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, high 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$_4$ 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 $a = 6.802\text{Å}$, $b = 8.875\text{Å}$, $c = 7.053\text{Å}$, $\alpha = 90.0^\circ$, $\beta = 102.12^\circ$, $\gamma = 90.0^\circ$.

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-tetrahedral structure, with the two tetrahedra sharing a common oxygen atom. There are three distinct oxygen sites, with different symmetries, and therefore different coordination.

![](image)

Figure 1—Yb$_2$Si$_2$O$_7$ structure, (001) plane. Yb (light blue), Si (dark blue), Oxygen (red). In each tetrahedron, type O1 atoms are shared with another tetrahedron. Of the remaining three atoms, one is type O2 and two are type O3.

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 in space or time.
- 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 were 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 $v_{j} e^{-E_{j}/k_{B}T}$ in which $v_{j}$ and $E_{j}$ are the hopping rate and migration barrier energy for a hop between lattice or interstitial sites A and B respectively, and $k_{B}$ is the frequency factor, typically assumed to be between $10^{11}$ and $10^{13}$.

KMC procedure for diffusive hopping (continued)
- The probability for each possible hop can be computed from the hopping rate, with $P_{j} = v_{j} e^{-E_{j}/k_{B}T}$ 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 $\Delta t = \frac{v}{\sqrt{2 \pi}}$, where $v$ is a random number, $0 < v < 1$.
- 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, $<\Delta r^2>$, averaged over all vacancies, is computed.
- The diffusion $D$ is obtained from the Einstein relation $<\Delta r^2> = 2D_{o}t$.

- In the case of vacancy-mediated diffusion, it is convenient to track vacancies rather than oxygen atoms. In this case the oxygen diffusivity $D_{o}$ is obtained by multiplying the number of oxygen vacancy and atomic hops:

$$D_{o} = 1 \times 10^{-3} C_{V}$$

where $C_{V}$ is the concentration of vacancies.

Because the coordination of the three types of oxygen atoms is complex, we have investigated a variety of potential diffusion paths. We consider three types of paths:

1. Paths connecting atoms within a single tetrahedron.
2. Paths connecting atoms in different tetrahedra of a double-tetrahedron complex.
3. Paths connecting atoms in different double tetrahedron complexes.

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.

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 $10^{12}$ events, and each diffusivity is an average over ten runs.