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First principles and classical molecular dynamics studies for oxygen grain boundary diffusion in sapphire

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High temperature mechanical properties of polycrystalline materials are strongly related to the atomic transportation phenomena, namely diffusion. α-Al_2O_3 is one of the most utilized structural materials and the high-temperature mechanical properties are known to be dominated by a short-circuit diffusion along grain boundaries (GBs). So far, the behavior of oxygen self-diffusion in Al_2O_3 has been intensively investigated. However, the atomistic migration mechanism at GBs has not been clarified in detail. In order to discuss the origin of GB diffusion mechanism of Al_2O_3, we investigated oxygen vacancy formation energetics at GBs by first principles projector augmented wave calculation and effective atomic diffusion paths along GB by classical molecular dynamics (MD) simulation.

In this study, three different GBs, Σ11 ($10\bar{1}1$), Σ13 ($10\bar{1}4$) and Σ37 ($\bar{1}018$) were constructed. Calculated atomic configurations around GB plane were shown in Fig.1. The supercells containing 200 (Σ11), 240 (Σ13) and 480 (Σ37) atoms were used for calculating the defect formation energy by first-principles calculation. In this case, one oxygen atom was removed from the supercells to introduce a vacancy. For obtaining the optimized structures all atoms in the supercells were fully relaxed.

For the classical molecular dynamics (MD) simulations, vacancies were randomly introduced from the extended supercells. After reaching the adequate equilibration of the systems, oxygen trajectories were investigated by the statistical MD simulations using the empirical pair-potential[1] under NEV unsembles.

We calculated the oxygen vacancy formation energies of 10 sites in Σ13 GB. It was found that there is clear site-dependency of the vacancy formation energy, and the vacancies are more preferably formed at the GBs than that in bulk. Furthermore, in order to find the preferential defect formation site at the GB, ΔE_f was defined as the differences of defect formation energies between the bulk-like region (O10) and GB. The absolute values of ΔE_f and the strains were plotted as a function of distance from the GB as shown in Fig.2. From the overall features, it was found that the strains tend to decrease as increasing the distance from the GB, and simultaneously, the ΔE_f also decreases. This indicates that the defect energetic at the GB is closely related to these structural distortions at the GBs[2].

In the presentation, the results obtained for other grain boundaries will be also shown to discuss the effective atomic migration paths predicted by MD simulations and the relationship with those structural distortions.

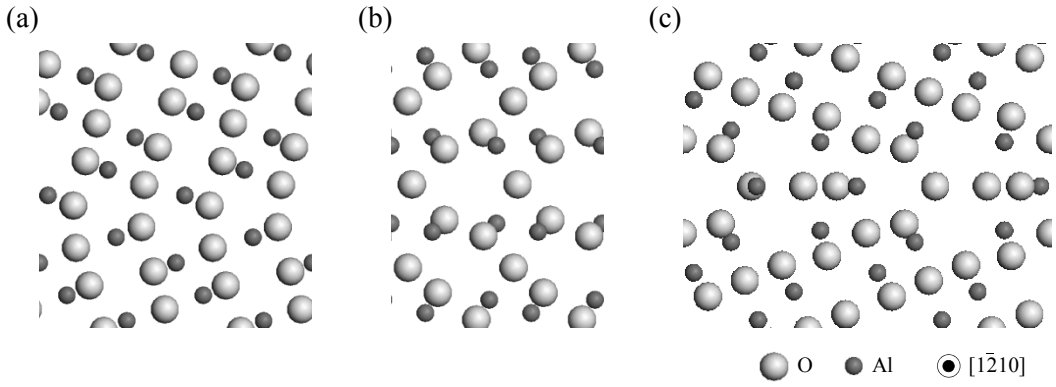

Fig. 1 Atomic configurations viewed from [1$\bar{2}$10] direction of (a) Σ11, (b) Σ13 and (c) Σ37 grain boundary. Each structure was determined by static lattice calculation and first principles calculation as the most energetically stable structure.

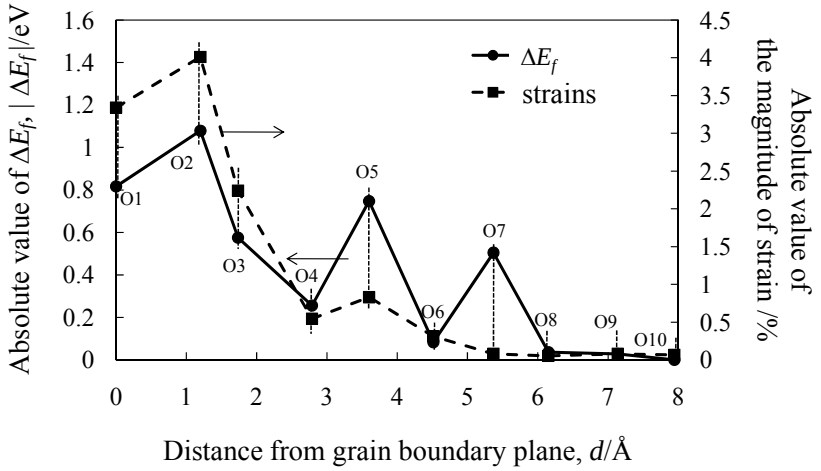

Fig.2 Absolute value of ΔE_f (circles) and the magnitude of strain (squares) as a function of distance from GB plane.

References

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