Classical and Hybrid Density-Functional/Classical Molecular Dynamics Study of Dislocation Core in Alumina Ceramic

Kenji Tsuruta¹, Toshiyuki Koyama² and Shuji Ogata³

¹Graduate School of Natural Science and Technology, Okayama University, Okayama 700-8530, Japan
²Computational Materials Science Center, National Institute for Materials Science, Tsukuba 305-0047, Japan
³Graduate School of Engineering, Nagoya Institute of Technology, Nagoya 466-8555, Japan

We perform molecular-dynamics simulations to investigate the atomic and electronic structures of a basal edge dislocation in α-Al₂O₃. The core structure consisting of two non-stoichiometric partial dislocations, which has been recently proposed by an experiment, is examined by an empirical interatomic-potential model and by a hybrid quantum/classical approach. The atomic rearrangements in the full and in the partial dislocation cores are analyzed. The local electronic structure in the full dislocation core is evaluated by the density-functional method applied for a quantum-cluster region in the hybrid simulations. Interaction potentials between partial dislocations are investigated by the classical model. Results preliminarily obtained show that the partials aligned normal to a basal plane ((0001)) has a short-ranged repulsive nature approximately within 8 Å.

Keywords: molecular dynamics, hybrid quantum/classical method, dislocation core, alumina

1. Introduction

Despite the industrial importance of ceramics as structural and electrical materials, the detailed structures of dislocations in oxides are still controversial mainly due to their complication of the basic crystalline structures. Recent progress of high-resolution electron microscopes has enabled one to obtain the atomic-level information in such nanostructures which had not been observed directly. Shibata et al. have reported recently their experimental analysis, based on the scanning transmission electron microscopy (STEM), on the structures and migration properties of a basal edge dislocation with the Burger’s vector \( \mathbf{b} = 1/3(\overline{1}120) \) in \( \alpha\text{-Al}_2\text{O}_3 \). They have also proposed a dissociation mechanism of the full dislocation core into a pair of partial dislocations with \( \mathbf{b}_1 = 1/3(0110) \) and \( \mathbf{b}_2 = 1/3(1010) \) by considering gliding and self-climbing along the direction normal to the basal plane. These proposed mechanisms of the dislocation motions should be confirmed from an atomistic-level theory and/or simulation.

Atomistic simulations have been playing important roles in unveiling the properties and the mechanisms of materials processes which are not accessible by experiments. Nowadays, classical molecular dynamics method based on empirical interatomic potentials can handle billions of atoms using parallel computers and has been used to study statistical properties of materials at finite temperatures. However, in using the method for delicate structures, such as defects and impurities in oxides, the accuracy and the transferability of the potential model has to be validated to assess the results, which is not always possible. The first-principles molecular-dynamics method, based on the density-functional (DF) theory, is a powerful tool to obtain detailed information on atomic and electronic structures in nanometer scale within experimental accuracy. It has, however, serious limitation in applying the method to analysis on extended defects in materials due to the scaling properties of computing time of the method, which is proportional to \( N^3 \) where \( N \) is the number of electron in the system. A dislocation pair, in which the number of atoms in a primitive unit exceeds likely one thousand, is such a system that the density-functional method is hardly applicable unless the extremely high-end supercomputers are available to use freely for months.

In the present study, we combine a classical molecular-dynamics (MD) and a hybrid quantum/classical MD approaches to study the dislocations in alumina. In the hybrid method, the core regions of dislocations, where the atomistic and electronic structures may be qualitatively different from those in bulk, are simulated by a cluster calculation based on the DF method whereas other crystalline regions are modeled by an empirical interatomic potential. This method has been applied successfully various system and phenomena such as hydrogen-atom diffusion in silicon at high temperatures and effects of \( \text{H}_2\text{O} \) on fracture initiation in silicon. In the present study, this method is applied to analyzing atomic and electronic structures of dislocation core in \( \alpha\text{-Al}_2\text{O}_3 \). The Mulliken’s atomic charges and the local density-of-states of the dislocation core are evaluated by the DFT calculation for the cluster. Partial dislocations and their mutual interactions are investigated via the classical MD simulations. The purpose of the analysis is to examine the stabilization mechanism of the partial dislocation pair observed recently by the STEM.

2. Computational Methods

The empirical interatomic potential for alumina, proposed by Vashishta et al., consists of two- and three-body terms: The two-body term includes steric-size effects, Coulomb interactions, charge-induced dipole, and van der Waals interactions. The three-body interaction potential is given by a product of spatial and angular dependent factors to correctly describe bond-bending and bond-stretching characteristics. The cohesive energy, elastic constants, bulk
modulus, melting temperature of the corundum phase, and basal slip process during impact damages is well described.\textsuperscript{11)}

MD simulations with the proposed interatomic potential for the liquid state are also in good agreement with the experimental results obtained through neutron and x-ray structure factors.

