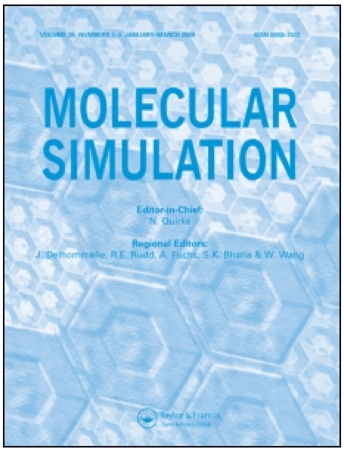

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Molecular Dynamics Simulation of the Model Grain Boundary Structure of Polycrystalline Materials

Hiroshi Ogawa[a]; Fumihiro Wakai[a]; Yoshio Waseda[b]
[a] National Industrial Research Institute of Nagoya, AIST, Nagoya, Japan [b] Institute for Advanced Materials Processing, Tohoku University, Sendai, Japan

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MOLECULAR DYNAMICS SIMULATION OF THE MODEL GRAIN BOUNDARY STRUCTURE OF POLYCRYSTALLINE MATERIALS

HIROSHI OGAWA[1], FUMIHIRO WAKAI[1]
and YOSHIO WASEDA[2]

[1]*National Industrial Research Institute of Nagoya, AIST,*
1-1, Hirate-cho, Kita-ku, Nagoya, 462 Japan
[2]*Institute for Advanced Materials Processing, Tohoku University,*
2-1-1, Katahira, Aoba-ku, Sendai, 980-77 Japan

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Molecular dynamics simulation of polycrystalline material has been carried out to investigate the atomic structure of grain boundary. We developed a simple method for expressing and analyzing the polycrystalline structure involving various grain sizes by introducing weighted Voronoi polyhedra. The three dimensional simulation exemplified by zirconia nanocrystals showed that the model structure is stable at elevated temperatures up to near the melting point. The feasibility of the present method was tested by analyzing the structure properties of polycrystalline, based on the mathematical expressions describing the grain boundary and inside grain regions.

Keywords: Polycrystalline; molecular dynamics; zirconia; grain boundary; Voronoi polyhedron

1. INTRODUCTION

Materials consisting of very small crystal grains are known to show some particular behaviors. A typical example is the superplastic deformation of metals which elongates up to several hundred percents without fracture under the tensile stress [1]. Ten years ago, one of the present authors (F. W.) found similar superplastic deformation behavior also takes place in ceramic materials at high temperature [2]. Such large deformation of bulk materials has been considered to be controlled by the slip of grains at the boundary in the rearrangement of the grain configuration. However, the mechanism of superplasticity seems to be more complicated [3] and further information is required with respect to atomic transports both inside and outside the grains. Molecular dynamics (MD) simulation appears to be useful for this purpose by making available information of microscopic transports. Such data is quite difficult to obtain from the experiments especially at high temperature.

Compared with the single crystal or amorphous case, simulation of polycrystalline includes difficulty mainly arising from its large system size. It is difficult to generate a realistic, three-dimensional structure of polycrystalline material since the time consuming is severe for a large system. Besides the works on primitive models on grain boundary structures such as the one-dimensional stacking of crystal layers [4] or two-dimensional polycrystals [5], fully three-dimensional simulation of polycrystalline has been carried out only very recently [6–8] in parallel with significant technical progresses in computer.

Phillpot *et al.* [6, 7] simulated the Lennard-Jones nanocrystals which is grown from 8 crystal seeds in the liquid phase of 55296 atoms. They carried out the MD simulation of more than 66 ps for generating the polycrystalline structure, and analyzed it as the simple stacking of box-shaped grains. Zhu and Averback [8] simulated the sintering process of fcc-copper polycrystals. They started the simulation with the initial system involving a few small crystals and vacant regions, and generated the sintered structure by compressing the system at 300 K for 20 ps. Although the required computational time for generating the polycrystalline structure must be large in these studies, the resultant structures are rather simple and appear to differ from actual polycrystalline cases of complex distribution of grains with various sizes. However, within the best knowledge of the present authors, method to generate and analyze the three-dimensional grain boundary is still far from complete. Hence, a new method for investigating the polycrystalline structure is strongly required.

