dot{r}_i &= p_i / m + \chi(r, p) r_i \\ \dot{p}_i &= f_i - \chi(r, p) p_i - \xi(r, p) p_i \\ \dot{V} &= 3V\chi(r, p)\end{aligned}$$

where r , p , m and f are the coordinate, momentum, mass and force of the moving atom, respectively, and V is the volume of the calculating cell. Dots represent derivatives of time. χ and ξ are Lagrangian multipliers and these functions of r and p are determined from equipartition law and virial theorem.

In this case, the change of shape in the calculating cell is isotropic. Also, the movement of atoms is controlled by using the Lagrangian multiplier to maintain the total kinetic energy in the system at a constant. In all calculations, the pressure and the temperature of the system are set to be 0.0 Pa and 582 K, respectively.

2. Inter-atomic potentials

It is still difficult to describe structural transformation itself at present. Therefore we employed a method described as follows. To model an fcc/bcc transformation, (a) the relaxation of the initial configuration of perfect and defected fcc crystals is done by using a potential (the Finnis-Sinclair (F-S) potential for copper⁽⁴⁾) that stabilizes the fcc structure, and then (b) the crystal is set to be transformed by changing the potential to a bcc stabilizing one (the F-S potential for bcc-iron⁽⁵⁾). The function types of the F-S potential are different between fcc and bcc. The structural transformation described by this combination of potentials is supposed to be a diffusionless type.

3. Verification of the calculating method

In this study the calculations for relaxation are executed 30000 MD steps (3.5 ns) using fcc potential. The stability of kinetic and potential energies, pressure and cell size, and the configuration of the atoms in a system are confirmed to verify the accomplishment of relaxation of the initial configuration. While applying the bcc potential, the energies are lowered gradually. The calculation after applying the bcc potential is carried out up to 120000 MD steps (13.3 ns).

4. Analysis methods

It is not easy to understand the detailed change in crystal structure from the appearance of a crystal alone. In the present study, we intended to render the spatial information of the process more apparent. Therefore Voronoi polyhedra analysis⁽⁶⁾ is utilized to visualize spa-

tial change of transformed region because bcc structure is known to be easily distinguished from fcc structure by using (0608) Voronoi polyhedra. To investigate the spatial changes with time, we identify the atoms, which remain the constituent of (0608) Voronoi polyhedron for an appropriate MD time, as bcc constituent atoms. Using Voronoi polyhedra analysis, the crystal structure is classified on an atomic scale.

The crystallographic orientations of transformed regions are analyzed by the configuration of the atoms that is confirmed as the bcc constituent. This procedure distinguishes three variants of formed bcc crystals by examining which {100} plane of the original fcc crystal is nearly parallel to the (001) plane of the formed bcc crystals.

5. Initial configurations

The initial configuration has fcc structure and the surfaces of the calculating cell are {100} planes. The cubic calculating cell of the perfect crystal contains 2048 ($8 \times 8 \times 8 \times 4$) atoms. Simple lattice defects are introduced to investigate the difference between crystals. Before the relaxation of the fcc structure, one and two half planes parallel to (001)fcc are removed. As a result of the relaxation, neighboring atoms close the vacant half planes and edge dislocations can be introduced geometrically.

III. Results

1. Spatial change with time in a perfect crystal

Firstly, we examined a perfect crystal to understand the general aspects of change in a crystal structure. **Figure 1** shows the spatial change with time in a perfect

Fig. 1 Spatial change with time in a perfect crystal. (a) 5000 MD steps, (b) 10000 MD steps, (c) 15000 MD steps, (d) 20000 MD steps. The gray level of lines distinguishes the variants of formed bcc crystals.

Fig. 2 Changes with time in the number of atoms that belong to bcc crystals of which (001) planes are nearly parallel to (010), (001) and (100) plane of perfect fcc crystal.

crystal. In the early stage of transformation (Fig. 1(a)), small regions start to transform to bcc structure. Some crystals grow larger, and small bcc crystals form and combine to be large clusters in some regions. The distribution of bcc crystals is uniform in the fcc crystal. Bcc clusters that have different orientations align alternately. The shape of the interface of each crystal is not a plane. It is noted that the changes in the crystal structure occur in the system set up by the NTP ensemble and the potential-change procedure employed in the present study.

The crystallographic orientation relationship that is observed experimentally in fcc/bcc crystals is satisfied in the crystals calculated. However it is difficult to determine which relationship (N-W or K-S) is satisfied because the exact direction of the plane is essentially dispersed in the atomistic estimation. It is noticed that the crystallographic orientation of one cluster is the same from the beginning of the transformation. The numbers of atoms that belong to each three variants of crystals are almost equal in a perfect crystal.

Figure 2 shows the changes in the number[†] of bcc constituent atoms with time. This figure demonstrates that the difference in the number of atoms belonging to a crystal that has different orientations is not large, except for the very early stage, as already noticed in Fig. 1. The sharp and periodic fluctuations of the number of bcc constituent atoms can be observed through the calculation in a perfect crystal.

