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Ab initio prediction of threshold displacement energies in ZrC

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ABSTRACT

The threshold displacement energies (E_d) of C and Zr atoms in ZrC have been determined using *ab initio* molecular dynamics simulation. The values of E_d have been predicted along the three main high-symmetry crystallographic directions [001], [011], and [111], and the averaged E_d values are 16 eV and 37 eV for the C and Si sublattices, respectively. We further explore the dependence of E_d on small deviations from these high-symmetry directions and on the presence of C vacancies, which are often encountered in ZrC_x alloys. The trends in values are explained in terms of the structural and chemical properties of ZrC. The predicted E_d values provide relevant parameters for future modeling of radiation damage in ZrC.

1. Introduction

Zirconium carbide (ZrC), due to its high temperature stability, oxygen gettering ability, chemical inertness and resistance to irradiation damage [1–3], is of interest as a radiation resistant structural material in the high temperature gas cooled reactor (HTGCR). However, the radiation responses of ZrC are still poorly understood, including both its high-temperature microstructural changes [4] and the origin of its superior resistance to amorphization. In fact, radiation-induced amorphization of ZrC has not yet been observed experimentally at any temperature or dose [1,4–10]. One of the key unknown parameters needed to model the irradiation response of ZrC, e.g., using SRIM simulations [11], is the threshold displacement energy (E_d).

E_d has several different definitions [12–15] and in this work we follow Ref. [15] and it is defined as the minimum kinetic energy required to produce a permanent defect on the same sublattice as the PKA, such as a stable Frenkel pair, which may or may not involve displacement of the PKA. Please see the Appendix for results following a somewhat different definition. The Kinchin–Pease and Norgett–Robinson–Torrens (NRT) models for Frenkel pair defect production under irradiation predict that Frenkel pairs will be produced by a high-energy ion in a quantity inversely proportional to the value of E_d [16]. The widely used SRIM code [11] for predicting defect production rates also requires E_d values as input. In addition, in some cases the E_d values have been associated with a material's amorphization resistance [17]. For example, in a molecular dynamics (MD) simulation of ion beam irradiation on GaN [18], the high E_d values were used to help explain the small initial damage and high dose to amorphization of GaN. It is possible that E_d values in ZrC (if they are sufficiently high) could be responsible for the unusual resistance of this material to amorphization. It is also of fundamental interest to explore if the unusual structural aspects of ZrC, in which C behaves almost like an interstitial and which can tolerate a very large number of C vacancies (a large x in ZrC_x), produces unusual values of E_d compared to nominally similar materials, e.g., SiC. In general E_d is not isotropic, which means that it can have different values for different crystallographic directions and for symmetry distinct atoms.

The value of E_d is difficult to measure experimentally, since a single defect is hard to create in irradiation experiments, and even if it can be generated, it is difficult to identify [12]. Among the computational methods, the molecular dynamics (MD) technique has been proved to be an effective and efficient way to predict threshold displacement energies [12,19,20]. MD simulations can be performed using classical interatomic potentials (which we will call Classical MD (CMD)) or *ab initio* calculations (which we will call *Ab*

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Initio MD (AIMD)). Although AIMD is far slower and more computationally demanding than CMD, it avoids the use of interatomic potentials, which have been suggested to be the largest source of errors in E_d values determined with CMD [21]. AIMD has previously been successfully applied to study E_d in SiC [12], GaN [20], and $Y_2Ti_2O_7$ [22].

Threshold displacement energies in ZrC have been previously estimated by Gosset et al. [5] who found E_d to be equal to 25 eV and 35 eV for C and Zr, respectively. However, these values were estimated based on experimentally observed values in TaC rather than in ZrC. E_d for ZrC has not been measured or calculated directly. Furthermore, no information about the anisotropy of E_d or the possible influence of ZrC_x ($x < 1$) off-stoichiometry on E_d is known.

In this work, we use AIMD simulation to calculate the E_d in ZrC. To explore anisotropy, we predict E_d along different directions for the primary knock-on atom (PKA), considering displacements both directly along high-symmetry and slightly off high-symmetry directions. We also investigate effects of the off-stoichiometric properties of ZrC_x ($0.6 < x < 0.98$) [2] by predicting the influence of C vacancies on E_d.

2. Methods

The AIMD simulations were performed with the Vienna Ab-initio Simulation Package (VASP) [23–26] in the framework of density functional theory (DFT) and the projector-augmented wave (PAW) method. The exchange-correlation was treated in the generalized gradient approximation (GGA), as parameterized by Perdew, Burke, and Ernzerhof (PBE) [27]. The PAW potentials were generated with the following valence electronic configurations: $5s4d5p$ for Zr and $2s^22p^2$ for C. An energy cut-off of 450 eV was used.

We used a $3 \times 3 \times 3$ cubic supercell of ZrC containing 216 atoms. The system-size convergence was verified by comparing the corresponding E_d values in a 64-atom cell with those in a 216-atom cell, as shown in Table A1 in the Appendix. It was found that the values agree within 5 eV except for Zr[001], where the 64 atom cell gives a large error due to a periodic boundary effect. This agreement suggests that the results for the 216-atom cell are well converged with respect to size to within a few eV or less. The large discrepancy for E_d(Zr[001]) in these two supercells is due to a “wrapping” error in the 64-atom cell, where the collision wraps across the periodic cell and the energy from the PKA effectively interacts with itself, causing a large reduction of E_d. No such obvious “wrapping” effects occurred for the 216-atom supercell simulations. In all AIMD runs, we use a single gamma point for the k-points.

