Atomic Structure and Transport Properties in α-Al2O3 [0001] Symmetric Grain Boundaries

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[Introduction]
High-temperature behaviors in ceramics (such as creep, grain growth, oxidation, sintering and so on) are frequently originated from mass-transport phenomena in microstructures. In particular, grain boundary diffusion, which is short circuit diffusion along grain boundaries, often plays a very important role in such behaviors. Polycrystalline ceramic materials contain various kinds of grain boundaries with different atomic structures. It is, therefore, important to clarify the relationships between grain boundary diffusivity and grain boundary structures for individual grain boundary. For this purpose, we fabricated five kinds of grain boundary models of α-Al2O3 by bonding two single crystals with specific geometrical configuration in order to find the relationship between the atomic structures and diffusion properties of grain boundaries.

As well as atomic column arrangement of grain boundaries, the segregation of rare earth element is known to be very effective for the improvement of high temperature properties of α-Al2O3 [1]. However, the reason of its improvement is still unclear. In this study, we also fabricated yttrium-doped bicrystal with the same geometry as the one of un-doped five bicrystals (Σ31{71140}/[0001]) in order to perform the direct and quantitative evaluation of “doping effect”.

[Experimental Procedures]
Detailed atomic structures were determined by combining the experimental studies (HRTEM) and the theoretical studies (Fig. 1). Subsequently, grain boundary diffusion coefficients of O and Ti were measured by tracer exchange and secondary ion mass spectroscopy (SIMS) depth profiling method (Fig. 2).

[Results and Discussion]
(Un-doped boundaries) It was found that grain boundary diffusivity of both O and Ti varied by the factor of more than 100 for the present grain boundaries and the measured diffusivity of each species was well correlated with Al-O bond density and free volume in the grain boundaries, respectively. It suggests that GB diffusion originates in the atomic-level disorder of grain boundaries and the mechanism of grain boundary diffusion is different depending on diffusion species. Such difference may be explained by the bulk diffusion mechanism (vacancy diffusion or interstitial diffusion).

(Yttrium-doped boundary) It was thus found that yttrium doping retards grain boundary diffusivity by approximately 10 times compared to the undoped boundary, while their activation energies were not greatly different (Fig. 3). This result supports either or both of the “site-blocking” and “swamp-out” mechanisms [2]. The relatively strong effect of yttrium segregation can be interpreted as a selective short-circuit diffusion and yttrium segregation in disordered areas of grain boundaries, which was directly confirmed by STEM-HAADF observation [3].

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[References]
FIG. 1. (a) A magnified HRTEM image, (b) a calculated atomic structure, and (c) a simulated image of $\Sigma 7\{4510\}$ boundary.

FIG. 2. Schematic illustrations of (a) a typical concentration profile and (b) an equi-concentration contour of a bicrystals after the tracer diffusion annealing. Both lattice diffusion coefficients and grain boundary diffusion coefficients can be determined from this “two-step” profile.

FIG. 3 Oxygen diffusion coefficients in $\alpha$-$\text{Al}_2\text{O}_3$ (○,□: Lattice diffusion coefficients of the undoped and the yttrium doped $\Sigma 31$ boundaries, respectively. ●,■: Grain boundary diffusion coefficients of the pristine and the yttrium doped grain boundaries, respectively). An effective thickness of grain boundary was assumed to be 1nm for both grain boundaries.