Kinetic Monte Carlo Simulation of Oxygen Diffusion in Ytterbium Disilicate

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ABSTRACT

Ytterbium disilicate is of interest as a potential environmental barrier coating for aerospace applications, notably for use in next generation jet turbine engines. In such applications, the transport of oxygen and water vapor through these coatings to the ceramic substrate is undesirable if high temperature oxidation is to be avoided. In an effort to understand the diffusion process in these materials, we have performed kinetic Monte Carlo simulations of vacancy-mediated and interstitial oxygen diffusion in Ytterbium disilicate. Oxygen vacancy and interstitial site energies, vacancy and interstitial formation energies, and migration barrier energies were computed using Density Functional Theory. We have found that, in the case of vacancy-mediated diffusion, many potential diffusion paths involve large barrier energies, but some paths have barrier energies smaller than one electron volt. However, computed vacancy formation energies suggest that the intrinsic vacancy concentration is small. In the case of interstitial diffusion, migration barrier energies are typically around one electron volt, but the interstitial defect formation energies are positive, with the result that the disilicate is unlikely to exhibit experience significant oxygen permeability except at very high temperature.

INTRODUCTION

Ceramic matrix composite (CMC) materials are under consideration for use in next-generation jet turbine engines, due to their thermomechanical properties. However these Si-based ceramics are susceptible to oxidation at high operating temperatures, and thus require the use of an environmental barrier coating. Ytterbium and Yttrium silicates are being considered for this role, and the diffusion of oxygen and water vapor through such coatings are of concern. [1] In this work, we describe combined ab initio and kinetic Monte Carlo (kMC) studies of oxygen diffusion in Ytterbium disilicate ($Yb_2Si_2O_7$). 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) [2].

β-Ytterbium disilicate exists in a monoclinic phase that is isostructural with thortveitite, stable from near room temperature to at least 1600C [3]. The space group of the monoclinic phase is C2/m (12), and the lattice parameters are a=6.802Å, b=8.875Å, c=4.703Å, and β = 102.07°[4]. The unit cell contains two $Yb_2Si_2O_7$ units, as shown in Figure 1. There are three distinct types of oxygen sites (O1, O2 and O3) within the cell. It can also be seen that all silicon atoms are tetrahedrally bonded to oxygens, and all oxygen atoms are contained within structures consisting of two tetrahedra which share a common vertex; there are no structural interstitial atoms, as there are in some other disilicates, notably Y_2SiO_5.

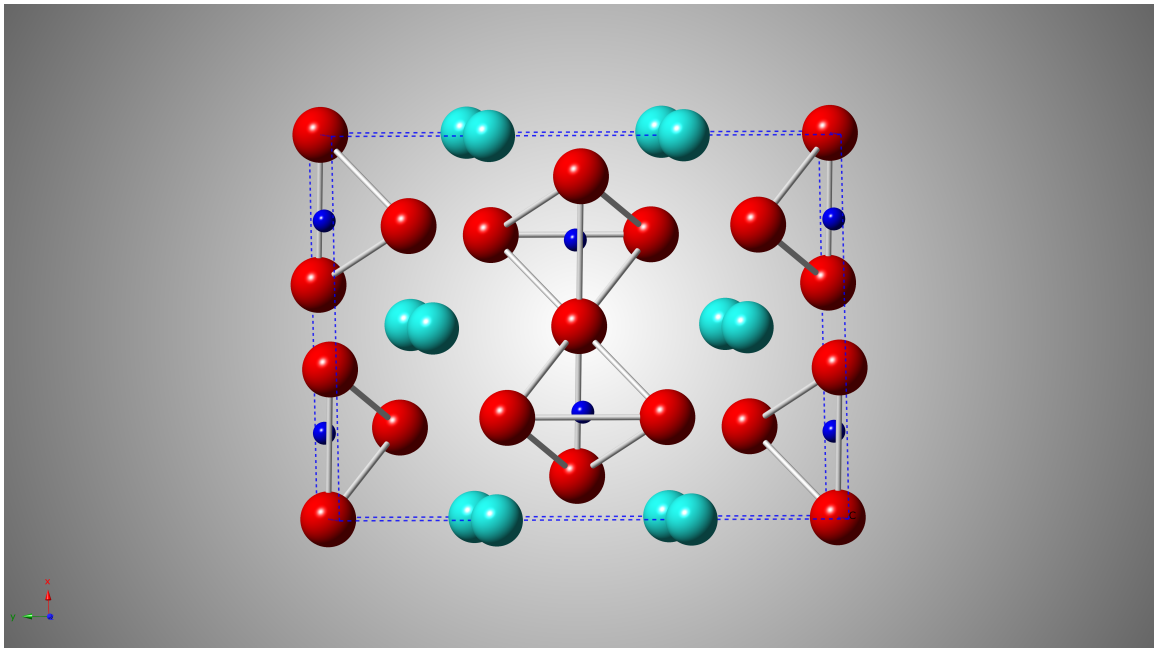

Figure 1—$Yb_2Si_2O_7$ structure, (001) plane. Yb (large, light blue), Si (small, dark blue), Oxygen (large, red). In each tetrahedron, type O1 atoms are shared with another tetrahedron. Of the remaining three atoms, one is type O2 and two are type O3.