We have recently developed a hybrid quantum-mechanical (QM)/classical (CL) method,\textsuperscript{12)} similar to what is called ONIOM method,\textsuperscript{13)} i.e. a quantum region is embedded in the (classical) total system via the “handshake atoms”. In the hybrid method, the total Hamiltonian of the hybrid system is defined as:

\[
H = H_{\text{MD}}^{\text{system}}(\mathbf{r}_{\text{all}}, \mathbf{R}_{\text{all}}) + \sum_{\text{QM regions}} [E_{\text{cluster}}(\mathbf{r}_{\text{QM}}), E_{\text{HS}}^{\text{CL}}(\mathbf{r}_{\text{QM/MD}})] - L_{\text{CL}}(\mathbf{r}_{\text{QM}}, \mathbf{r}_{\text{HS}}^{\text{CL}})]
\]

where the first term represents the Hamiltonian for the whole system modeled by the sum of kinetic energies of the nuclei and a classical interatomic potential, and the second and third terms in eq. (1) are the potential energy for “QM cluster”, modeled by a quantum-mechanical DF Hamiltonian, and that for “CL cluster” described by the classical interatomic-potential model, respectively.

In the second and third terms in eq. (1), the abbreviation “HS” on the atomic position (\(\mathbf{r}_{\text{HS}}\)) stands for the “Handshake atoms”, which bridge between the atoms in the outermost shell of the QM cluster and their nearest neighbor atoms in the original total system. Species of the “HS” atoms is chosen to be aluminum, as suggested in Ref. 7). We have adjusted the relative position of the HS atoms along the QM-CL atomic bond by minimizing the discrepancy of atomic forces on the QM atoms bonded with the HS atoms in the perfect crystal. In the present study, the cluster is assigned for a cylindrical region around a dislocation core. The periodic-boundary condition is therefore applied along the direction parallel to the dislocation, i.e. [1100] in Fig. 1.

For the calculations of QM cluster, we employ the real-space density-functional (DF) method.\textsuperscript{13)} The detailed scheme in this method has been published elsewhere.\textsuperscript{14)} Cartesian mesh points in real space are used to represent the Kohn-Sham (KS) orbitals and Hartree potential. The mesh size is set to be 0.29 Å, which corresponds to approximately a cutoff energy of 33 Ry in the plane-wave representation of the KS orbitals. Data on the mesh points are spatially decomposed, stored, and calculated in each computing nodes on a parallel computer. The kinetic-energy operators in the KS Hamiltonian are calculated by the finite-difference method with 6th order polynomials. Only valence electrons are considered with the normconserving pseudopotentials. The generalized gradient approximation to the exchange correlation potential of the electrons is adopted with the partial-core correction. Numerical solutions of the KS orbitals and of the Hartree field are obtained on the mesh points with the multigrid method\textsuperscript{15)} for accelerated convergence in the selfconsistent-field iterations. The effective charge on each atomic site is evaluated via the Mulliken’s population analysis,\textsuperscript{9)} where the wave functions for occupied states are projected onto atomic basis centered at each atomic site. The cutoff radius for the projection is chosen to be 5.29 Å.

3. Results

3.1 Atomic and electronic structures of a full dislocation core

Figure 1 depicts a pair of the full dislocations in the crystalline \(\alpha\)-Al\(_2\)O\(_3\), with the number of atoms 3420. Each full dislocation (\(b = 1/3(1120)\)) consists of a pair of an Al-terminated and an O-terminated partial dislocation. Each partial dislocation is the mixed dislocation with either \(b_1 = 1/3(0110)\) or \(b_2 = 1/3(1010)\) that is constructed by inserting the column of Al-O atomic half layers normal to (0001) with respected termination at the basal slip plane. In the present model in Fig. 1, the two partials are adjacent so that there is no stacking fault in the dipole of the full dislocations.\textsuperscript{3,4)}

To obtain a stable atomic structure of the system described above, we first remove the two adjacent A-O atomic half layers normal to the slip planes from the crystalline alumina, and then relax the system by the classical molecular dynamics (MD) with the steepest-decent algorithm.\textsuperscript{16)} The periodic simulation box is optimized simultaneously in the MD relaxation process. From the MD-relaxed system, we prepare the QM and CL clusters of cylindrical shape with radius of 14 Å, as shown in Fig. 1. These clusters involve 144 atoms with 21 HS atoms. We then apply the hybrid QM/CL MD method, described in the previous section, to stabilization of the system. We again employ the steepest-decent quenching process in the MD simulation.

