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Atomistic simulations of grain boundary transformation under high pressures in MgO

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ABSTRACT

This study focuses on transformation of grain boundary (GB) structures under high pressures up to 60 GPa by using a simulated annealing technique with molecular dynamics and lattice statics calculations for various symmetric tilt GBs (STGBs) of MgO. It is found that except for the $\Sigma 3(111)/[1\bar{1}0]$ that is a rather stable GB, all the STGBs studied transform into a metastable structure more than once at threshold pressures. In addition, the GBs with an open-core structure and small tilt angle are found to be more "flexible" to transform into different structures than the GBs with a dense structure. For polycrystalline MgO, therefore, GBs may also exhibit GB transformation under high pressures and flexible GBs may govern overall transformation and deformation. These findings also suggest that polycrystals sintered at high pressures consist of more pressure-resistant GBs than those at normal pressures.

1. Introduction

Grain boundary (GB) frequently has impacts on the material properties of polycrystalline oxides. For example, recent experimental studies with bicrystals and theoretical calculations have indicated that GB segregation (GBS) behavior [1–3] and GB diffusivity [4,5] vary with GBs, suggesting that microscopic or atomic-level GB characters, such as GB plane and atomic arrangement, play important roles in these GB phenomena. A better understanding of GB structure in the atomic level is a key issue for material design of polycrystalline oxides.

Nevertheless, it is still difficult to determine precisely atomic arrangements at oxide GBs, partly because intrinsic and extrinsic factors, which is either intentional or unintentional, can modify GB structures. Previous studies showed that "pure" GB structures obtained by calculations frequently contradict observations with transmission electron microscopy (TEM) and scanning TEM (STEM) even for well-defined symmetrical tilt GBs (STGBs) and such "pure" GBs are speculated to transform into different structures by various factors, e.g. the formation of Schottky pairs at GBs in NiO [6–8], GBS of unintentional impurities in MgO [9–11], and surface conditions of samples in Al_2O_3 [12–14]. Therefore, it is essential to understand structural deviation from pure GB structures under given conditions and environments, first of all.

Pressure is also a crucial factor that affects both the macroscopic and microscopic states of materials, and recent studies have explored new bulk phases under high pressure for a wide variety of oxides [15–18]. GB structure under high pressure has been also studied as an interesting issue for theoretical study and basic materials science. In this case, it is difficult to experimentally observe the pressure dependence of GB structure, and thus previous studies employed theoretical calculations to STGBs for MgO as a prototype oxide system and indicated that the STGBs are transformed into different structures under high pressures up to 100 GPa [19–22]. In addition, these studies showed that the formation energy of vacancies at GBs decreases as pressure increases, indicating that pressure can promotes the creation of point defects at GBs. However, the previous studies focused only on simple well-defined STGBs, namely the $\Sigma 5(210)$, $\Sigma 5(310)$ and $\Sigma 17(410)$ GBs with the [001] tilt axis, all of which have the open-channel structures identical to each other. At present, it is still unclear whether GB-structural transformation reported for the simple well-defined GBs is the general phenomenon for GBs of MgO or not.

In order to tackle this issue, we investigate high-pressure transformation for thirteen STGBs of MgO with the [001] and $[1\bar{1}0]$ tilt axis, which cover various types of GB structures at zero pressure, by using simulated annealing (SA) with molecular dynamics (MD) and lattice statics calculations. The remaining part of this work consists of the following sections: the next section describes details of construction of

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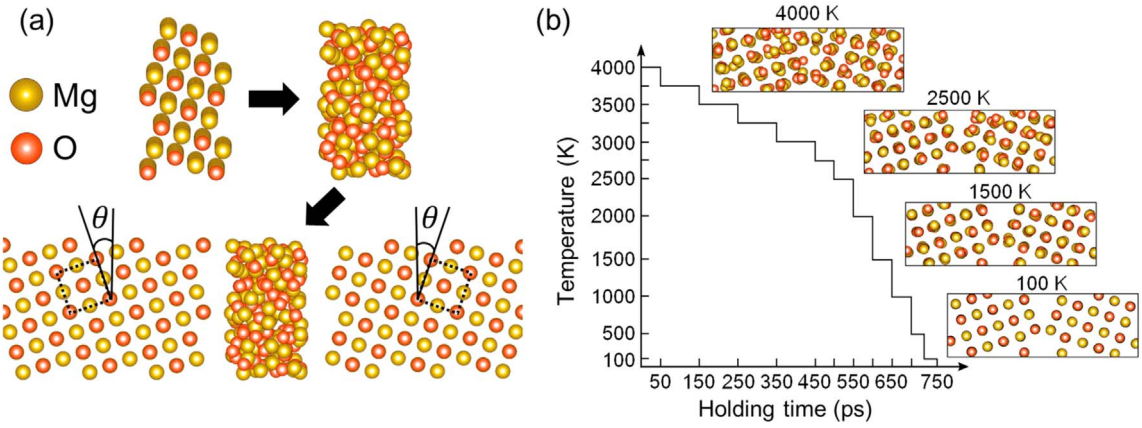

Fig. 1. (a) Schematic illustration of a starting GB model with a disordered structure sandwiched by two grains with a misorientation angle 2Θ. First, a MD simulation is run with a single-crystal model a 8000 K to disorder the atomic arrangement completely. Then, the structure is inserted between two grains that are individually tilted by a misorientation angle of $\theta°$. (b) Conditions of the SA technique with MD simulations in terms of temperature and holding time, and snapshots of atomic arrangement at each of the temperature during MD simulations.

a GB model and computational conditions for SA techniques. Section 3 discusses results of GB structures obtained at high pressures and changes in GB energy and excess volume. In addition, the effect of temperature on the formation of metastable GB structures is also discussed. The final section is devoted to conclusions of this work.