2. Spatial change with time in a crystal containing a dislocation

Secondly, we examined a crystal that contains a dislocation to check its effects on the change in crystal structure. Figure 3 shows the spatial change with time in a crystal containing a dislocation. In this crystal, the fcc structure also transforms to bcc. In the early stages of the transformation (Fig. 3(a)), some regions around the dislocation core, which is represented as the line across the

Fig. 3 Spatial change with time in a crystal containing a dislocation. (a) 5000 MD steps, (b) 10000 MD steps, (c) 15000 MD steps, (d) 20000 MD steps. The gray level of lines distinguishes the variants of formed bcc crystals.

Fig. 4 Changes with time in the number of atoms that belong to bcc crystals of which (001) planes are nearly parallel to (010), (001) and (100) plane of fcc crystal containing a dislocation.

calculating cell in Fig. 3, start to transform to bcc structure. All bcc clusters formed are larger than those formed in a perfect crystal. Even in the later stage of the transformation (Fig. 3(d)), there is an aperture around the dislocation. It is noted that almost all the bcc crystals have the same orientation. Therefore it can be understood that the crystallographic orientations are strictly controlled in a crystal containing a dislocation. The shape of the interface of formed crystals is nearly plane in contrast to the that of the perfect crystal. The crystallographic orientation relationship is also satisfied in this crystal.

Figure 4 shows the changes in the number^{††} of bcc constituent atoms with time. It can be seen that the number of atoms belonging to crystals of only one orientation is high and increase and the other numbers are quite low. In contrast to the results of the perfect crystal, the numbers increase steadily.

[†] Precisely, this is the number of triangles that are constructed by the three bcc-constituent atoms and are used to represent the orientation of the bcc crystal.

^{††} Same as pointed out in Fig. 2.

Fig. 5 Changes with time in the percentage of bcc constituent atoms in a perfect crystal and crystals containing dislocations.

3. Changes in the number of bcc constituent atoms with time in various crystals

Figure 5 shows a comparison of the changes in percentage of the total number of bcc constituent atoms in a perfect crystal with that of crystals containing dislocations. In a perfect crystal, the percentage of bcc constituent atoms in all atoms saturates to be about 40% and does not proceed after 40000 MD steps. On the other hand, in a crystal containing one dislocation, the percentage rises to 64% and saturates at the time of 70000 MD steps. Moreover, in a crystal with two dislocations, the percentage rises to 87%.

IV. Discussion

In the present study, it is clarified that the method that changes inter-atomic potential can describe structural transformation. In the case of results obtained by Parrinello-Rahman's procedure, one original crystal changes to one transformed crystal⁽¹⁾. The present calculations indicate that formed crystals that have different orientations align alternately and uniformly in a perfect crystal and crystals that have the same orientation form around the dislocation. These aspects indicate that this procedure also illustrates the detailed difference that arises from initial conditions.

The number of bcc constituent atoms increases steadily in a crystal containing two dislocations. On the other hand, the percentage of bcc constituent atoms saturates to be about 40% in a perfect crystal (Fig. 5). Considering this difference, it is thought that the formed small bcc crystals in a perfect crystal (Fig. 1) are the appearance of fluctuation and are not nuclei. It suggests that the existence of a dislocation determines whether nucleation occurs or not.

It is fundamentally difficult to compare experimental knowledge with calculated results because of differences in the scale of size and time. However, if we consider the final state obtained by the calculation, we may compare these two kinds of information. The calculated results of this sort are that: (a) formed crystals can grow only around the dislocation, (b) the crystallographic orientation relationship that is observed experimentally in

fcc/bcc crystals is satisfied, and (c) the orientation of formed crystals is restricted around the dislocation. These results coincide with the general aspects of the experimental observations of diffusional transformations. The nucleation sites of diffusionless transformations are not obvious in spite of significant experimental efforts. It is thought generally that a transformation of this type nucleates heterogeneously⁽⁷⁾. The results of the process of bcc crystal formation in crystals containing dislocations (Fig. 3) suggest that the nucleation site of diffusionless transformation is the strain field around the dislocation and is not the dislocation core. This point must be clarified by the introduction of more realistic defects in the calculating crystals.

V. Conclusions

Using the molecular dynamics method, which employs a pressure-temperature-constant condition and potential-change procedure, the spatial changes during the nucleation process of structural transformation in computer-modeled metallic crystals are investigated and the results are as follows:

(1) Structural change occurs in the system modeled by the NTP ensemble and potential-change procedure employed in the present study.

(2) The crystallographic orientation relationship that is observed experimentally in fcc/bcc crystals is satisfied in the crystals calculated.

(3) In a perfect crystal, structural transformation starts uniformly and formed crystals that have different orientations align alternately. However, the change in the number of bcc constituent atoms saturates at about 40% in all atoms and the structural transformation does not proceed. It is thought that this is the state of fluctuation.

(4) In a crystal containing a dislocation, structural transformation starts around the dislocation and it is clearly observed that the crystallographic orientation of formed crystals is restricted. The number of bcc constituent atoms increases steadily in a crystal containing two dislocations. This is the nucleation process.

(5) Whether nucleation of structural transformation occurs or not is clearly distinguished by the initial state of a crystal.

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