KINETIC MONTE CARLO METHOD

"Infrequent event" systems are those in which the events of interest are temporally separated from each other by relatively long periods during which no such events take place. Diffusive hopping is an example of such a system. The kinetic Monte Carlo (kMC) simulation method is particularly suited for the study of such systems, and can be orders of magnitude more efficient than molecular dynamics [5]. The method considers in detail the events of interest but treats the evolution of the system between such events only statistically. The kMC method does not produce detailed atomic trajectories, but can be used to calculate certain properties such as diffusivities quite efficiently [5]. A detailed description of the method is beyond the scope of this paper, but is provided by Voter [5].

Diffusion via the hopping of atoms among crystalline or interstitial sites is common, and such diffusion is usually considered a thermally activated process at all but the lowest temperatures [6]. Such a model, along with the simulation method described here, has been used to accurately simulate oxygen diffusion in similar materials, e.g. yttria-stabilized zirconia [7]. The hopping rate for a diffusive hop between sites A and B is given by $\nu_{AB} = \nu^0 \exp(-E_{AB}/k_B T)$, where ν_{AB} and E_{AB} are the hopping rate and migration barrier energy, respectively, and ν^0 is a frequency factor representative of atomic vibrational frequencies. ν^0 is typically assumed to be on the order of $10^{13}s^{-1}$. When the hopping rate is known, the hopping probability can be obtained, with $P_{AB} = \nu_{AB}/\Gamma$, in which Γ is the sum of hopping rates for all hops accessible to the system.

A model system is established, typically consisting of a number of random walkers that may represent oxygen vacancies or interstitial oxygen atoms. An event catalog is then created which contains information on the direction and magnitude of all hops, along with the corresponding hopping probabilities. The simulation proceeds iteratively, with a sequence of events chosen stochastically from the catalog. A chosen event is executed, and the event catalog updated; entries describing hops no longer accessible are replaced by entries describing hops newly accessible to the system. After each such event, the simulation clock is advanced stochastically by an amount $\Delta t = -\ln(R)/\Gamma$, with $0 < R \leq 1$ a random number. After a sufficient number of events have been executed, the diffusivity D can be obtained from the Einstein relation $<R^2> = 6\ D\ t$, where t is the total elapsed simulation time. In the case of vacancy-mediated (though not interstitial) diffusion, it is convenient to track the motion of vacancies, rather than atoms, in which case the simulation produces the vacancy diffusivity. In the case of vacancy-mediated diffusion, it is convenient to track the motion of vacancies rather than atoms; the resulting vacancy diffusivity may be converted to atomic diffusivity by multiplying the vacancy diffusivity by a concentration factor $C_v/(1-C_v)$, where C_v is the vacancy concentration.

RESULTS AND DISCUSSION

All calculations were performed using density functional theory (DFT) incorporating the plane-wave pseudopotential scheme as implemented in the Quantum Espresso [8] and VASP [9] suites of computer codes. The calculations used functionals incorporating the Generalized Gradient Approximation [10] of Perdew, Burke and Ernzerhof , and were carried out using a 1x1x1 periodic cell. While it might be advantageous to use a larger supercell so as to allow atomic relaxations to take place over a larger volume, the 1x1x1 cell is fairly large, containing 22 atoms. Given the large number of potential diffusion paths that were investigated, the use of larger supercells was deemed impractical. Higher-fidelity calculations of barrier energies for a smaller number of low-energy paths are in progress.

We first performed an optimization of the lattice constant *a*, keeping the ratios *b/a* and *c/a* and the angle β as reported by Smolin [3]. The value obtained was 7.043Å, larger than the value reported by Smolin by 3.5 percent, consistent with the known tendency of the Generalized Gradient Approximation to underbind.

Vacancy Mediated Diffusion

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 the two tetrahedra of a double tetrahedron complex.
(3) Paths connecting atoms in different double tetrahedron complexes.

