

Molecular dynamics simulation on the grain boundary structure of polycrystalline zirconia

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Molecular dynamics simulation of polycrystalline material has been carried out to investigate the atomic structures of grain and grain boundary. The model structure exemplified by zirconia nanocrystals was found to be stable at elevated temperatures by three-dimensional simulation. The phase transition phenomena including tetragonal to cubic and melting were reproduced. The feasibility of the present method was also tested by analyzing the structure variation at the grain boundary and self-diffusivity of ions.

1. INTRODUCTION

Superplastic deformation is one of the particular behaviors found in polycrystalline metallic materials composed by very fine grains [1]. Ten years ago, one of the present authors (F. W.) found similar superplastic deformation also takes place in ceramic materials at high temperature [2]. Large deformation of bulk materials observed in these phenomena has been considered to be controlled by complex dynamical behaviors of grain boundary structure [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 which is quite difficult to obtain from experiments especially at high temperature.

Compared with the single crystal or amorphous case, simulation of polycrystalline frequently includes difficulty mainly arising from the computer ability. Since the time consuming is severe for a large system, simplified model structures, for example one-dimensional stacking of crystal layers or two-dimensional polycrystallines, have been used [4,5]. Fully three-dimensional simulation of polycrystallines has been carried out only very recently [6,7] in parallel with significant technical

progresses in computer. Phillpot et al. [6] simulated the Lennard-Jones nanocrystalline which is grown from 8 crystal seeds in the simulation box filled with the liquid phase of about 55,000 atoms. Zhu and Averback [7] simulated the sintering process of fcc-copper by compressing the simulation box including crystalline and vacant regions, by using about 9,000 atoms. Ogawa et al. [8] simulated the polycrystalline, cubic zirconia composed of grains of which radii are not uniform by using newly proposed model structure. In this work, the authors extended the previous work [8] to tetragonal zirconia, and tried to obtain information on dynamical aspects including self-diffusion of atoms.

2. MOLECULAR DYNAMICS SIMULATION

The model structure used in this work was composed by four, infinitely long grains. The size of the simulation box is approximately $7.6 \times 8.0 \times 2.5$ nm, and the periodic boundary conditions were applied to the system toward x , y and z directions. The grain regions are filled by atoms by changing the axis orientation which satisfy the periodicity and continuity toward z direction. Atomic arrangement of tetragonal zirconia was assumed for the crystal structure

since yttria-stabilized zirconia is the first ceramic material of which superplasticity was found [2]. Minor elements such as yttria were omitted in this work for simplicity. The total number of atoms is about 12,000.

The interatomic potentials of Dveldi and Cormack [9] were adopted which was constructed based on the energy surfaces of monoclinic, tetragonal and cubic structures. The force calculation was carried out based on the rigid-ion part of the potential only, and the shell term was neglected by the reason of computer resources. Temperature of the system was controlled by Nosé's thermostat [10]. The diagonal part of the pressure tensor were adjusted to 0.1 MPa by using the Andersen's method [11] for each direction. Other details of the calculation are almost identical to our previous simulation studies [8,12].

3. RESULTS

3.1. Phase transitions

In order to investigate the temperature variation of polycrystalline structure, the computational sample was heated up from 300K

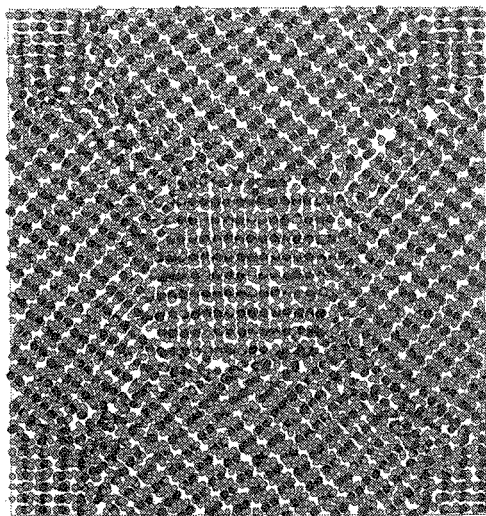


Fig.1 Snapshot of the simulated sample at 1500K as the projection to x - y plane. (Gray = O, black = Zr.)

