Kinetic Monte Carlo Simulation of Oxygen Diffusion in Ytterbium Disilicate

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Introduction

Silicon-based ceramic components for next-generation jet turbine engines offer potential weight savings, as well as higher operating temperatures, both of which lead to increased efficiency and lower fuel costs. Silicon carbide (SiC), in particular, offers low density, good strength at high temperatures, and good oxidation resistance in dry air. However, reaction of SiC with high-temperature water vapor, as found in the hot section of jet turbine engines in operation, can cause rapid surface recession, which limits the lifetime of such components. Environmental Barrier Coatings (EBCs) are therefore needed if long component lifetime is to be achieved.

Rare earth silicates such as Yb$_2$Si$_2$O$_7$ and Yb$_2$SiO$_5$ have been proposed for such applications; in an effort to better understand diffusion in such materials, we have performed kinetic Monte Carlo (KMC) simulations of oxygen diffusion in Ytterbium disilicate, Yb$_2$Si$_2$O$_7$. The diffusive process is assumed to take place via the thermally activated hopping of oxygen atoms among vacancy or interstitial sites. Migration barrier energies are computed using density functional theory (DFT).

β-YTTERBIUM DISILICATE STRUCTURE

β-Ytterbium disilicate exists in a distorted monoclinic phase that is stable from near room temperature to at least 1600°C. The space group is C2/m [11]; with lattice parameters a = 8.620 Å, b = 8.872 Å, c = 4.703 Å, α = 90.0°, β = 102.12°, γ = 90.0°.

The unit cell, which contains two eleven-atom Yb$_2$Si$_2$O$_7$ chemical units, is shown in Figure 1. All oxygen atoms are contained within a double-tetrahedron structure, with the two tetrahedra sharing a common oxygen atom. There are three distinct oxygen sites, with different symmetries, and therefore different coordination.

KINETIC MONTE CARLO METHOD

• The KMC method is designed to investigate the dynamical evolution of a system.

• It is particularly well suited for the study of “infrequent event” systems, in which the events of interest are widely separated spatially or temporally.

• It treats the events of interest in detail while incorporating only the average behavior of the system between events.

• It is often substantially more efficient than molecular dynamics simulations for such systems.

KMC procedure for diffusive hopping

• Events of interest are thermally activated diffusive hops among vacancy or interstitial sites. Migration barrier energies are computed using density functional theory (DFT). All hops are assumed to be uncorrelated.

• A Yb disilicate computational cell is created that includes vacancy and interstitial concentrations appropriate for the simulation temperature.

• All potential hops within the cell are identified and the event hopping rates are computed as $\nu_{\text{ hopping}} = \nu_0 \exp(-E_{\text{ barrier}} / k_B T)$ in which $\nu_0$ and $E_{\text{ barrier}}$ are the hopping rate and migration barrier energy for a hop between lattice or interstitial sites A and B respectively, and $\nu_0$ is the frequency factor, typically assumed to be between $10^{13}$ and $10^{16}$.

Results and Discussion

The lattice constant a was optimized using DFT, assuming the ratios b/a and c/a and angle β were as reported by Smolak. All calculations were performed using the VASP density functional code, with projector augmented wave pseudopotentials, and using the generalized gradient approximation (GGA). The value obtained was 7.543 Å, larger than value reported by Smolak by 3.5%, consistent with DFT-GGA's tendency to underbond.

Vacancy-mediated diffusion

Vacancy site preferences were determined by computing the energies of relaxed unit cells having vacancies at O1, O2, and O3 sites. The O1 site is lowest in energy, and the O2 and O3 site energies were larger by 0.67 eV and 0.61 eV, respectively.

Vacancy formation energies were found to be 3.95 eV, 4.06 eV and 4.02 eV for the O1, O2 and O3 vacancy sites, respectively. The intrinsic concentrations of vacancies at the three oxygen sites were computed as $C_v = \exp\left(-\frac{E_v}{k_B T}\right)$ where the values range from $10^{-10}$ at 1000°K to $10^{-9}$ at 2000°K. In all cases, the intrinsic vacancy concentration is so small that oxygen permeation in the pristine material is unlikely to be problematic.

Diffusion Paths and Barrier Energies

Oxygen coordination histograms for the three oxygen sites are shown in Figure 2a-c. O1 sites have the simplest coordination, with nearest neighbors lying within the two tetrahedra that form the Si$_2$O$_7$ complex.

O2 and O3 sites show more complex coordination. Within the same tetrahedron, the O1-O2 and O1-O3 distances are slightly smaller than O2-O3 and O3-O3 distances, indicating a distorted structure. A second neighbor shell involves atoms in other complexes, but the interatomic distances are not much larger than the intra-tetrahedral ones. The O2 sites' third neighbor shell is much further away, while the O3 sites show neighbors lying within a broad range of distances.

KMC Simulations

A kinetic Monte Carlo code developed in our laboratory was used, along with the energy barriers as described above. Simulations were performed at temperatures of 1000°K, 1250°K, 1500°K, 1750°K, and 2000°K, with 1750°K being close to the target operating temperature of components to be protected by these coatings. Each run consisted of 5 x $10^{8}$ events, and each diffusivity is an average over ten runs.

Interstitial Diffusion

Defect formation energies for oxygen atoms located at various interstitial sites were computed. The formation energy in this case is defined as the difference between the energy of a cell containing an interstitial atom, and the sum of the energies of a perfect cell and an oxygen atom in its reference state. Three stable interstitial points were identified via structural minimization, and the interstitial formation energy was calculated for each, with values between 1.4 eV and 2.3 eV. The magnitude of these energies indicates that the concentration of interstitial oxygen atoms, which is larger than the concentration of vacancies, will still be relatively low.

Interstitial migration barriers were computed for several possible diffusion paths; the migration barriers are about 1 eV, indicating that the diffusivity is considerably larger than the case for vacancy-mediated diffusion, and this has been confirmed in preliminary KMC simulations.

When both the diffusivity and interstitial concentration are considered, it appears that the interstitial diffusive flux through the material will be larger than the vacancy-mediated flux, but will be small enough that it will likely not be of major concern for the proposed application.

Conclusions

Vacancy-mediated oxygen diffusivities from kinetic Monte Carlo simulations are small, as long as only intrinsic oxygen vacancies are considered. The addition of extrinsic vacancies to the simulations can produce diffusivities orders of magnitude larger, though it is not known whether such vacancies exist in the required numbers in the real material.

Predicted interstitial diffusivities are considerably larger than vacancy mediated diffusivities. The interstitial defect formation energies are positive, suggesting that the concentration of interstitial defects in Yb$_2$Si$_2$O$_7$, while larger than the vacancy concentration, will be small enough that significant oxygen permeability via this mechanism is unlikely to occur.

Yet to be considered are more complex diffusion mechanisms, for example, diffusion along paths connecting vacancy and interstitial sites; this mechanism is currently under investigation.

Table 1—Low-energy hopping paths

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<th>Path type</th>
<th>Location</th>
<th>Forward barrier, eV</th>
<th>Reverse barrier, eV</th>
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<td>1.38</td>
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</table>

Figure 3—Vacancy-mediated oxygen diffusivities