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Theoretical study of Lu segregation in Σ13 Al_2O_3 grain boundary

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In this study, atomic structure and Lu segregation behavior of the pyramidal Σ13 twin grain boundary in Al_2O_3 were investigated by empirical theoretical calculations. The stable structures of the pristine grain boundary were predicted by the systematic static lattice calculations. Segregation energies for Lu at the grain-boundary core sites were found to be not constant, but very site specific. The present result indicates that Lu segregation should occur in very ordered manner along the grain-boundary core region.
Key words: Al_2O_3, Lu, Grain boundary, segregation, static lattice calculation

1. INTRODUCTION

Polycrystalline alumina (α-Al_2O_3) is one of the most commonly used structural ceramics because of its outstanding high-temperature mechanical and chemical stability. For its usage at high-temperatures, creep deformation becomes critical issue. It has been reported that small amount of dopant addition (e.g. rare-earth elements) dramatically improved the creep resistance of polycrystalline α-Al_2O_3 [1]. Bulk α-Al_2O_3 has extremely low solubility limit for these cations, and therefore such dopants tend to segregate to the grain boundaries or form secondary precipitates at grain junctions. These segregated dopants seem to affect the grain boundary sliding behavior, which is considered as the dominant mechanism of high-temperature creep deformation in fine-grained alumina [2, 3]. However, it is still unclear why these segregated dopants can modify the grain boundary strength at elevated temperatures.

To understand the dopant mechanism in Al_2O_3, atomic-scale understanding of grain boundary structures and dopant segregation must be essential. Among various dopant systems, the addition of Lu has been reported to have the strongest effect on the retardation of high-temperature creep deformation in Al_2O_3 [1]. On the other hand, the pyramidal Σ13 twin grain boundary is known to have quite periodic, sufficiently disordered structure and relatively high grain boundary energy as compared to the basal Σ3 twin boundary and the rhombohedral Σ7 twin boundary [5]. Previously, the Σ13 boundary has been used for theoretical analysis of Y, Sc and La segregation [4], and the stable segregation sites were independently predicted for the above three dopants systems. However, theoretical analysis of Lu segregation has not been performed, although Lu is the most effective dopant. In this study, grain-boundary segregation behaviors of Lu at the pyramidal Σ13 twin grain boundary were systematically investigated by theoretical approach based on the empirical static lattice calculations.

2. COMPUTATIONAL PROCEDURE

In this study, static lattice calculations based on empirical interatomic potentials were used to investigate the grain-boundary structure and segregation behavior. First, the stable atomic structures of pyramidal Σ13 grain boundary were systematically estimated under constant pressure condition by the static lattice calculation using GULP program code [6.7]. Here, Buckingham-type

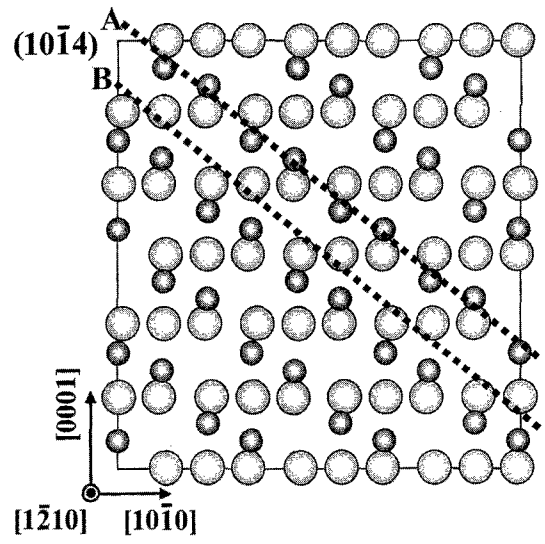

Fig. 1. Crystal structure of α-Al_2O_3 viewed from [1$\bar{2}$10] directions. Large and small circles represent oxygen and aluminium atoms, respectively. The dashed lines mark the two terminated planes, A: Al-terminated and B: O-terminated plane.