The main purpose of this paper is to describe a simple method for expressing and analyzing the model grain boundary structure of polycrystalline materials by introducing the weighted Voronoi polyhedra. This includes the simple mathematical expressions and high applicability to complex configurations of grains with various sizes. The usefulness of the method on generating and analyzing polycrystalline structures will be demonstrated by applying to the zirconia nanocrystals case, as an example.

2. MODEL STRUCTURE OF POLYCRYSTALLINE MATERIALS

Let us consider N grain centers $\mathbf{P}_i (1 < i < N)$ in three dimensional space $\mathbf{R}$. The Voronoi polyhedron V_i around $\mathbf{P}_i$ is given by the set of points in $\mathbf{R}$ closer to $\mathbf{P}_i$ than other centers as, [9]

$$V_i = \{\mathbf{r} \in \mathbf{R} \mid d(\mathbf{r}, \mathbf{P}_i) < d(\mathbf{r}, \mathbf{P}_j), \quad j \neq i\}, \tag{1}$$

where $d(\mathbf{r}, \mathbf{P}_i)$ denotes a *distance* between $\mathbf{r}$ and $\mathbf{P}_i$. Definition of d is not unique, and when we use the following definition the resultant V_i is called weighted Voronoi polyhedron [10]:

$$d(\mathbf{r}, \mathbf{P}_i) = |\mathbf{r} - \mathbf{P}_i|^2 - w_i^2, \tag{2}$$

where w_i represents a *radius* of center $\mathbf{P}_i$. The face of V_i which is shared with the neighboring polyhedron V_j is planner and perpendicular to the line $\mathbf{P}_i\mathbf{P}_j$ as is in the case of ordinary Voronoi polyhedra. The boundary plane, however, does not cross the mid-point of $\mathbf{P}_i\mathbf{P}_j$ and shifts toward the grain of which radius is smaller. The schematic diagram of these situations is shown in Figure 1.

The geometries of weighted Voronoi polyhedra appear to describe the cofigurations of actual grains in polycrystalline materials. If the grain grows

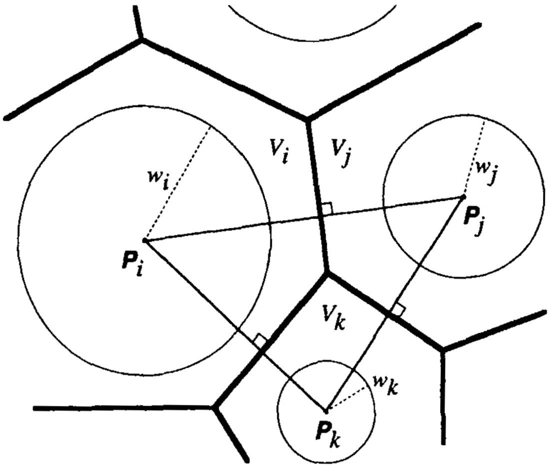

FIGURE 1 Two-dimensional schematic diagram of the weighted Voronoi polyhedra defined by $\mathbf{P}_i$ and w_i.

homogeneously from each nucleation center, the resultant grain shape could be expressed by a polyhedron-like one of which faces are almost perpendicular to the lines between neighboring nucleation centers. The faces are not always located at the mid points to the centers due to the difference in the staring times of grain growths. Such similarities can be explicitly given without particular adjustments by using only $4N$ geometrical parameter, $\mathbf{P}_i$ and w_i.

After defining the geometry of grain boundary, we must set the orientation of crystal axes in each grain region. The Euler angle, $\mathbf{E}_i = (\phi_i, \theta_i, \psi_i)$, can be used to denote such orientation, hence another $3N$ values are necessary. The values can be chosen continuously if we permit the mismatch of atomic configuration at the boundary which is corresponds to the ordinary polycrystalline case. Further $3N$ parameters are also needed to denote the translational shift $\mathbf{t}_i$ between the grain center and the origin of crystal unit cell. Through these procedures, the three dimensional space can be divided into N grains and uniquely filled by atoms by using $10N$ parameters, $\mathbf{P}_i$, w_i, $\mathbf{E}_i$ and $\mathbf{t}_i$.

