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Rare-earth segregation at Σ13 grain boundary in alumina

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Alumina ceramics (α-Al_2O_3) are utilized in many high-temperature applications because of their high structural and chemical stability at severe conditions. It is well known that small amount of dopant addition (e.g. rare earths) effectively retard the high-temperature creep deformation of fine-grained polycrystalline Al_2O_3. Yoshida et al. reported that 0.045mol % Y_2O_3-doped Al_2O_3 shows a creep rate approximately two orders of magnitude slower than that in pristine Al_2O_3 at 1250°C [1]. Rare earth addition is thus promising for obtaining better property alumina ceramics. However, even until recently, the dopant mechanism has not been well understood because the atomic location and structure of rare earths were not identified in alumina ceramics. By the recent Z-contrast scanning transmission electron microscopy (STEM) observations, it is now recognized that the added dopants preferentially segregate into grain boundaries and occupy very specific atomic sites [2]. These experimental breakthroughs open up the possibility of understanding the dopant mechanisms in alumina grain boundaries [2]. In the present study, we further develop our rare earth dopant study by using well defined model grain boundary [3,4], and investigate the grain-boundary segregation behavior of several rare-earth dopants systematically.

In this study, Σ13 pyramidal twin grain boundary with rotation axis of $[1\bar{2}10]$ was selected as a model grain boundary. In this grain boundary, the boundary plane is {1014} and the structural periodicity is relatively short along the GB. Y-doped and pristine Al_2O_3 bicrystals were fabricated by diffusion bonding at 1500°C for 10 hour in air. In the case of Y-doped bicrystals, yttrium acetate tetrahydrate solution with concentration of 0.02 mol/l was coated on one side of the polished surfaces, and then sandwiched by the other crystal during diffusion bonding. HRTEM and STEM observations were performed by using a JEM-4010 (400kV) and a JEM-2100F(200kV) with CEOS Cs corrector.

Fig. 1 (a) and (b) show the HRTEM images of the grain boundaries fabricated in this study. FIG. 1 (a) corresponds to the pristine grain boundary and (b) to the Y-doped grain boundary. It is clearly seen that there are no secondary phases such as amorphous phases, and the two crystals were well bonded at atomic level to form atomically flat grain boundaries. These results suggest that the present bonding condition can successfully form Σ13 pyramidal twin grain boundary. Comparing two HRTEM images, apparent differences can be seen, especially in the vicinity of the boundary core region. These differences must be closely related to the Y segregation. From the stable atomic structures predicted by the static lattice calculations as well as first-principles calculations, experimental HRTEM image of Fig. 1 (a) seems to be the O-terminated structure with glide-mirror symmetry [3,4]. From the calculated grain-boundary energies, the Al-terminated structure is more stable than the O-terminated case and each calculated structures are shown in Fig. 2. It is considered that, due to the present fabrication condition, the meta-stable O-terminated grain boundary is preferred in the present experiment.

To investigate the atomic level location of rare earth atoms in the boundary, we used high angle annular dark field (HAADF) STEM to directly image rare earth atoms along the boundary. By the HAADF STEM, we found that rare earth atoms occupy very specific sites along the boundary. These results suggest that the grain boundary segregation behavior of rare earths in alumina is closely related to the atomic structures of the grain boundaries.

References

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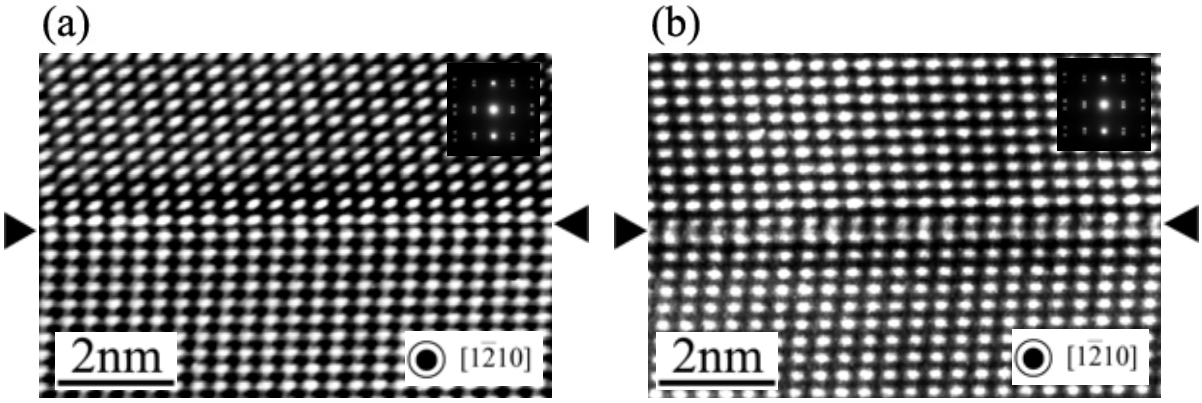

FIG. 1. HRTEM images of (a) pristine and (b) Y-doped Σ 13 grain boundary. Arrows indicate the position of grain boundaries.

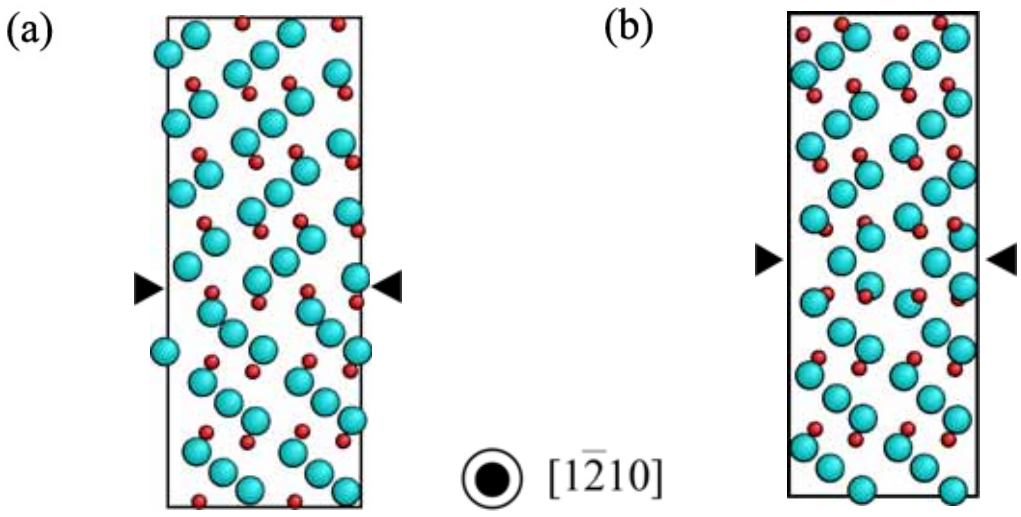

FIG. 2. Theoretically predicted Σ13 grain boundary structures. Arrowed regions are the grain boundary.(a)Al-terminated structure (b) O-terminated structure [4].