First-principles calculation on the atomic structure of yttrium doped Σ13 grain boundary in alumina

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Alumina (α-Al_2O_3) has proved to be of full potentiality in the field of high working temperature devices owing to its excellent chemical stability and mechanical property. High temperature performances of alumina, particularly the high temperature creep behaviors have been intensively studied [1]. It was suggested that grain boundary (GB) sliding should be one of the key processes of high temperature creep deformation in alumina, and GB diffusion might be one factor to control GB sliding. By way of controlling the GB diffusion and thus sliding, a small amount of foreign cation dopants, such as rare earth elements, could leave strong suppression on creep behavior in alumina [2]. This might be because these dopants distribute at specific sites, for instance the GBs, changing the atomistic structures and chemical bonding nature locally, and consequently bringing changes in macroscopic properties. Therefore, knowing where dopants lie is quite imperative for understanding the GB strengthening issue induced by the dopants. However, it is not a facile task until recent bi-crystal method and HAADF-STEM observations have made it feasible to identify of heavy foreign elements at specific GB.

In this work, we made a theoretical approach to the structure and property of yttrium segregated GB in alumina. We took Σ13 pyramidal twin GB as a model. From previous HAADF-STEM observations, Y-distribution along the GB was explicitly confirmed at an atomic scale. The GB mainly shows a one-layer Y-segregated structures [3]. To elucidate the details of the segregation phenomena we first made efforts to establish the model of this one-layer structure and performed further investigation on defect formation at the doped GB. A part of the supercell used in the modeling is shown in Fig.1. We doubled pristine oxygen-terminated supercell along [1-210] and vertical to the GB so as to restrain the interaction between adjacent GBs and adjacent vacancies caused by the periodical boundary condition utilized in the calculation method. Dopant segregation energy is defined by the following formula:

$$E_{seg}=\{(E_{GB}^{nY}-E_{GB}^{pure})-n(E_{Bulk}^{Y}-E_{Bulk}^{pure})\}/n$$

Here, n equals 4 because four cation atoms are substituted by yttrium in the present model. Calculated segregation energies are shown in Fig. 2a, indicating that doping Y atoms into the first layer or the third is the most stable. These two cases give out almost the same structure since the GB layer has shifted towards the doping layer during the structure optimization when dopants were introduced into the third layer. As in Fig. 2c, both the first and the third layer substitution cases show that cations around yttrium shaped into a hexagon with two convex sides, which go in well accordance with the observation in Fig. 2b [3]. When the second layer is substituted, neighboring cations form two concave sides. In the fourth layer substitution case the GB structure shows an obvious transition feature. When the fifth layer or the sixth layer becomes the doping

layer, the surrounding cations formed one concave and one convex side, which resemble the structures in the bulk alumina. Summing up the above, we can consider that further than the fifth layer, lattice behaves more like a bulk. The three nearest layers can be seen as GB zone and the fourth layer as a transition zone. With obtained models we further performed calculations of defect formation energies. Results show that Y-doped GB region is more difficult to produce oxygen vacancies than pure GB.

To conclude, we obtained plausible models for atomistic structures of Y-segregated Σ13 GB in alumina. We found that these yttrium dopants at the GB can curb the formation of oxygen vacancy. In the future, it is hopeful to enlighten the mechanism of creep behavior and mechanical property with theoretical method.

References
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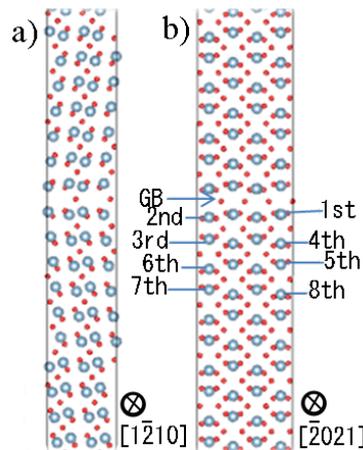
Fig. 1 A part of the structure model of Σ13 alumina GB used in this calculation. a) [1-210] projection. b) [-2021] projection.
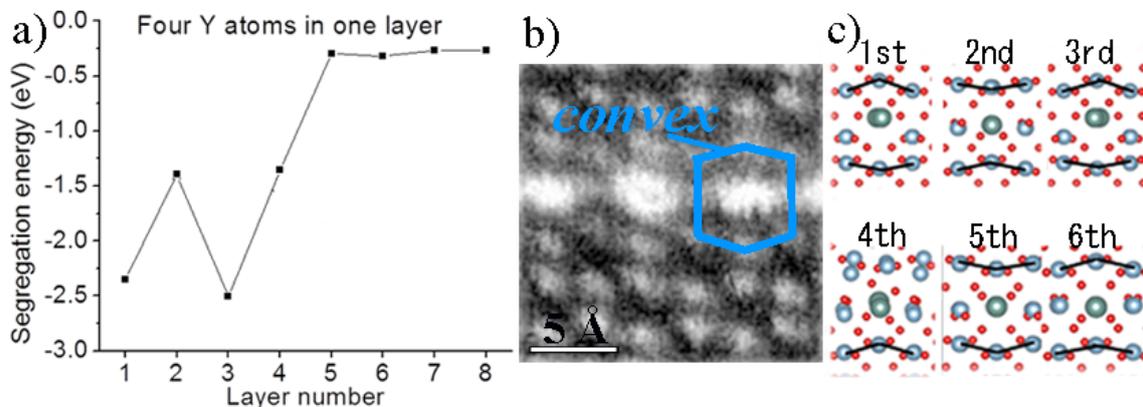

Fig. 2 a) Dopant segregation energy with respect to doping layer. b) Magnified STEM image of the GB region along [-2021] projection. c) Local atomic structure around the Y atoms after relaxation.