In MD simulation of bulk materials, it is ordinary to use the periodic boundary conditions to the MD basic cell, hence $\mathbf{P}_j$ in eq. (1) denotes not only the one in the basic cell but also those in replica cells. In order to prohibit the boundary between the *same* grain, more than eight grains should be given in the simulation cell. The grain size must be selected carefully because the actual size of grain in real materials is often too large to handle by MD simulation. Too small grain sizes, on the other hand, are also unrealistic since the number of atoms on the grain surface is getting larger. If we permit the situation that the ratio of atoms existing on the grain surface to whole atoms is less than 30%, one grain consists of at least about 8000 ($= 20^3$) atoms, hence more than approximately 60000 atoms are required.

The number of atoms can be reduced by introducing the infinitely long grain which is made by neglecting the boundary between V_i and those in replica cells toward a particular, say z, axis. In this case, the total number of atoms is reduced in proportional to the side length L_z of the simulation box. However, this process involves certain constraint on L_z and Euler angles θ_i and ψ_i so as to maintain the continuity of atomic arrangement at the grain boundary.

3. MOLECULAR DYNAMICS SIMULATION

The model employed in this work does not depend on composition or crystal symmetry. We selected cubic zirconia (ZrO_2) without hesitation since yttria-stabilized zirconia is the first ceramic material of which superplasticity was found [2]. The Coulombic potentials of Born-Mayer type proposed by Dveldi and Cormack [11, 12] were used. This potential model was constructed based on the energy surfaces of cubic, tetragonal, and monoclinic structures of zirconia. The original form of the potential includes the rigid ion part and the shell term. Due to the limited computer resources, we ignored the shell term in the present simulation because our main purpose is to test the usefulness of the new model structure. Reliability of the MD simulation adopting such simplified potential model was already discussed by Li and Hafskjold [13].

The model structure of polycrstalline zirconia was generated by the procedure mentioned above. About 13000 atoms were arranged in the simulation box whose size is approximately 7.6 nm × 7.6 nm × 2.5 nm by using the geometrical parameters given in Table I. We assumed four infinitely long grains of which diameters appeared on the xy plane are approximately 3 and 5 nm. The ratio of atoms on the grain surface is approximately 25% in this model. The initial structure of polycrystals includes several unrealistic atomic arrangements: for example very close atomic pairs at the grain boundary. The potential energy released by close atomic pairs are quite likely to alter the structure at the beginning of MD simulation. Hence we must eliminate such unrealistic structure in order to start the MD simulation safely. A part of inconveniences is reduced by selecting more preferable values for $\mathbf{t}_i$ in try-and-error manner. However, the most straightforward way is to pick up the close neighboring atoms within a certain cut-off radius. In this work, we marked the atoms located in a distance shorter

TABLE I Values of the geometrical parameters used in this study. The values of $\mathbf{P}_i$ and t_i are normalized by the side lengths of the simulation box and the crystal unit cell, respectively

i	*1*	*2*	*3*	*4*
P_i^x	0.75	0.25	0.25	0.75
P_i^y	0.25	0.75	0.25	0.75
P_i^z	0	←	←	←
w_i/nm	2.2	2.2	1.4	1.4
φ_i	$3\pi/4$	$\pi/4$	0	$-\pi/2$
$\sin\theta_i$	$\sqrt{1/3}$	←	←	←
ψ_i	$\pi/4$	←	←	←
t_i^a	0.1	←	←	←
t_i^b	0.1	←	←	←
t_i^c	0.1	←	←	←

than 0.2 nm. This method is very simple and convenient, but a demerit that the number of atoms cannot be adjusted to a desired value should be stressed. This is particularly important in the case of two- or multi-component system so as to keep the stoichiometry. The resultant number of atoms in the model structure is 12528 (8352 oxygen and 4176 zirconium atoms).