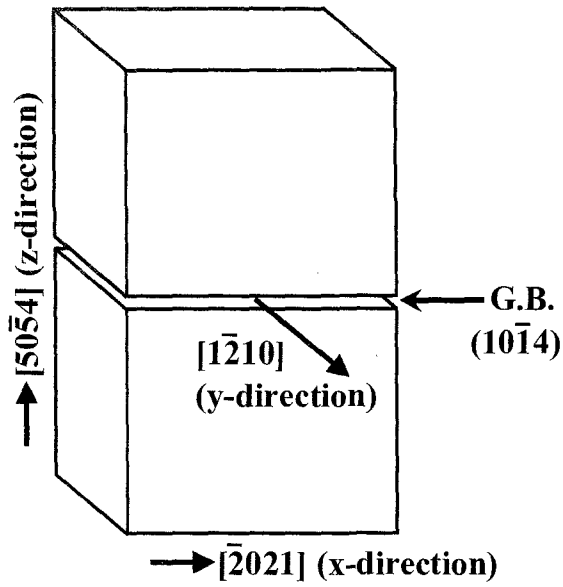

Fig. 2. Schematic illustration of a grain boundary supercell used in this study.

two-body ionic potentials with the potential parameters proposed by Lewis and Catlow were employed [8]. The validity of this potential parameter for Al_2O_3 has been confirmed elsewhere [5,9]. The supercell containing pyramidal Σ13 twin grain boundary were constructed by cutting α-Al_2O_3 corundum structure with (10$\bar{1}$4) plane and rotated one grain by 180° around the normal direction to the grain boundary plane, [50$\bar{5}$4] axis respected to the other grain. As shown in Figure 1, two terminations can be considered in the (10$\bar{1}$4) plane, namely Al-termination or O-termination [5]. Therefore, when constructing the supercells, the two type terminations must be taken into account. We assumed that the supercells preserve the stoichiometry because the formation energy of nonstichiometric defects in α-Al_2O_3 is extremely high [11]. The number of atoms in these supercells was selected to be 120. This size is confirmed to be large enough to reproduce the properties of Al_2O_3 [5]. Figure 2 illustrates the supercell geometry used for the present calculations. In order to obtain the most stable atomic structure, the rigid body translations of the two grains were systematically changed, and then the cell were fully relaxed to find the local or global energy minimum. Using the calculated total lattice energy, grain-boundary energies (energy per boundary area, in J/m^2) were estimated according to the following equation,

$$E_{GB} = (E_{tot,GB} - E_{tot,bulk})/A_{GB} \quad (1)$$

Where E_{GB} is the grain boundary energy, $E_{tot,GB}$ and $E_{tot,bulk}$ are the total energies of the supercells the grain boundary and bulk which contain 120 atoms respectively. A_{GB} is the grain boundary area. Thus obtained grain-boundary energies were plotted against the translation states, and then the local energy minimum structures were identified.

Lu segregation energies at the grain-boundary sites were also estimated by the static lattice calculations. Al sites in the supercell were systematically substituted by Lu atoms, and their total energy were calculated. We defined the segregation energy, E_{seg}(Lu) (eV/grain boundary), according to the following equation,

$$E_{seg}(\mathrm{Lu}) = -\{E_{GB}^{pure} + 2E_{bulk}(\mathrm{Lu})\}/2 + \{E_{GB}(\mathrm{Lu}) + 2E_{bulk}^{pure}\}/2 \quad (2)$$

Here, E_{bulk}(Lu) is the total energy containing one Lu atom in bulk cell containing 60 atoms. E_{GB}(Lu) is the total energy containing one Lu atom in one grain boundary. This segregation energy means energy gain when Lu atom moves from bulk region to specific site in the grain boundary. Therefore, negative segregation energy indicates that the segregation of Lu atom is energetically favored.

3. RESULTS&DISCUSSION

For the structural optimization of the pristine boundary, two-grains were mutually shifted by a translation vector $\boldsymbol{T}$ in the grain boundary plane. Lateral translation component $T_1\mathbf{x}+T_2\mathbf{y}$ is a two-dimensional vector within the two-dimensional grain boundary plane in the supercell. T_1 and T_2 are fractional coordinates with respect to the supercell lattice vector $\mathbf{x}$ (= [$\bar{2}$021])