Three steps are used for the AIMD simulations. In the first step, the system is equilibrated at 300 K using a Nose-Hoover thermostat (the equilibration runs). The time step is 1fs and the equilibration time lasts 1 ps. In the second step, a series of initial kinetic energies are added to the PKA to attempt to generate Frenkel pairs (the production runs). No thermostat is used in this step. The time step is 0.1fs, which was found to give a maximum displacement during one AIMD time step of about 0.02 Å, as measured in simulations for C PKA with an initial kinetic energy of 50 eV. We believe this time step is small enough as this associated maximum displacement is lower than the maximum displacement of 0.1 Å recommended by Corrales et al. [28] for calculations of excess energy in displacement cascades. After simulating for about 0.2 ps, we are able to observe whether a Frenkel pair will form or not at the given kinetic energy and thereby roughly estimate the value of E_d. To determine E_d, a velocity corresponding to the kinetic energy (E_k) was given to a C (or Zr) PKA atom. The PKA velocity was initially aligned along the three main crystallographic directions: [001], [011], and [111], as shown in Fig. 1(a) and (b). We have also checked the effects of tilting the velocity direction slightly off the high-symmetry directions (by a small angle of about $\alpha \approx 2°$). To define the tilted directions, we use the unit vector triplet ($\mathbf{e}_x$, $\mathbf{e}_y$, $\mathbf{e}_z$) to describe the velocity directions. As we know, the unit vectors along the [001], [011], and [111] are (0, 0, 1), (0, sin45°, cos45°), and (sin55°cos45°, sin55°sin45°, cos55°), respectively. The corresponding unit vectors along the [001]_tilted, [011]_tilted, and [111]_tilted are (0, sin2°,cos2°), (0, sin47°, cos43°), and (sin57°cos45°, sin57sin45°, cos53°), respectively.

In the third step in the AIMD simulations, for the initial kinetic energies around the estimate E_d from step two, longer time simulations with a time step of 1fs with a thermostat at 300 K are performed for the evolution of produced defects (the evolution runs). The stability of Frenkel pairs is tested for about 3 ps. If a stable Frenkel pair is formed in AIMD simulations, the system is then subsequently relaxed at 0 K to reach the stable configuration to ensure that the Frenkel pair is stable. To determine E_d, simulations are performed for each kinetic energy (E_k) value given to the PKA atom and E_d is set at the lowest value where a Frenkel pair is formed.

Initially all three steps are performed for each case on a course grid of energies with an energy interval of 5 eV in order to approximately determine E_d, which requires at most 10 simulations (one at each E_k value). Then about five runs with an energy interval of 1 eV around the approximate E_d determined from the coarse grid are conducted to improve the precision so that the value where the Frenkel pair is formed is accurate to within 1 eV. Once the value for E_d is known, a final longer time AIMD simulation (for about 1 ps) is checked to make sure the Frenkel pair is stable. This 1 eV range of possible values is then used as the estimated errors bars in Tables 1 and 2.

3. Results and discussion

3.1. E_d for impulses along the high-symmetry crystallographic directions

Table 1 and Fig. 2 report the results of E_d of C and Zr atoms along the main high-symmetry crystallographic directions in ZrC. Results for SiC [12,14] are also included for comparison. We include directions [111] and $[\overline{111}]$ as they are different in SiC, although they are equivalent for ZrC. We note that as the structures of ZrC and SiC are rocksalt and zincblend, respectively, the different directions do not correspond to the same environments. Therefore, differences in E_d between the two systems may be due to both their different chemistries and their different structures, and any interpretation of the origin of these differences must at least take both possibilities into account. It is shown that E_d is strongly anisotropic. It is easiest to displace C atom along the [111] direction (E_d(C[111]) $\approx 7 \pm 1$ eV) and most difficult along the [011] direction (E_d(C[011]) $\approx 20 \pm 1$ eV). This ordering can be rationalized in terms of the structure and chemistry of ZrC. In particular, the low value along the [111] direction can be explained by the fact that when the C PKA was displaced along this direction it moves into a region of significant open space and rapidly begins to form bonds with the second nearest-neighbor C atoms before colliding with the third nearest-neighbor Zr atom. This bonding effect, which stabilizes the [111] direction, does not occur in the other directions. Along the [011] direction, the C PKA kicks out its second nearest neighbor C atom along the [011] direction, the C PKA goes back to its original lattice site, and the kicked-out C atom forms a C–C dumbbell with the sixth nearest neighbor C atom of the original PKA site. Along the [001] direction (E_d(C[001]) $\approx 19 \pm 1$ eV), the C PKA impacts a Zr atom, which rebounds the C atom backward due to the much greater mass of Zr. The returning C atom passes near its original lattice site, and then it deviates further from the lattice site while it vibrates back and forth. Eventually, this C atom becomes a C