In the MD simulation, the equation of motion was integrated by using the Verlet algorithm [14] with the time step of 2 fs. The force calculation was optimized by the neighbor-list and the Ewald sum methods [14]. Temperature of the system was controlled by Nosé's thermostat [15], and the heating and cooling rates of ±25 K/ps were used to proceed to different temperatures. The diagonal part of the pressure tensor were adjusted to 0.1 MPa by using the Andersen's method [16] for each direction. Other details of the calculation are almost identical to our previous simulation studies [17, 18].

4. SELECTED RESULTS ON THE POLYCRYSTALLINE STRUCTURE

Global Structure

In order to obtain the thermally relaxed polycrystalline structure, the computational 'sample' was heated up from 300 K to 2500 K at 0.1 MPa and held for 80 ps. During this process, the simulation cell expanded by 102.3%, 102.9% and 100.9% toward x, y and z directions, respectively. Such anisotropic expansion is considered to be caused by the difference in atomic configurations at grain boundaries. The size of the grain, on the other hand, changed during the heating process. After eliminating the thermal expansion effect, the radii of larger ($i = 1$, 2) and smaller ($i = 3$, 4) grains were found to increase and decrease by about 0.2 nm, respectively. The simulated density of the polycrystalline is 5.48 Mg/m^3 at 2500 K which is fairly consistent with the measured density value of cubic zirconia [19].

The stability of the model structure was examined by changing the temperature to be 2500 K, 3000 K, and 3500 K. In the case of polycrystalline structure, the stability at high temperature is not trivial because the disorder at the grain boundary possibly causes thermal instability. Ths snapshots of the simulated sample after keeping the system for 80 ps at 2500 K and 3000 K are shown in Figure 2. The simulated structure at 2500 K keeps the image of polycrystals. In the snapshot is also shown the boundaries of weighted Voronoi polyhedra with modified values of radii which represents

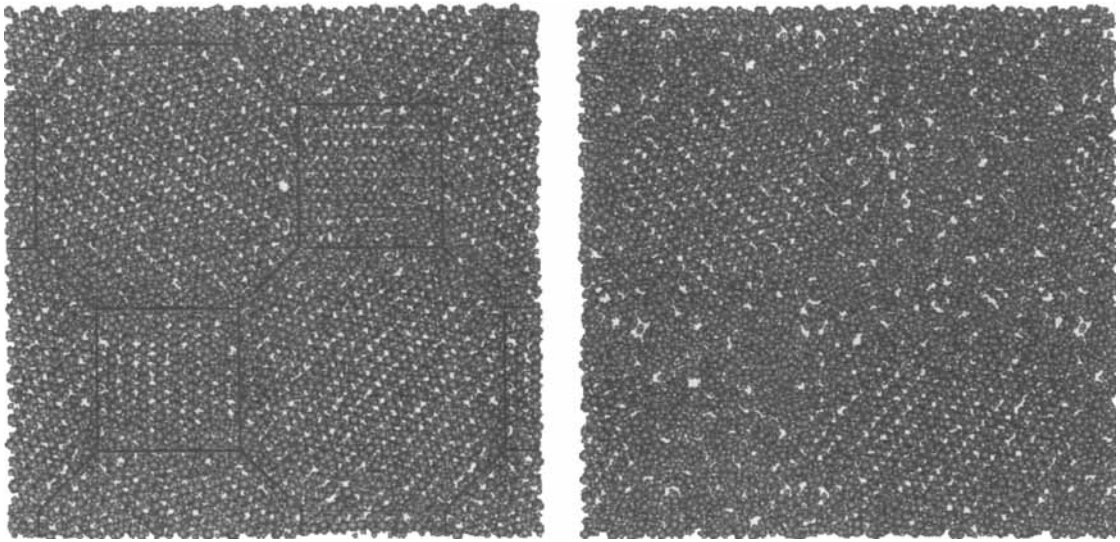

FIGURE 2 Snapshots of the simulated structures at 2500 K (left) and 3000 K (right) after the relaxation period of 80 ps. Oxygen and zirconium atoms are displayed by blue and orange spheres, respectively. Grains in each snapshot distribute in turns of $i = 2, 4$ (upper) and $i = 3, 1$ (lower) from left to right, respectively, and are surrounded by their replicas. Size of the displayed region is about 10 nm × 10 nm. The boundaries of weighted Voronoi polyhedra at 2500 K are shown by the green lines. See Color Plate II.