Vacancy formation energies (VFEs) for oxygen vacancies located at each of the three oxygen site types were calculated. The VFE is defined as the energy difference between a perfect crystalline cell, and the sum of the energies of a cell containing an oxygen vacancy, and a single oxygen atom in its reference state. The oxygen reference state energy was taken to be one-half the energy of an isolated diatomic oxygen molecule. All atoms in the disilicate cell were allowed to fully relax. The VFEs for oxygen sites types 1,2 and 3 were calculated to be 3.59 eV , 4.0 eV and 4.20 eV, respectively. The vacancy formation energies are large enough that the concentration of intrinsic oxygen vacancies will be small, even at high temperatures, suggesting that, regardless of the magnitude of the diffusivity, oxygen permeation through these coatings will be small.

However, the operating environment experienced by coatings of these materials can be extreme. In addition to high temperatures, coatings may experience attack by foreign substances, notably reactive glasses, which can cause significant structural and chemical modification of the disilicate surface. Because the chemistry of such processes is not well understood, the presence of extrinsic oxygen vacancies cannot be ruled out, and we include kMC simulations carried out for situations where the extrinsic oxygen concentration is substantially larger than the intrinsic concentration.

The migration barrier energy is defined as the energy difference between a cell containing a hopping oxygen at its initial position, and a cell with the oxygen atom at the saddle point along the diffusion path. Because of the complexity of the monoclinic unit cell, it is not obvious which paths will involve low-energy barriers. We therefore calculated paths for all hops involving atoms within 10 a.u. of each vacancy. Such paths are numerous enough that the use of computationally intensive saddle point search methodologies such as the nudged elastic band (NEB) method is impractical. Approximate saddle point locations were determined by computing a number of energies along the straight path between a hopping atom's initial and final positions. Once the maximum energy along the path was located, the energies of a small cluster of points at or near the maximum energy point were computed, and the location of the approximate saddle point was obtained using a polynomial fit of the energies in the plane perpendicular to the initial path.

Migration barrier energies range from 0.6eV to 7.4eV. The lowest-energy paths are those connecting two O3 atoms, and O3 and O2 atoms, within the same tetrahedron. The smallest barriers for paths between different complexes are in the range of 1.7eV to 3.5eV, making these the rate-limiting hops.

Diffusivities are shown in Figure 2 for temperatures ranging from 1000K to 2000K, for both the intrinsic vacancy concentration, and assumed extrinsic concentrations of 10^{-3}, 10^{-5} and 10^{-7}. It is clear that, in the absence of extrinsic vacancies, the vacancy-mediated diffusivity is small.

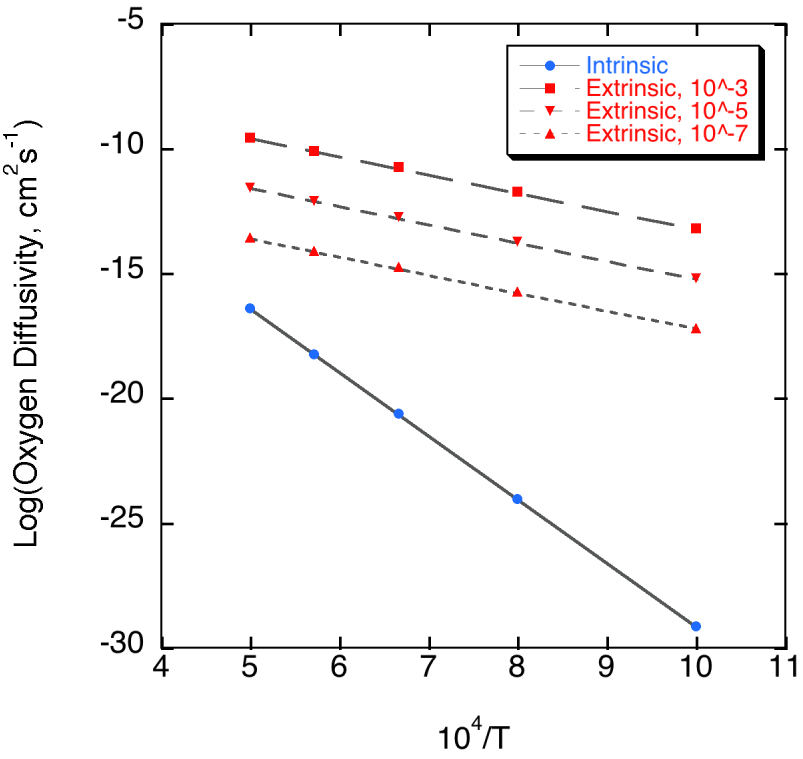

Figure 2—Vacancy mediated diffusivity versus temperature

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.

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

While the interstitial defect formation energies are smaller than the vacancy formation energies, the concentration of interstitials will be larger than the concentration of intrinsic vacancies. However, the concentration is small enough that oxygen permeation is likely to be small as well.

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 $Yb_2Si_2O_7$, 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.

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