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 oxygen vacancy sites or among 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 (12), with lattice parameters a = 6.802Å, b = 8.875Å, c = 4.703Å, α = 90.0°, β = 102.12°, γ = 90.0°.

The unit cell, which contains two tetrahedron 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 $v_{AB} = \exp(-\Delta E/RT)$ in which $\Delta E$ and $E_0$ are the hopping rate and migration barrier energy for a hop between lattice or interstitial sites A and B respectively, and $v$ is the frequency factor, typically assumed to be between $10^{11}$ and $10^{12}$.

KMC procedure for diffusive hopping (continued)

• The probability for each possible hop can be computed from the hopping rate, with $P_{AB} = \frac{v_{AB}}{\sum v_{ij}}$, where $i$ is the sum of hopping rates for all possible hops in the computational cell. Event displacement vectors and probabilities for all hops accessible to the system are included in an event catalog.
• An event is chosen from the catalog stochastically, based on the event probabilities, and executed. The execution of such an event makes a number of new events accessible to the system, while a number of previously-accessible events become inaccessible.
• Event probabilities for the newly-accessible events are computed. The newly-accessible events and probabilities are added to the event catalog, and the newly-inaccessible events and probabilities are deleted.
• The simulation clock is advanced stochastically by an amount by $\Delta t = \frac{1}{\sum v_{ij}}$, where $\Delta t$ is a random number, $0 < \Delta t < 1$.
• The process proceeds until an appropriate number of events have been executed.

• When the simulation has finished, the total elapsed time, $t$, and the mean square displacement, $<R^2>$, averaged over all vacancies, is computed.
• The migration diffusion D is obtained from the Einstein relation $<R^2> = 6Dt$.

Results and Discussion

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 sites were larger by 0.86eV and 0.81eV, respectively.

Vacancy formation energies were found to be 3.59eV, 4.06eV, and 4.05eV for the O1, O2, and O3 vacancy sites, respectively. The intrinsic concentration of vacancies at the three oxygen sites were computed as $C_v = \exp(-\Delta E/RT)$, where $\Delta E$ is the vacancy formation energy. Values range from $10^{-11}$ to $10^{-10}$ at 2000K.

Oxygen coordination histograms for the three oxygen site types are shown in Figure 2. Oxygen coordination histograms for oxygen sites (a) O1, (b) O2, (c) O3.

Path 1—Oxygen coordination histograms for oxygen sites (a) O1, (b) O2, (c) O3.

Diffusion Paths and Barrier Energies

Oxygen coordination histograms for the three oxygen site types are shown in Figure 2. 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 O2-01 and O2-03 distances are slightly smaller than O2-02 and O2-03 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' first neighbor shell is much further away, while the O3 sites show neighbors lying within a broad range of distances.

The lowest-energy paths for each possible interatomic path are shown in Table 1. Within a tetrahedron, the lowest-energy paths are the O3-03 and O2-03 sites. The barriers for paths involving an O1 site are substantially larger, indicating that diffusive hops involving O3 sites are the most probable. Hopping paths between sites on different tetrahedra in the same complex are in general not energetically favorable. Intercell complex hopping involving O1-03, O2-02 and O2-03 paths are higher in energy than the most intracell complex hops, indicating that intercomplex hops will likely be the rate-limiting process.

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 1000K, 1250K, 1500K, 1750K, and 2000K with 1750K being close to the target operating temperature of components to be protected by these coatings. Each run consisted of 5 x $10^5$ events, and each diffusivity is an average over ten runs.

Interrstitial 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 perfect 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 sites 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, which is larger than the concentration of vacancies, will still be relatively low.

Interrstitial migration barriers were computed for several possible diffusion paths; the migration barriers are about 1 eV, indicating that the diffusivity is considerably larger than is 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 diffusivity 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>1.5</td>
<td>2.0</td>
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<td>1.5</td>
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<td>0.8</td>
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