the grain boundary position in the simulated sample by the accuracy of about 0.1 nm. At 3000 K, which is just above the melting point of zirconia ($\approx$2960 K [20]), the thickness of the boundary layer increases and the smaller grains ($i = 3, 4$) seem to be melted. A liquid like structure without any crystal region was obtained at 3500 K. Although the precise value of the melting point of the simulated sample cannot be estimated by the present results alone, we may safely say that the polycrystalline structure is undoubtedly well-recognized for simulation even at temperatures near the melting point.

Grain Boundary Layer

Atomic configuration at the grain boundary is the most informative parts of the present simulation. Coordinates related to the grain boundary are simply expressed when we use the weighted Voronoi polyhedra for the model structure. For an atom at **r**, the distance u_{ij} from the boundary between V_i and V_j is calculated by,

$$u_{ij}(\mathbf{r}) = \{d(\mathbf{r},\mathbf{P}_j) - d(\mathbf{r},\mathbf{P}_i)\}/2\,|\mathbf{P}_i - \mathbf{P}_j|, \tag{3}$$

where the positive value of u_{ij} is defined toward V_i. Using this relation, inside region of the grain is divided into the sliced layers $B_i(s,s')$ as,

$$B_i(s,s') = \{\mathbf{r}\in\mathbf{R}\,|\,s < u_{ij}(\mathbf{r}) < s', \quad j \neq i\}. \tag{4}$$

Schematic diagram of various regions expressed by this formula is given in Figure 3.

As for examples of the structure analysis, the number density of each element, the O/Zr ratio, and the coordination number of each atomic pair were investigated as functions of the distance from the boundary. They were counted and averaged in each sliced region $B_i(s - \Delta s/2, s + \Delta s/2)$ for all grains. The cut-off distances for counting the coordination numbers of O – O, Zr – O and Zr – Zr pairs were assumed to be 0.3, 0.32 and 0.43 nm, respectively, and the value of Δs was chosen to be 0.01 nm.

The results are shown in Figure 4. The structural inhomogeneity at small s (boundary) region is clearly seen in the figure as deviations from the property in lager s (crystal) region. The number densities of both element decrease by about 10% at the region of $s < 0.5$ nm. The oscillatory feature of crystals seems to still remain in the boundary region although the amplitude of oscillation is small compared with the crystal region. The O/Zr ratio

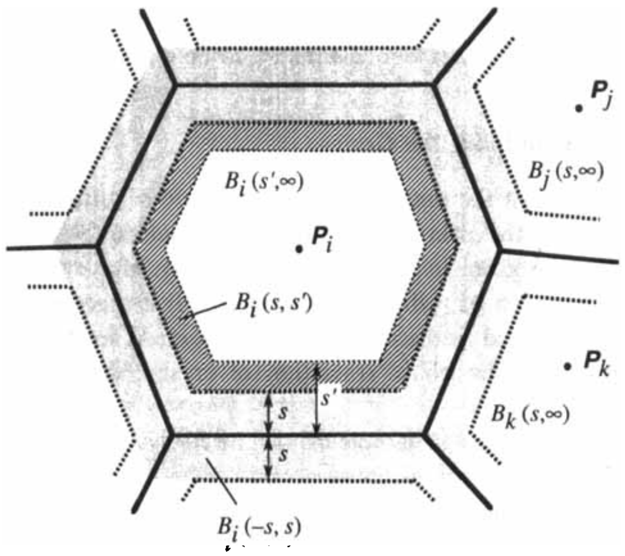

FIGURE 3 Schematic diagram of the sliced layer $B_i(s,s')$ and its variations.