to 3000K with the rate of 20 K/ps. In Fig. 1 is shown the snapshot of simulated structure at 1500K. The grain boundary of the simulated sample seems to be stably held at this temperature. At 3000K, which is just above the melting point of zirconia (≈ 2960 K), the thickness of the boundary layer increases and the two smaller grains are almost melting.

In course of heating the sample from 1500K to 3000K, all grains transform to high-temperature phase, cubic zirconia. The phase transitions of crystals started at one of the smaller grains at about 2000K and completed for all grains at about 2300K. These values are lower than, but not so far from the experimental value, ≈ 2650 K. Although the precise value of the transition temperature cannot be estimated in the present simulation due to the finite heating rate, it may be considered that the present simulation reproduces the fundamental characteristics of the temperature variation of atomic arrangement in the grains.

3.2. Grain boundary layer

Glassy layers at grain boundary of nm order in polycrystalline zirconia were firstly pointed out by TEM observation by Rühle et al. [13]. In the present simulation, layers with disordered atomic arrangements are also found at the grain boundary as shown in Fig. 1. In order to obtain further information on such layers, the number density of each element were evaluated as a function of the distance from the boundary. All boundaries were taken into account and averaged for 60 ps. The results at 1500K are shown in Fig. 2. The disorders at the grain boundaries are clearly seen in the figure as the deviation from the property in crystal region. The number densities of both element decrease by about 10% near the boundary. The oscillatory feature of crystals seems to still remain near the boundary although the amplitude of oscillation are small compared with those in crystal region. The thickness of the boundary layer is estimated to be roughly 1 nm which is comparable with the TEM observation [13]. Although we should mind that the boundary layers in the real material are formed by impurities such as silicates [13],

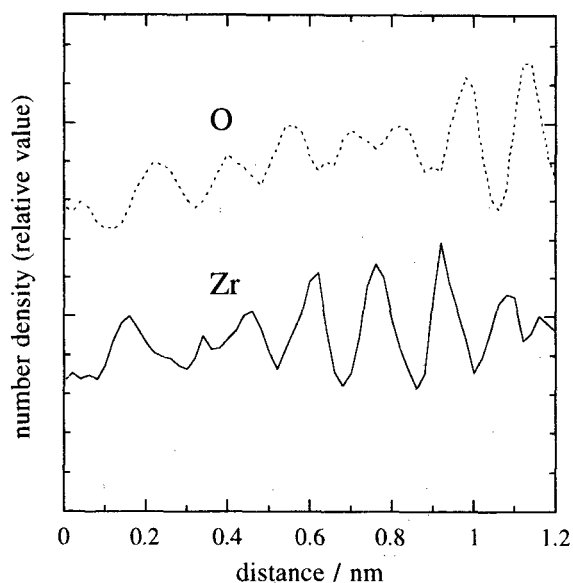


Fig. 2 Number densities of oxygen and zirconium at 1500K as functions of the distance from the grain boundary.

the similarity between the results of simulation and experiments is remarkable.

3.3. Atomic diffusion in polycrystalline structures

Because zirconia ceramics are widely used as oxygen sensors, self-diffusion of ions in zirconia crystal has been investigated by MD simulation [14]. On the other hand, atomic diffusion in polycrystalline materials are also interested in relation to high temperature creep or superplasticity [3]. In these cases, self-diffusivities of atoms both inside the grain and at the grain boundary have important meanings. Both types of diffusion are recognizable in the present simulation: oxygen diffusion between sites in cubic crystal grain, and random motions of both elements at the boundary.

