Vortex on the Surface of a Very Small Crystal during Martensitic Transformation

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Vortices of trajectories of atoms on the surface of a crystal are found as a transient pattern in the numerical experiment to study martensitic transformation in an ideal crystal which has its surface as a sole lattice defect, but no other internal lattice defect. An empirical instability condition for the appearance of the vortex is interpreted in terms of the dependence of the excitation energy of a vortex on its size. [S0031-9007(99)08438-0]

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Various kinds of pattern formation in systems driven away from equilibrium beyond the critical instability condition have been reviewed by Cross and Hohenberg [1]. The first order phase transformation usually can proceed under any degree of deviation from equilibrium, as far as sufficient time is allowed for. However, the spinodal decomposition and the martensitic transformation (MT) are two special examples of the first order phase transformation, which can be initiated only for a given degree of deviation from equilibrium. In the spinodal decomposition, the critical instability condition for the high temperature phase has been explicitly given by the Cahn-Hilliard theory in terms of the thermodynamical variables [2] and the associated pattern, which has to be transient because the deviation from thermal equilibrium goes down with the progress of the phase transformation, has been quantitatively studied in terms of the time dependent Ginzburg-Landau equation [3]. However, in MT although the equivalent critical instability condition is empirically well defined in terms of the critical temperature, usually called M_s, an explicit expression for the instability condition similar to that of Cahn-Hilliard is not yet given but has been expected to involve both the thermodynamical variable related to thermal lattice vibrations [4] and lattice defects [5]. Since any crystal in the real world inevitably contains different kinds of lattice defects simultaneously, it has been extremely difficult to obtain an explicit expression for the critical instability condition and hence to study quantitatively the transient pattern which is supposed to appear when the critical instability condition is met. In this Letter, we report results of a numerical experiment on the critical instability condition in MT and the transient pattern in ideal small crystals which contain only one kind of lattice defect, i.e., the surface of crystals, but no other internal lattice defects, although many preceding numerical attempts trying to simulate MT in more realistic model crystals than the present one have already been carried out [6].

MT in small crystals with less than 10^4 atoms without internal lattice defects is investigated by use of the standard molecular dynamics (MD) based on the 5th order Gear algorithm [7]. The interatomic potential used in MD is the special version of embedded-atom-method (EAM) potential for Fe due to Johnson and Oh [8]. The numerical value of the integration step has been chosen as 4% of the shortest lattice vibration period with this potential, which is approximately 1.6×10^{-13} sec. The total kinetic energy is scaled to the value corresponding to the set temperature at every ten numerical integration steps. This potential makes the face-centered-cubic structure (fcc) of Fe metastable and the body-centered-cubic structure (bcc) stable, the difference of potential energy between fcc and bcc being 0.03 eV/atom at 0 K. Because this potential does not explicitly include the magnetic contribution to the potential energy, we cannot reproduce the change of the relative stability of fcc against bcc with temperature. As far as we use this EAM potential, we cannot approach the instability condition by lowering temperature of a crystal from high temperature as in the standard experimental procedure to study MT. Instead, we have to approach the critical instability condition for MT by increasing temperature or amplitude of thermal lattice vibration [9].

Since no previous information is available for the critical instability condition for MT in ideal small crystals without internal lattice defects, we must explore its whereabouts before we can study the formation of transient pattern. Metastable fcc crystals with nearly spherical shape surrounded by different kinds of crystal facets with 453, 1055, 2093, 3559, and 5729 atoms are prepared and relaxed so that appropriate surface relaxation takes place. Then the temperature is raised at a constant rate of 4.59 K/ps, while the potential energy of crystals is monitored. The temperature where a sudden drop of the potential energy associated with the change of crystal structure from fcc to bcc occurs is marked as T_{ms}. T_{ms} is different from M_s, which is obtained when temperature is lowered in the real experimental situation where the relative stability between fcc and bcc changes with temperature, while in the EAM potential used here it is locked to the constant

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value. T_{ms} obtained from repeated numerical experiment are plotted against N, the number of atoms in crystals, in Fig. 1. Although the explanation of the dotted line in Fig. 1 will be given later in connection with the associated transient pattern formation, Fig. 1 indicates the existence of the critical instability condition for MT, which is dependent on N in crystals without internal lattice defects. The scatter of T_{ms} comes from randomness in the thermal lattice vibration which is introduced into the initial condition for MD as a random small deviation from perfect equilibrium at 0 K.