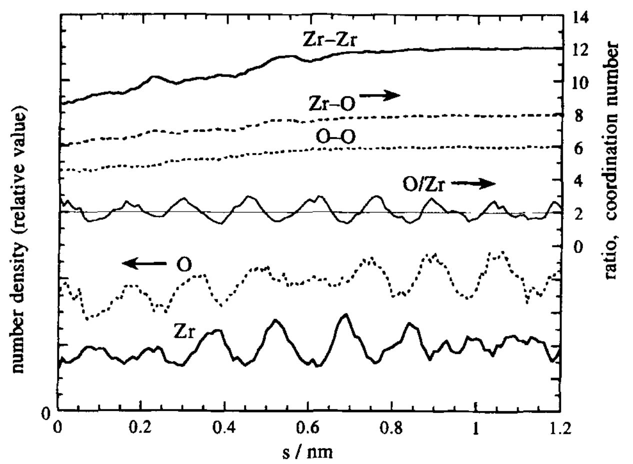

FIGURE 4 Plots of the number density of each element, the O/Zr ratio, and the coordination number of each atomic pairs as functions of the distance from the boundary.

also shows a similar behavior. The deviations of coordination numbers are recognized in slightly wider region, $s < 0.7$ nm. By considering these results, the total thickness of the disordered layer at the boundary is estimated to be roughly 1 nm. This result is comparable with those of TEM observations on yttria-stabilized zirconia [21] or other ceramic material [22] of which boundary layer thicknesses were estimated to be a few nm.

Structure Variation Inside the Grains

Detailed analysis on the time dependent structure of grains has frequently been excluded in the past because the mathematical definition of grain regions cannot be given in a straightforward way. However, our patience for such analysis can be reduced by using eq. (4) if the weighted Voronoi polyhedron is adopted as the model configuration. As for the examples, the grain rotation and the phase transition of crystal structure were investigated.

Each grain in the present sample can rotate freely around z axis since the periodic boundary conditions cause no limitation on φ_i. In fact, small tiltings of grains from the original orientations (which are multiples of $\pi/4$) are recongnized in Figure 2. Orientation of each grain was evaluated by using the atomic coordinations in the region defined by B_i (0.5 nm,∞). In Figure 5 are shown the time variation of rotation angles for all grains at 2500 K. Grains were found to rotate within the range of about ± 1°. The variation of the rotation angle seems to be small for larger grains ($i = 1$, 2) compared with smaller ones probably due to their large moments of inertia. Correlation of the time variation of rotation angle between different grains is not clearly recongnized in the figure. In fact, the maximum value of the cross correlation factor was calculated to be 0.39 between $i = 2$ and 3 which is considered to be statistically insignificant.

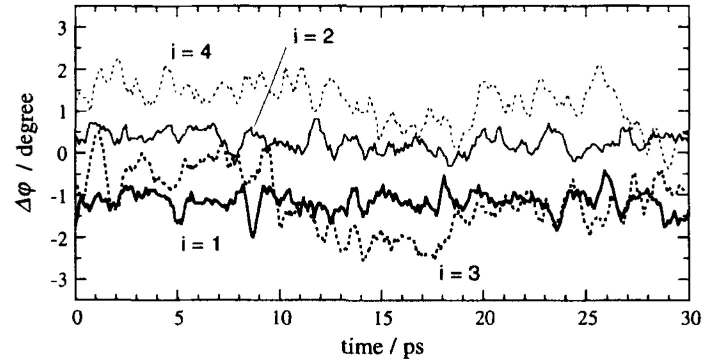

FIGURE 5 Time variations of rotation angles of grains during 30 ps at 2500 K. Deviations from the initial values given in Table I are plotted.

The inside grain region, B_i (s, ∞), is also conveniently used for picking up and displaying the atomic configuration of crystal. Since the cubic structure of pure zirconia is stable only at high temperature, the low temperature phase must be realized by cooling the computational sample. In the case of the present sample, all grains transformed to the tetragonal phase during the cooling process from 2500 K to 1000 K. The atomic configurations before and after the phase transition are shown in Figure 6 by picking up the inside grain region of B_2 (0.5 nm, ∞). After the phase transition, the crystal elongated toward c axis and the oxygen atom distribute on two sites. By averaging the atomic coordinations in this region, the positional parameter of oxygen, z_0, was evaluated to be about 0.17 which is fairly close to the experimental value, 0.185 [23].