In order to evaluate the self-diffusion coefficients of these types separately, we marked the atoms inside the grain and at the boundary layer of which thickness of 0.5 nm. Mean square displacement (MSD) of each element was counted by using the trajectory data of marked atoms during 60 ps. So as to avoid unnecessary

confusions, atoms in the transient region between 0.25 to 1 nm from the boundary plane at the beginning were excluded in the calculation. The MSD's at 2500K are shown in Fig. 3. The MSD of oxygen at the grain boundary shows almost linear dependence on time. Other MSD's, on the other hand, show rather irregular behaviors typical to short range diffusion.

The self-diffusion coefficients of oxygen are estimated by the linear regressions of MSD's to be 3.4×10^{-11} and 5.7×10^{-10} m²/s inside the grain and at the grain boundary, respectively. The former value seems to be too small compared with the extrapolated value of experimental data on oxygen diffusivity, on the order of 10^{-10} m²/s, in yttria-stabilized zirconia [15]. Such discrepancy may be explained by the fact that very few oxygen vacancies exist in pure ZrO₂ crystals which play important roles for the oxygen diffusion in zirconia crystals. The self-diffusion coefficient at the grain boundary, on the other hand, seems to be in the same range with the experimental values.

Diffusivities of zirconium were estimated to be 2×10^{-12} and 4.3×10^{-11} m²/s inside the grain and at the grain boundary, respectively. The former value has no significant meaning and

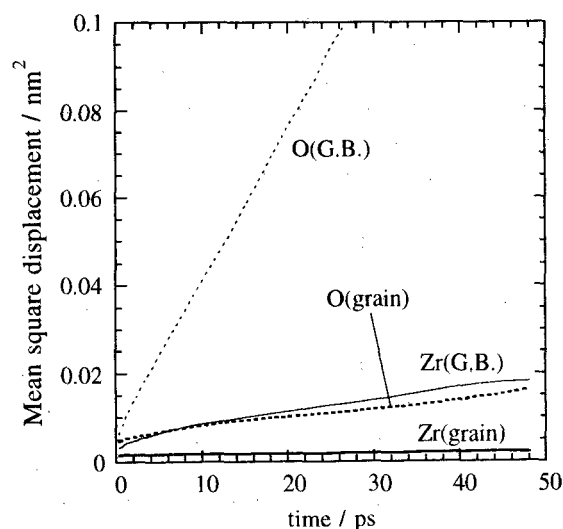


Fig. 3 Mean square displacements of oxygen and zirconium observed in regions of inside grains and the grain boundary (G. B.) layer.

can be assumed to be zero. The latter is, however, comparable with the calculated oxygen diffusivity inside the grain, although the reliability of the values should be checked by further experiments.

4. DISCUSSION AND CONCLUSION

The present MD simulation extracted several interesting information on the polycrystalline zirconia for both static and dynamical aspects as shown in above. Although the adopted configuration of grain boundary is much simpler compared with those in actual samples, similarities concerning to the phase transitions and the grain boundary layer were found between them. In this sense, the technique used in this work is expected to be also useful in more realistic simulation employing, for example, fully three-dimensional arrangement of grains or composition including impurities such as yttrium. It seems to be necessary to take impurity elements into account in order to reproduce precise characteristics on atomic transports, as pointed out in above.

On the other hand, most significant difference between the actual and simulated samples must be the size of grains. We must be careful on the fact that large number of atoms belong to the surface regions of grains in the MD simulation. Roughly speaking, about 25% of atoms are on the grain surface in the present case. Such situation is considered to be different from that in actual polycrystalline sample composed by micron or sub-micron grains. Hence, some particular technique for extrapolating the simulation results to larger scales should be developed.

In conclusion, the present authors stress that the MD simulation appears to be useful for investigating the structure and dynamical behaviors of polycrystalline materials in microscopic levels. It would be interesting to extend the present method to more realistic

ceramic systems, and the usefulness and validity will be tested in a wider base.

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