From the relationship plotted in Fig. 1, MT in the crystal nearly spherical shape consisting of 453 atoms is expected to take place when the temperature is kept around 200 K. The temperature of this crystal is raised from 2 K at a constant rate until it reaches 200 K and is kept there afterwards. The change of potential energy is plotted as function time in Fig. 2(a). It fluctuates around the value corresponding to fcc lattice until about 56 ps, when it suddenly starts to drop, indicating the onset of MT, until it reaches the value corresponding to bcc lattice. The average configuration of atoms in the crystal is checked by calculating the radial distribution function, as shown in Fig. 2(b), which shows the characteristic of fcc lattice before the onset of MT and that of bcc after the completion of MT.

Tadpolelike marks are used to study what kind of trajectories of atoms lead to the onset of MT. The head of each tadpole represents the position of an atom at the end of a short period, which corresponds to 800 integration steps (about 5.12 ps), and the end of its tail represents the position of the same atom at the beginning of the same period. Here, the position of an atom is defined as the average of the 77 integration steps, in order to filter out a random high frequency component of the thermal vibration. The displacement of an atom in the crystal is represented by a tadpole swimming headway. In this way, trajectories of atoms on the surface of the crystal viewed from the [111] direction are shown in the left column of Fig. 3 and those on the (111) cross section through the center of the crystal are shown in the right column of Fig. 3. For the period between 48.6 and 53.8 ps which precedes the time of onset of MT, trajectories of a few atoms on the lower part of the surface are beginning to show a vortex but atoms on the cross section do not show any appreciable displacement comparable to lattice spacing. Between 53.8 and 58.9 ps, the trajectories of atoms on the surface starts to show more than one vortex centered around different ⟨111⟩ facets, which contact each other at their peripheries. At this period, atoms on the cross section start to show appreciable displacement in comparison with lattice spacing. It is to be noticed that this period between 53.8 and 58.9 ps coincides with the time when the sudden drop of the potential energy is noticed. This time is understood to mark the onset of MT in this crystal. Between 58.9 and 64.0 ps, the contact between vortices centered on different facets takes place, and atoms on a different part of the same (111) cross section, which has not shown any appreciable displacement previously, now start to show displacement coinciding with the further drop of the potential energy.

The process of MT described above is one particular example of many runs including the crystal with a different total number of atoms and with different shapes but always without internal lattice defects. In all these cases, the onset of MT is always preceded by the appearance of a combination of contacting vortices on the surface of a crystal. However, the number of vortices, which appear on the surface of crystals, does not depend on the size of the crystal. In crystals with nearly spherical shapes, the size of critical vortices remains approximately equal to the radius of crystals. This is related to the property of these vortices that their centers must be around the boundaries between ⟨111⟩ and other facets on the surface. Since the distance between these facet boundaries increases proportionally to the radius of crystals, the size of critical vortices increases proportionally to the size of crystals, while the number of vortices remains constant independent of their size.

The question is how this transient vortex of trajectories of atoms is related to the onset of MT. If an isolated

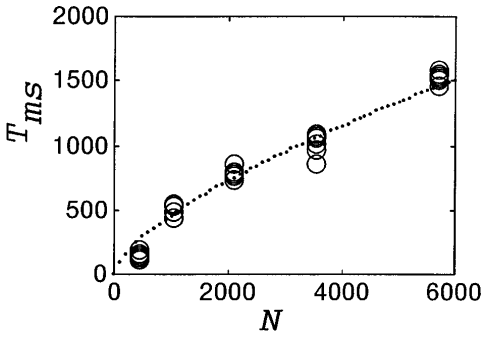

FIG. 1. T_{ms} indicates the temperature (in K) where the instability sets in while the temperature of the crystals with N atoms is being raised at rate of 4.52 K/ps. The dotted line indicates the thermal energy T_{ms} (in K), which is necessary to excite vortices with size approximately equal to the diameter of the crystals.