5. DISCUSSIONS AND CONCLUSION

The model polycrystalline structure generated by using weighted Voronoi polyhedra is found to induce several merits in the simulation as shown in above. The most significant feature of the present method is the simplicity of mathematical description for defining the model structure of polycrystalline material by using only $4N$ values, $\mathbf{P}_i$ and w_i. It may be stressed that this number of parameters is the least for describing the grain positions and sizes. By changing the parameter values, we can generate a wide variety of

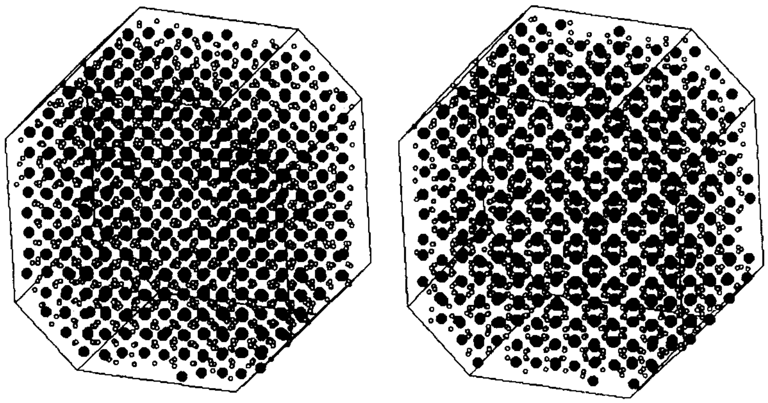

FIGURE 6 Variation of the crystal structure before (left, 2000 K) and after (right, 1500 K) the phase transition. Only the atoms in the region B_2 (0.5 nm, ∞) are displayed. Oxygen and zirconium atoms are denoted by open and filled circles, respectively.

model structures including fully three-dimensional distribution of grains with various sizes. Such a point is very convenient compared with other possible definition of grain boundary geometry, for example the simple stacking of the space-filling polyhedra such as the truncated octahedra [24]. Not only the random boundaries exemplified in this study, coincident boundaries can also be generated by properly selecting the additional 6N parameter values, $\mathbf{E}_i$ and $\mathbf{t}_i$.

The second feature of the present method is the similarity between the Voronoi cell and grain configurations in actual materials. The faces of weighted Voronoi cells are perpendicular to the lines between neighboring cell centers, and their distances from the centers are roughly proportional to the cell radii w_i. These conditions are reserved in the actual polycrystalline structure if it is constructed by the homogeneous grain growth. In this sense, the present model enables us to provide a good candidate for an initial configuration of the simulation. Although the usefulness and reliability of the structure should be confirmed by an actual MD simulation at finite temperature with a sufficient relaxation period. The model structure must be rejected if the structure relaxed to a different configuration. Even in that case, however, an improved model structure can be defined by adjusting the geometrical parameters to the relaxed configuration.

The present model has another important merit to make the structure analysis easier. By using eqs. (1) and (2), we can easily find which grain does a certain atom belongs to at any time in the simulation. The structure properties are also evaluated as a function of the distance from the boundary by using eqs. (3) and (4). Such simplicity in the structure analysis was hardly obtained by another description of the grain boundary especially for three-dimensional system. It may also be suggested that the special boundary regions shared by three or four grains, which are often called as the triple junction or the glass pocket, can be expressed by using eq. (4) as $B_i(-s, s) \bigcap B_j(-s, s) \bigcap B_k(-s, s)$, etc.

In conclusion, the present authors stress that the model structure generated by using the weighted Voronoi polyhedra appears to be very effective and convenient for the MD simulation of polycrystalline materials. A complex structure of grain boundaries can easily be generated and analyzed. The potential capability of this new method may not be overemphasized. Thus, it would be interesting to extend the present method to other ceramic systems, and the usefulness and validity will be tested in a wider base.

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