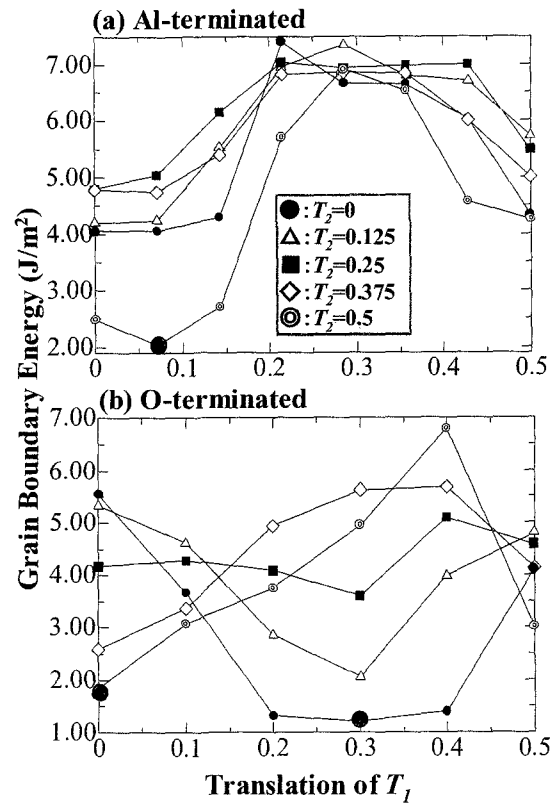

Fig.3. Calculated grain boundary energies with (a) Al-terminated and (b) O-terminated structures versus rigid-body translation of T_1 and T_2. The lowest energies states are indicated by the large doted circles.

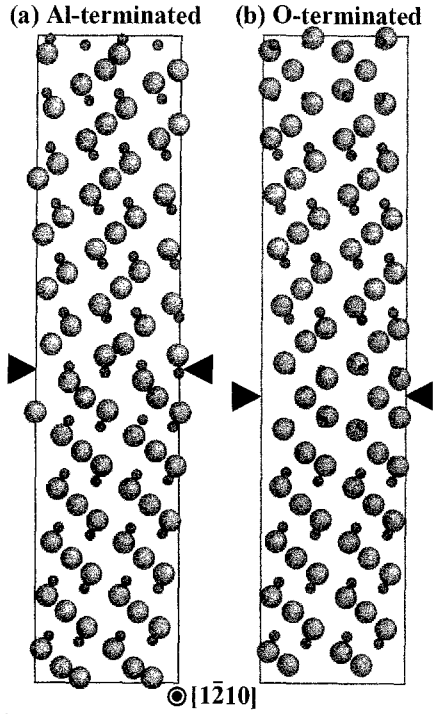

Fig. 4. Relaxed stable atomic structures of (a) Al-terminated and (b)O-terminated grain boundary viewed along [1$\bar{2}$10] direction.

and y (= [1$\bar{2}$10]), respectively. In this study, two-grainswere translated by steps ΔT_1=0.07 and ΔT_2=0.125 for Al-terminated, ΔT_1=0.10 and ΔT_2=0.125 for O-terminated supercell. Due to the periodic boundary condition, T_1 and T_2 were calculated up to 0.5. Figure 3 (a), (b) show the calculated grain-boundary energy as a function of the translation states in Al-terminated or O-terminated grain-boundary supercell, respectively. It can be found from the results that there are three stable structures. In the Al-terminated case, (T_1, T_2) = (0.07, 0.5) is the most stable translation state, while in the O-terminated case, (T_1, T_2) = (0, 0.5) and (0.3, 0) are stable translation states. However, the structures of (T_1, T_2) = (0.07, 0.5) in Al-termination and (T_1, T_2) = (0.3, 0) in O-termination are found to be identical structure. Therefore, two local stable structures can be found in this boundary. The two stable structures of Al and O-termination cases are shown in Figure 4(a), (b). Calculated values of the grain boundary energy are 1.20J/m^2 for Al-terminated and 1.84J/m^2 for O-terminated respectively. The most stable Al-terminated grain boundary was thus selected as the model grain boundary for simulating Lu segregation. The Al sites for Lu substitution are defined in Figure 5. We define that Al sites in the lower grain is in A-domain, while those in the upper grain is in B-domain. Although one supercell has 48 Al sites, there are coupled equivalent sites and thus 24 substitution sites were considered as shown in Figure 5. Figure 6 shows a plot of segregation energies versus distances from the grain boundary core. While most sites showed positive values of segregation energies, two sites with very low segregation energies can be found. This result clearly shows that the Al-terminated Σ13 grain boundary