2. Computational details

Fig. 1 shows a schematic picture of construction of a GB model and computational conditions of MD simulations. We employ SA techniques with MD to obtain energetically stable and metastable GB structures under pressures up to 60 GPa. An initial GB model under zero pressure is constructed by inserting a disordered bulk structure between two grains tilted at a given misorientation angle. The disordered structure is created by holding a single-crystal model at 8000 K for 20 ps. The first SA starts at 4000 K with the NVT condition to suppress the expansion of the disordered structure and to solidify the structure. Then the NVT condition is switched to the NPT condition at $T < 4000$ K to allow a simulation box to change its lattice constants. At this stage, the temperature is decreased in a stepwise manner with a temperature decrement ΔT of 250 K at $T \geq 2500$ K or 500 K at $T < 2500$ K. A holding time at the temperature is set to 100 ps at $T \geq 3000$ K, 50 ps at 1000 K $\leq T < 3000$ K, or 25 ps at $T < 1000$ K. After a MD runs for 25 ps at 100 K, the GB structure is numerically optimized with a conjugate gradient algorithm of a static lattice energy minimization. This study uses an empirical potential set of the Buckingham type reported in a previous study [23]. The cut-off radius of the empirical potential is set to 20 Å. The formal charges of a Mg and O ion are assumed to be +2 and −2, respectively. All calculations in this work are performed with the LAMMPS code [24].

The second SA starts at 3000 K using the zero-pressure GB structures, which obtained from the first SA, at a pressure from 2 GPa to 60 GPa with an interval of 2 GPa. The temperature is decreased stepwise with $\Delta T = 250$ K at $T \geq 2000$ K or $\Delta T = 500$ K at $T < 2000$ K, and a holding time is set to 50 ps at $T \geq 1000$ K and 25 ps at 500 K and 100 K. Finally a numerical optimization is performed at the same pressure as that of the SA. In addition, the effect of pressure release on the GB structure is studied. A GB structure obtained under a high pressure is again numerically optimized at zero pressure, and its atomic arrangement and GB energy are evaluated.

The advantage of the SA techniques used in this work is that atomic diffusion is effectively promoted by thermal fluctuation whose magnitude depends on a given temperature. As a result, it becomes easier to overcome energy barrier for GB transformation between different GB structures, which allows us to search a wide range of possible stable and metastable structures within limited time. On the other hand, the disadvantage is that SA simulations are sometimes trapped into local-minimum GB structures at which atomic arrangements are significantly disordered even after geometrical optimizations. In this work, such highly disordered GBs are not considered as a metastable GB structure and excluded.

In order to understand systematically the pressure dependence of GB structure, we study several STGBs with the [001] and $[1\bar{1}0]$ tilt axis varying their misorientation angles and thereby atomic arrangements at the GBs. Table 1 lists the STGBs studied in this work and their GB energy and excess volume per GB area at 0 GPa. The structural features and energetics of these STGBs will be discussed in detail elsewhere. The GB energy at pressure P, $\Delta E^{\mathrm{GB}}(P)$, is evaluated by the following equation:

$$\Delta E^{\mathrm{GB}}(P) = \frac{E^{\mathrm{GB}}(P) - nE^{\mathrm{BULK}}(P)}{2A(P)} \quad (1)$$

where $E^{\mathrm{GB}}(P)$ and $E^{\mathrm{BULK}}(P)$ are the lattice energy at pressure P of a GB model and an unit cell of MgO, respectively, n is the number of unit cells contained in the GB model, and $A(P)$ is the GB area at P. It should be noted that $\Delta E^{\mathrm{GB}}(P)$ corresponds to the increase of internal energy per GB area, not the Gibbs free energy, since $\Delta E^{\mathrm{GB}}(P)$ does not consider the contribution of entropy and PV term. Nevertheless, it is possible to understand the trend of the pressure dependence of GB structure by

Table 1
STGBs studied in this work and their GB energy and excess volume per GB area for the most stable GB structures. These values are obtained under zero pressure.

Grain boundary	Misorientation angle 2Θ (°)	GB energy (J/m^2)	Excess volume per GB area (Å)
Σ65(810)/[001]	14.3	1.78	0.90
Σ13(510)/[001]	22.6	1.95	1.13
Σ5(310)/[001]	36.7	1.95	1.23
Σ5(210)/[001]	53.1	1.76	0.99
Σ13(320)/[001]	67.4	2.06	0.39
Σ61(650)/[001]	79.6	1.41	0.25
Σ65(551)/[1$\bar{1}$0]	16.1	2.28	0.30
Σ33(441)/[1$\bar{1}$0]	20.0	2.49	0.35
Σ9(221)/[1$\bar{1}$0]	38.9	2.74	0.66
Σ11(332)/[1$\bar{1}$0]	50.5	2.65	0.50
Σ3(111)/[1$\bar{1}$0]	70.5	0.86	0.01
Σ17(223)/[1$\bar{1}$0]	93.4	2.68	0.44
Σ3(112)/[1$\bar{1}$0]	109.5	2.52	0.91