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Local Phonon Thermal Conductivity in the Vicinity of Σ5 (310)/[001] Symmetric Tilt Grain Boundary in ZrO_2

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Zirconia-based materials have various properties, such as high chemical stability, high toughness, and low thermal conductivity. Owing to these properties, the zirconia based materials are of prime candidates for thermal barrier coatings (TBCs), which protect gas turbine blades from high temperature under oxidation environment [1]. In order to increase operating temperature of the TBCs, lower thermal conductivity is essentially needed. With lower thermal conductivity, operating temperature can be raised, which contribute to higher energy conversion efficiency. Attention should be paid to grain boundary (GB), since most industrial materials are made of polycrystals. From earlier studies, it has been known that thermal conductivity decreases as the number density of GB increases, or, in other words, as grain size gets smaller [2]. However, origins of the decrease in thermal conductivity in the vicinity of GB are still unclear since it is very difficult to analyze local thermal conductivity in the vicinity of GB. The aim of this study is to quantitatively analyze the decrease in thermal conductivity in the vicinity of GB by atomic-level computational analyses.

In order to calculate phonon thermal conductivity, it is necessary to reproduce phonon scattering, since various kinds of phonon scattering are origins of the decrease in phonon thermal conductivity. In this study, the phonon thermal conductivity was obtained by a perturbed molecular dynamics calculations [3], which enable calculations and theoretical analysis of thermal conductivity to reveal underlying mechanism that govern thermal conduction. We calculated phonon thermal conductivity using the model of tetragonal ZrO_2 with Σ5 (310)/[001] symmetric tilt GB (hereafter referred to as GB model) and the single crystal model for comparison. One of the reasons why we chose of this GB is that the GB energy is medium, originated from medium magnitude of structural distortion with dangling bonds in the vicinity of the GB. The three-dimensional detailed atomic arrangement in vicinity of this GB is determined by previous study [4].

In this study, the pair-potential parameters proposed by Schelling *et al.* were used [5]. At first, the atomic configurations were annealed by molecular dynamics at 2000 K, followed by thermalization at desired temperature, 1500 K for 150 ps without the perturbation to ensure that they are at thermal equilibrium. Then, under the perturbation, heat flux was monitored for 300 ps and averaged over last 250 ps to calculate phonon thermal conductivity. In order to improve statistical accuracy, calculations were carried out in five different perturbations. Before dealing with GB model, we evaluated the phonon thermal conductivity at single crystal model and analyzed the dependence of the phonon thermal conductivity on temperature and yttria concentrations. It is confirmed that the phonon thermal conductivity was decreased with the increase of temperature and concentrations of yttria indicating that phonon scattering was reproduced well, which ensures the reliability of phonon thermal conductivity calculations in this study.

Figure 1 shows calculated partial phonon thermal conductivity of the GB model perpendicular to the GB plane in comparison with that of the single crystal model as a function of distance from GB plane. The partial thermal conductivity of Zr and O, which quantifies contribution of each ionic species to overall thermal conductivity, is shown in the figure instead of total thermal conductivity, and summing up all the partial thermal conductivities over constituting elements is equal to overall total thermal conductivity, which can be measured in experiment and thus can be compared with experiment, if present. In the single crystal model, phonon thermal conductivity is almost constant with some fluctuation due to numerical error, regardless of distance from GB plane, as it is expected. In the GB model, in contrast, phonon thermal conductivity decreased as approaching GB plane, and showed minimal value on the GB plane.

The atomic arrangements and vibrational states of atoms in the region within ca. 6.5 Å from the GB plane were different from those of outside the region, i.e., in grain interior in the GB

model. The atomic arrangements and vibration states of atoms in grain interior in the GB model were the same as those in the whole regions of the single crystal model. Nevertheless, phonon thermal conductivity of grain interior in the GB model was lower than that of single crystal model. This indicates that the phonon scattering occurred not only in the GB region, where static and dynamics structure is different from bulk, but also in grain interior, where the static and dynamic structure is the same as in bulk, since the phonons are spatially spreaded waves like wavelets. In other words, phonons are scattered not only on the two-dimensional GB plane but also at three-dimensional region in the vicinity of GB from a microscopic viewpoint.

In summary, atomic simulations have been carried out in order to investigate phonon thermal conductivity in the vicinity of GB by perturbed molecular dynamics. Phonon thermal conductivity was decreased, as approaching GB, and exhibited minimal value right on the GB. Thermal conductivity of GB model was lower than that of single crystal model not only in the GB region but also in grain interior, which have the same atomic arrangement and vibration states of atoms as in the single crystal model. These results indicate that introduction of GB would be more effective on the microscopic level than expected on the macroscopic level where GB is understood as the two-dimensional one.

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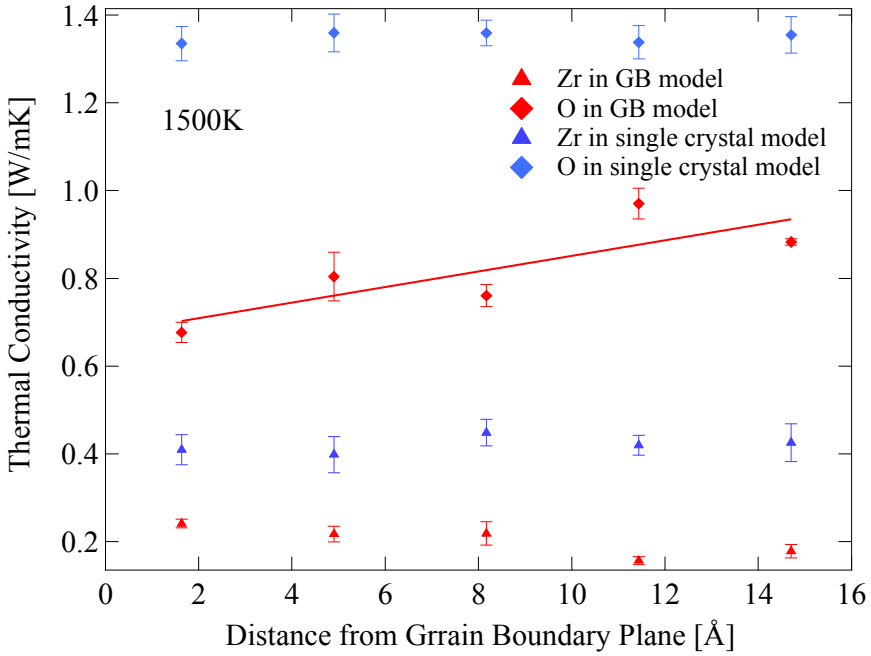

FIG. 1 Local partial thermal conductivities in the vicinity of GB in GB model and single crystal model. Standard deviation were calculated with five calculations with different perturbations and the line was obtained by liner fitting.