Supporting Online Material for

Grain Boundary Strengthening in Alumina by Rare Earth Impurities

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Methods and Materials

**Z-contrast imaging in the STEM.** We use atomic resolution Z-contrast imaging in the scanning transmission electron microscope (STEM) to show the arrangement of the cation columns at the boundary. The Z-contrast images were obtained using the JEOL 2100 with spherical aberration coefficient of ~0.5mm giving an optimum probe-size of ~1.3 Å (S1). A high-angle annular dark-field (HAADF) detector with an inner angle greater than 50 mrad was used. In these collection conditions, the image contrast of an atomic column in the incoherent Z-contrast image is approximately proportional to the square of the average atomic number (Z). This means that the bright spots in Fig 1 represent the Al columns; the O columns are not visible in these micrographs. The two intensely bright spots in figure 2 correspond to atomic columns containing Y.

**Static Lattice Calculations using GULP.** To simulate the Σ 31 boundary, we used static lattice calculations via the general utility lattice program (GULP) (S2). Here, a simulation cell containing two crystal slabs with a total width of about 5 nm width was used, containing 1240, while imposing three-dimensional periodic boundary conditions. Initial atomic positions were determined using coincident site lattice (CSL) theory. In order to take account of rigid body translations of the grain boundary, one of crystal slabs in the simulation cell was rigidly shifted parallel to the grain boundary plane. To consider the relaxations due to interatomic interactions, two-body Buckingham type ionic potentials parameterized by Catlow and James (S3) were employed. Atomic positions and the volume of the simulation cell were optimized under a constant pressure of 0.1 MPa. For each translation state of the grain boundary model, the grain boundary energy was calculated, and a most stable atomic structure was obtained.
To calculate the substitution of Y to various cation sites, the lowest energy translation state for the undoped case was used as a starting point. Y was then substituted at various sites, and for each case the boundary was allowed to relaxation again by the Buckingham potentials. The formation energy $E_f$ of $Y_{Al}$ was obtained by

$$E_f = (E^Y_{GB,Al} + \mu_{Al_2O_3} - E^{Al}_{GB,Al} - \mu_{Y_2O_3})/2$$  \hspace{1cm} (1)$$

$E^Y_{GB,Al}$ means a total energy of an Y-doped model, and $\mu_{Al_2O_3}$ and $\mu_{Y_2O_3}$ are total energies per molecule of bulk Al$_2$O$_3$ and Y$_2$O$_3$. $E^{Al}_{GB,Al}$ is the total energy of undoped $\Sigma$ 31 with the lowest-energy translation state.

**Comparison of the Grain Boundary Energies.** Our results show that the doping of Y ions to the GB increases the mechanical strength of the GB by strengthening the bonding at the grain boundary. Stronger bonding should lower the total energy of the grain boundary. Therefore, it is interesting to compare the energies for the pristine and Y-doped GBs. To calculate the GB energy for the undoped case is trivial. As described in the text, we investigated the atomic structure of the pristine GB using a 700-atom supercell. The GB energy is obtained from the difference between the total energy of the 700-atom supercell containing supercell and that of a perfect crystal model of same size. We find a GB energy of 3.93 J/m$^2$. The fairly large GB energy reflects the complexity of the Sigma 31 GB.

To calculate the Y-doped GB energy is a bit more involved since the total energy of the Y-doped GB much be compared with the total energy of a bulk Al$_2$O$_3$ crystal
containing Y. The 700-atom supercell used to calculate the Y-doped GBs contains two GBs, each containing 4 Y ions. Thus to obtain the Y-doped GB energy we must subtract the total energy of bulk Al₂O₃ containing 8 Y ions, in which the total number of atoms in the bulk state should be 700. Calculation of a 700-atom supercell containing 8 Y ions in bulk Al₂O₃ is technically straightforward but requires a significant computational cost. As an alternative, we have calculated the energies of an 80-atom supercell with and without a single Y ion at the center, and have calculated the excess energy of the Y-doped GB \( \gamma_{Y:GB} \) in the following way:

\[
\gamma_{Y:GB} = \left( E_{tot} - 8E_{Y:AlO} - \frac{6}{8}E_{AlO} \right) / 2S_{GB}
\]

where \( E_{tot} \) is the total energy of the 700-atom Y-doped GB supercell, \( E_{AlO} \) is the total energy of an 80 atom supercell containing pure Al₂O₃, \( E_{Y:AlO} \) is the total energy of an 80-atom supercell containing 1 Y ion, and \( S_{GB} \) is a GB area. The final result for \( \gamma_{Y:GB} \) is 3.48 J/m². It is noted here that additional calculations using a larger bulk supercell (containing 120 atoms) with a hexagonal symmetry yielded very similar results and ensured that the accuracy of the GB energy calculated above is less than 0.01 J/m². Comparing the Y-doped and pristine GBs, we see that the Y-doped GB energy is lowered by 0.45 J/m² upon Y-doping. This gives further evidence that the Y-O bonds at the Y-doped GB are indeed stronger than the corresponding Al-O bonds.

**First Principles Calculations using VASP.** The Vienna *Ab initio* Simulation Package (VASP) (S4, S5) is used for all geometry relaxations. We used GGA-Perdue-Wang-PAW potentials with one general k-point and an energy cutoff of 400 eV. The energy and the residual force on each atom were converged to 0.001eV, 0.01eV/Å respectively. In general, it takes 35 to
40 VASP relaxation steps to reach convergence. The calculations on the 700-atom supercell of the $\Sigma=31$ grain boundary model for both the Y-doped and undoped cases were carried out on the ORNL supercomputer (Cheetah) using up to 256 nodes at a time.

Additional ball and stick models of the 7-membered rings in both the undoped grain boundary and the Y-doped grain boundary are shown here in figures S1A and S1B. By comparing these illustrations with Figure 4 will aid in observing the increase in bonding coordination from the undoped case to the Y-doped case. The total number of oxygen bonded to the Al ions in the middle column is 19, yielding a coordination of 4 for two of the Al ions and 5 for the other two Al ions. Due to the boundary conditions of the supercell, only 26 of the 27 Y-O can be seen by comparing the illustrations. The full 27 bonds yields a coordination of 6 for one of the Y ions and a coordination of 7 for the remaining three Y ions.

**Figure S1:** Ball and stick models drawn from a tilted perspective for the 7-membered ring (A) in the undoped case and (B) in the Y-doped case.