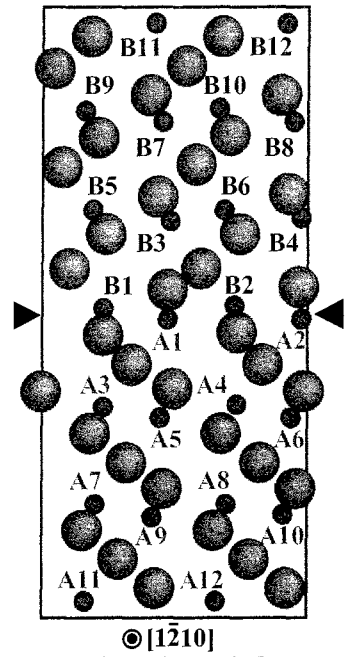

Fig. 5. Substitution sites of Lu atoms in the Al-terminated grain boundary supercell.

provides some favorable sites for Lu segregation, namely **A1** and **A2**, which are located in the very vicinity of the boundary core. It is interesting to point out that **B1** and **B2** had no tendency of Lu segregation, although they were also situated in the very core of the boundary. Since the valency of Lu and Al is the same, and Lu has larger ionic radius (0.86Å) than Al (0.53Å), structure relaxation should be related to the size mismatch between Lu and Al. According to the relaxed structure, Lu atoms tend to move toward the nearest open spaces lying on the (0001) basal plane, and first neighbor O atoms also accommodate their positions to try to keep the stable Lu-O bond lengths. Al atoms are coordinated with six O atoms with specific two bond length, b_s=1.84Å and b_l=1.96Å in Al_2O_3 perfect crystal. While the stable average bond length of Lu-O in the present potential model (Lu_2O_3) is 2.22Å, in the present relaxed structures, average bond length of Lu-O is estimated to be b_s=2.10Å and b_l=2.23Å at the **A1** and

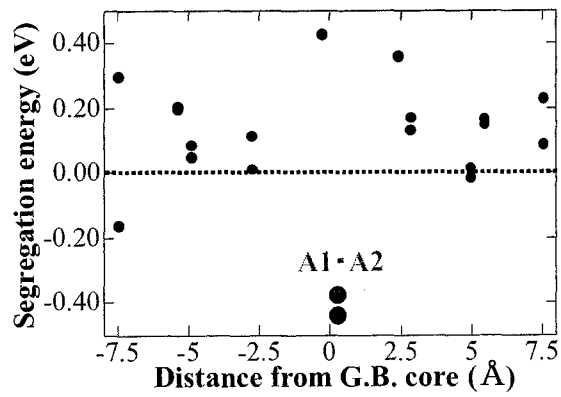

Fig. 6. Segregation energy versus distance from grain boundary core to the each substitution sites. Below dotted line, grain boundary segregation is energetically favorable.

A2 sites, while b_s=2.02Å and b_f=2.18Å at the **B1** and **B2** sites. Apparently, **A1** and **A2** site have closer Lu-O bond lengths with the stable Lu-O bond lengths than the **B1** and **B2** sites. This result suggests that even in the core region, Lu accommodation is site specific, and some sites can more easily accommodate the size mismatches between Lu and Al. According to the present theoretical analysis, Lu segregation thus will be very site specific, and probably depend on the amount of Lu atoms in the real grain boundary. It will be very interesting future work to estimate how these segregation sites develop with increasing Lu content at the grain boundary, and compare with experiments such as bicrystal experiments.

4.SUMMARY AND CONCLUSION

In this study, stable grain-boundary structure and segregation sites of Lu at the pyramidal Σ13 twin grain boundary were systematically investigated by the static lattice calculations. The Σ13 grain boundary has two stable structures with different terminations, and the Al-terminated structure was found to be the most stable structure. It was shown that Lu atoms segregate to the specific sites in the grain boundary core region, but not all sites in the core showed the tendency for segregation. This may be due to the difference in local environment of the grain-boundary sites, and thus difference in size mismatch accommodation of larger Lu atoms.

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