Atomic structure of the relaxed dislocation core is also depicted in Fig. 1. During the relaxation processes, the atoms surrounding the core tend to move slightly along the slip plane so as to adjust the local mismatch of the Al-O sequences normal to the plane. On the other hand, the atoms exposed to the core surface are remained under-coordinated, i.e., five fold at Al sites and three fold at O sites, whereas six fold at Al and four fold at O in the crystal.

Local electronic structure is characterized by results of the DF calculation of the QM cluster. Figure 2(a) shows histogram of the electronic eigenlevels in the relaxed QM cluster compared with the density-of-states (DOS) in the bulk.
crystal. An analysis reveals most of the eigenstates above the highest-occupied level ($E_F$) are localized at the cluster surface, meaning that these states are mainly artifacts due to the cluster calculation adopted in the present method and are not expected to affect significantly the ground-state properties of the system. Also, it implies that existence of the under-coordinated atoms on the dislocation core is signaled by the levels below the highest-occupied level appeared above valence-band top of the bulk DOS.

Figure 2(b) depicts results of the Mulliken’s population analysis\(^9\) of the QM cluster. The deviations of the effective charge on each atom around the dislocation core from the crystalline value for each species are plotted as a function of distance from the center of the core. This figure clearly shows that deviations of charge transfer in O atoms are smaller than those in Al atoms. Moreover, large deviation of Al charge remains beyond the first shell from the core surface despite that the under-coordinated Al atoms exists only on the innermost shell. This may be attributed to the non-directional nature of bonding to the O atoms whereas an Al-O bonding is highly direction-dependent around the Al atom. Small distortion of molecular unit around Al atoms affects localized $d$-states significantly. It results in exchange of electronic occupations among $s$, $p$, and $d$ states so as to adjust bonding strength against the local distortion.

### 3.2 Interaction between partial dislocation cores

Experimentally,\(^3,^4\) the basal dislocation in $\alpha$-alumina is observed to dissociate into two partial dislocations at low temperature, i.e. $1/3\{11\overline{2}0\} \rightarrow 1/3\{01\overline{1}0\} + 1/3\{10\overline{1}0\}$, and to recombine at high temperature. To quantify this phenomenon from the atomistic analysis, we estimate an interaction energy between dislocations within the classical interatomic-potential model. Figure 3 illustrates the atomic positions of the $\alpha$-alumina systems with partial dislocations inserted with various mutual distances along [0001]. We prepare the initial conditions for each partial dislocation similarly as described in the previous section for the full dislocation. We then relax the systems by the MD quenching based on the classical potential model.

Figure 4 depicts potential energy per atom as a function of the partial-core distance, $\Delta z$, defined in Fig. 3(d). The figure shows asymptotic increase of the energy for distance beyond 7.5 Å. This observation is consistent with that as the distance between these partials increases, energy of the stacking-fault (SF) formed on the $\{11\overline{2}0\}$ plane between these partials increases. On the other hand, at shorter distance than 7.5 Å, it exhibits a weak repulsive character of the interaction energy between the partials. The energy required to sustain an adjacent pair of the partials is larger than that required for each individual partial. This may be due to large stress...
intensity around the core of the full dislocation. This is a unique feature found in the present analysis, but it should be verified by more accurate interaction models.

4. Concluding Remarks

Combining the classical interatomic-potential model and the hybrid density-functional/classical molecular dynamics, we have investigated the atomic and electronic structures in the stoichiometric dislocation core in $\alpha$-Al$_2$O$_3$. The core structure consisting of two non-stoichiometric partials is found to be locally stable. The electronic density-of-states in the cluster calculated by the real-space density-functional method has indicated a signature of the under-coordinated atoms in the core surface. The Mulliken’s population has been calculated to characterize the local electronic structure around the dislocation core. It has revealed the large deviation of the local electronic states on Al atoms around the core from that of bulk value whereas the electronic states for O atoms remain qualitatively unchanged.

The interaction energy between dissociated partial dislocations is also calculated in the classical model. It has indicated an attractive character between partials due to the existence of the stacking fault between pair of the partials. A short-ranged repulsive like potential has, on the other hand, been observed for distance below 7.5 Å. These features may be attributed to the multiple effects, such as a strain field around the dislocation core, the stacking fault between two partials, and a long-ranged Coulomb interaction between line charges on the non-stoichiometric dislocation cores. Further analysis on these elements is in progress using the hybrid method with larger QM cluster and a variable-charge interatomic model.

Acknowledgement

This work was supported by Grant-in-Aid for Scientific Research on Priority Areas “Nano Materials Science for Atomic Scale Modification 474” from MEXT of Japan.

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