

First principles study on vacancy formation and diffusion behaviors in α -Al₂O₃ grain boundary

Tetsuya Tohei¹, Yuito Watanabe¹, Naoya Shibata¹, Yuichi Ikuhara^{1,2}

¹Institute of Engineering Innovation, The University of Tokyo, Tokyo, 113-8656, Japan

²Nanostructures Research Laboratory, Japan Fine Ceramics Center, Nagoya, 456-8587, Japan

α -alumina (α -Al₂O₃) is well known to maintain high mechanical strength, toughness, and corrosion resistance up to high temperatures, which are advantageous for application as high temperature structural materials. Rapid short-circuit diffusion process via grain boundaries in alumina is crucial for the material's high temperature properties such as creep deformation, densification in sintering, grain growth, and so on. Although diffusion phenomena along alumina grain boundary (GB) have been extensively studied, many questions remain unresolved [1][2]. In this study, we investigated atomic structures, vacancy formations and migration behaviors in alumina grain boundary by first principles theoretical calculations in attempting to understand the grain boundary diffusion phenomena from an atomistic scale.

In this work, we focused on Al₂O₃ Σ 11 (1-210)/[10-11] GB as a model grain boundary system. Stable atomic configuration of the GB was firstly searched by the method of rigid body translation employing static lattice calculations (GULP code). Then accurate atomistic structure of the GB was evaluated by first principles calculations within the framework of density functional theory (DFT). We used plane wave basis PAW method (VASP code) for structure optimization and total energy calculations. Supercells containing about 400 atoms were used for the calculations. Since oxygen diffusion in α -alumina is considered to occur mainly via oxygen vacancies, understanding the oxygen vacancy formation behavior is essential. Formation energies of isolated oxygen (O) vacancies were calculated for various atomic sites around the GB and the bulk region. For simulating diffusion phenomena, we employed two classes of theoretical methods: First we performed classical molecular dynamics (MD) simulations to estimate dominant diffusion paths in alumina Σ 11 GB. For the MD calculations extended supercells with the GB and composed of about 3600 atoms were used, with several oxygen vacancies introduced into the atomic sites with low vacancy formation energies at the grain boundary. Then accurate geometry and activation energies for the dominant atomic migration paths were calculated by nudged elastic band (NEB) method using the first principles PAW method [3].

Figure 1 (a) shows the stable atomic configuration of the Al₂O₃ Σ 11 (1-210)/[10-11] GB. Based on this structure, formation energies of vacancies for different O sites (numbered as 1 - 18) were calculated. Figure 1 (b) shows the dependence of the relative vacancy formation energy on the distance from the GB plane. It is found that O vacancies are more preferably formed at the GB (especially O sites #9 and 10) than in the bulk-like region (sites #1 - 4 and 15 - 18). It has been found that the vacancy formation energy is closely related to the structural distortions and electronic

state at the GB. Next, we investigated the migration behaviors of oxygen vacancies at the GB by MD simulations and first principles NEB calculations. From the MD trajectories of the oxygen vacancy sites, it was confirmed that diffusion of oxygen vacancies predominantly occurs along the grain boundary. Careful inspection of the trajectories revealed that the predominant oxygen diffusion is occurring mainly among four preferable oxygen sites. Then dominant grain boundary diffusion path found in the present calculation can be classified into four kinds of elementary migration paths among four different oxygen sites. Quantitative evaluation of migration energies by NEB calculations found that some of atomic migration paths at the grain boundary actually show lower energy barriers compared to the bulk migration paths, which is consistent with the previously reported experimental observations and present MD simulation results. Possible reasons for the observed tendency in energetically favorable or unfavorable migration paths are discussed in terms of local atomistic coordination around the migrating oxygen sites.

Acknowledgements:

The authors gratefully acknowledge the financial support by a Grant-in-Aid for Scientific Research on Innovative Areas "Nano Informatics" (Grant No. 25106003) from Japan Society for the Promotion of Science (JSPS).

References

- [1] A. H. Heuer, *J. Eur. Ceram. Soc.*, **28**, 1495-507 (2008).
- [2] T. Nakagawa *et al.*, *Scr Mater.*, **65**, 544-547 (2011).
- [3] N. Takahashi *et al.*, *Phys. Rev. B*, **82**, 174302 (2010)

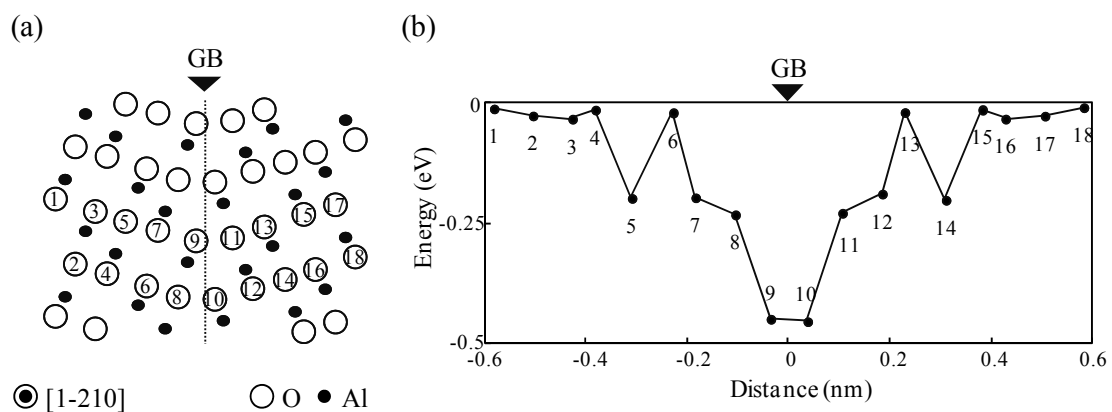


FIG. 1. (a) Atomic configuration of alumina $\Sigma 11$ (1-210)/[10-10] grain boundary viewed from [1-210] direction and (b) relative formation energies of oxygen vacancies as a function of distance from the grain boundary