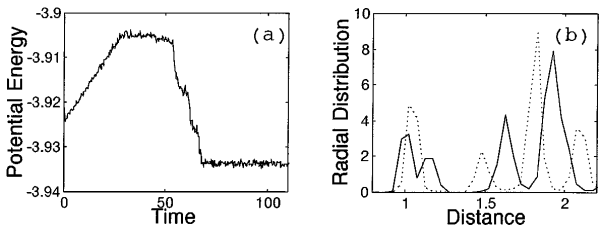

FIG. 2. (a) Change of potential energy (eV/atom) of the crystal vs time (ps). (b) Radial distribution vs distance. The dotted line is that observed at 46 ps, indicating fcc. The full line is observed at 69 ps, indicating bcc.

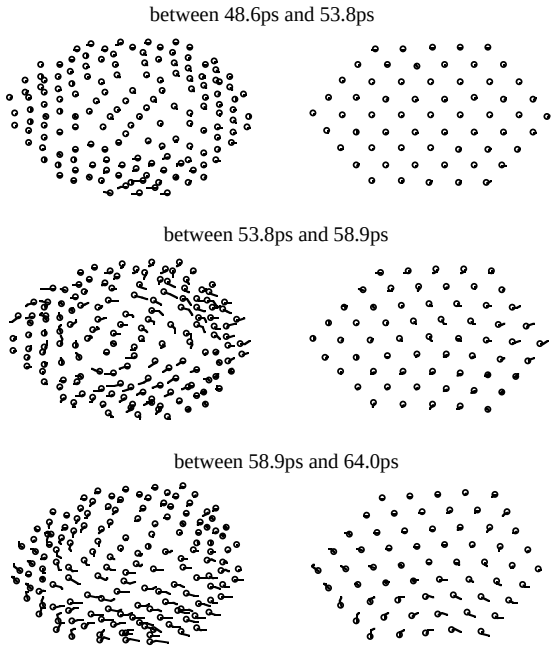

FIG. 3. Trajectories of atoms on the surface of the crystal on the surface viewed from the [111] direction are shown in the left column and those on the (111) cross section in the right column using tadpolelike marks.

vortex were to penetrate into the inside of a crystal, it would introduce rotation dislocations (disclinations) into the crystal [10], which would incur a huge increase of the potential energy of the crystal. However, if the vortices appear in a quartet, they induce the displacement of atoms around the center of a quartet as schematically shown in Fig. 4. The vector sum from the displacement from the rotation from the four vortices is zero for the atoms in the center, but that for the atoms in the vertical column is towards the center and that for the atoms in the horizontal line is away from the center. This is exactly the displacement necessary to induce the Bain deformation, elongation in the one direction and contraction in the other direction of an fcc lattice, opening the way towards bcc lattice. Because the EAM potential energy for Fe being used here is such that makes the initial fcc crystal metastable and the final bcc crystal stable, it is expected that, once a small nucleus of bcc crystal is created by the Bain deformation on the surface, its penetration into the inside of the crystal will keep on lowering the potential energy of the crystal signaling the onset of MT. While the presence of a quartet of vortices is more than sufficient for the onset of MT, the presence of a doublet of vortices must be at least necessary, because an isolated vortex will induce a disclination into the inside of the crystal and also because of the conservation of rotation on the surface.

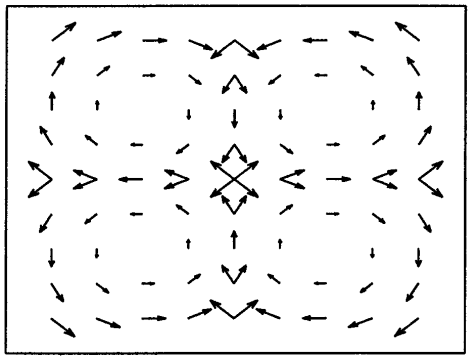

FIG. 4. The Bain deformation is induced in the center when a quartet of vortexlike displacement is introduced into the neighboring parts of a crystal.

In order to produce the Bain deformation on the surface of the crystal from contacting vortices, the vector summation of displacement must be assumed to take place only between the peripheries of the vortices. This means that the interior region of the surface atoms covered by a vortex is rotating as a rigid disk. Accordingly, the energy necessary to excite a vortex that serves to introduce the Bain deformation on the crystal surface can be estimated using elementary mechanics of a rigid body. The energy necessary to excite rigid body rotation of a thin circular disk of radius R and thickness h and density ρ with angular velocity ω is $\pi\rho hR^4\omega^2/4$. On the other hand, the amount of angular displacement at periphery of the disk is prescribed by the amount of displacement b for the Bain deformation, which is independent of the size of the disk. Accordingly, the necessary angular velocity ω for the disk to obtain this displacement b at its periphery during the period Δt is given by $b/R\Delta t$. Hence, the energy necessary to induce Bain deformation at peripheries of four vortices is estimated to be of the order of $\pi\rho hR^2b^2/\Delta t^2$. Since the size of vortex R, which is proportional to $N^{1/3}$ in crystals with nearly spherical shape, is approximately equal to the radius of crystals, the order of the magnitude of thermal energy necessary to excite vortices on the surface of the crystal is estimated as $6.24 \times 10^{-23}N^{2/3}$ J or $4.55N^{2/3}$ K. This is the dotted line in Fig. 1. Thus, the critical thermal energy T_{ms} is understood to represent the thermal energy necessary to excite the vortices of the critical size on the surface of nearly spherical crystal with N atoms. This indicates that the critical stability against MT of a crystal increases with its size if it does not contain internal lattice defects. This is considered to be in good accord with the results of a recent experiment on the increased stability of crystals against MT in the nm range [11], because dislocations, which are known to the most potent lattice defect for MT [5], are expected to be pushed out of the crystal due to their line tension in crystals with diameter in the nm range.

The study of the two dimensional sine-Gordon equation [12] suggests that vortices are possible for the flat surface of a crystal with arbitrary symmetry. However, the vortices observed in the present numerical experiment are not on a flat surface but are always located around the

boundaries between the different facets. This indicates a substantial decrease of their excitation energy when they are located around facet boundaries, which are considered as *defects on a defect (surface)*.

The presence of an excited transient state prior to the onset of MT has been proposed on the basis of the analysis of a systematic experiment on MT in various kinds of metals by Kakeshita and co-workers [13]. What is described above is understood to provide one concrete atomistic picture of the excited state which can exist on the surface of a small crystal without any internal lattice defects. How lattice defects other than surface are involved in setting up the critical instability condition and the associated transient pattern remains to be investigated. On the other hand, the recent advances in the experimental study of crystal surface by x-ray specular reflectivity [14] will prompt us to study further one specific case of MT in the situation where only the surface is present as a lattice defect, in order to establish quantitatively the critical instability condition for MT similar to that for spinodal decomposition.

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[9] This procedure can also be interpreted in terms of the transformation-temperature-time (TTT) curve frequently used in the metallurgical science as follows. We are studying MT in the lower part of the TTT curve instead of the upper part of TTT curve where MT is usually observed. In the former the thermal activation process is the sole factor in determining the instability of the low temperature phase. In the latter, although the thermal activation process is a fundamental process, the strong temperature dependence of the difference of cohesive energy between fcc and bcc structures induces the opposite dependence of the instability condition on temperature to that observed in the former.

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