First-principles study of native point defects and diffusion behaviors of helium in zirconium carbide

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ABSTRACT

The potential native point defects and diffusion behaviors of helium impurities in zirconium carbide (ZrC) are discussed by first-principles calculations. It is found that C-related defects are easier to form in energy than Zr-related defects, consistent with experimental observations. By comparing incorporation energies at various sites, the energetically favored location for helium in intrinsic ZrC is determined to be the Zr substitution site. The positive but small incorporation energy suggests that helium is at the edge of solubility in ZrC. It is revealed that Zr-vacancy assisted diffusion mechanism for helium plays a dominant role in ZrC system with a small energy barrier of 0.70 eV. Besides, helium is likely trapped in Zr pre-existing vacancies, which may impact on the mechanical properties and dimensional stability of ZrC materials.

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1. Introduction

Zirconium carbide (ZrC) is being considered as a candidate material for high temperature nuclear applications due to its exceptional thermal and electrical conductivities, ultra-high melting point of 3600 K, good resistance to fission products attack, and low neutron absorption cross-sections [1—4]. Experimentally, ZrC has been proven to be a structural and fission product diffusion barrier coating material for TRISO (tri-isotropic) coated nuclear fuel used in high temperature reactors [5—7]. The over-coated ZrC layer on the kernel [UO_2] can successfully retain Cs, Ag, Eu, and Ce isotopes over the entire annealing temperatures from 1200 °C to 1500 °C. In particular, during 1000 h long post irradiation heating at 1600 °C, the fractional release of Cs metal isotope reaches the level of about 10^{-4} for the ZrC coating layer, comparing with that of 10^{-1} for the currently used silicon carbide (SiC) coating layer [4,5], making ZrC as a candidate material for high power density high temperature reactor (HTR) fuels operating at temperatures >1873 K, which is considered a limit for SiC TRISO technology at present [8].

Though the irradiation performance of the ZrC coated fuel shows encouraging advantages, the knowledge on the fundamental properties of ZrC under irradiation remains quite insufficient both experimentally and theoretically. Previous experiments have shown that ZrC_x ($x < 1$) is stable with broad compositional homogeneity (38—50 at. % of C at 500 °C) [9,10]. Theoretically, Li et al [11] developed an interatomic empirical potential of Zr/C to study the vacancy formation and migration energies in ZrC. Brutzel et al. [12] studied the primary radiation damage and the associated defect produced in a stoichiometric mono crystalline ZrC matrix from the classical molecular dynamics simulations. Although the classical molecular dynamics investigations can provide meaningful results of the defect formation in ZrC, the accuracy is quite limited by the quality of the interatomic potentials. Relatively, the first-principles calculations based on the density functional theory (DFT) are able to produce reasonable ground—state parameters quantitatively for ZrC [4,13—15] with respect to experimental results, which provide a possible way to investigate the structural properties of ZrC under irradiation and fission products damage conditions.

Helium atoms are easily produced in neutron-irradiated materials due to α transmutation reactions, and tend to accumulate in vacancies to form helium bubbles. If this is the case, the vacancy mobility decreases while the accumulation of additional vacancies and helium atoms enhances [16,17], which may significantly affect the mechanical properties and dimensional stability of materials used in nuclear energy system [18—23]. The potential use of ZrC for nuclear applications makes it important to determine the incorporation and diffusion properties of helium in ZrC system. However, to our knowledge, such a detailed investigation has not been

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performed yet. Thus, in this paper, we will systematically study the intrinsic point defects and helium behaviors in bulk ZrC to deeply understand its structural stability. The rest of the paper is organized as follows. The first-principles computational method is briefly introduced. Then the calculation results are presented and discussed. Finally, a summary of the study is given.

2. Computational method

Our calculations are self-consistently performed within DFT in the framework of the projector-augmented-wave (PAW) method [24], with a generalized-gradient approximation (GGA) exchange-correlation functional in the Perdew-Burke-Ernzerhof (PBE) form [25], as implemented in the Vienna *ab initio* simulations package (VASP) [26]. Twelve electrons $(4s^2\,4p^6\,4d^2\,5s^2)$ for zirconium, four electrons $(2s^2\,2p^2)$ for carbon, and two electrons $(1s^2)$ for helium are taken into account as valence electrons. We employ supercell containing 64 host atoms to simulate point defects and helium migration in the ZrC matrix. To check the convergence of the formation and migration energies, we have also considered the $2 \times 2 \times 3$ and $3 \times 3 \times 3$ ZrC supercell, containing 96 and 216 host aotms, respectively. The energy cutoff for the plane-wave basis set is selected as 500 eV, and the integration over the Brillouin zone is carried out on $5 \times 5 \times 5$ k-point meshes generated by the Monkhorst-Pack scheme [27], which is sufficient for energy convergence of less than 1.0 meV per atom. During the calculation of the total energy of defective structures, the shape and size of the supercell are fixed while the fractional atomic coordinates are relaxed until the Hellmann-Feynman forces are less than 0.02 eV/Å.

3. Results and discussion

3.1. ZrC structure and ground state properties

Here we consider the rocksalt (B1) crystal structure of ZrC with space group Fm$\overline{3}$m (No. 225). The Zr atoms are located at the cube's corner points and the C atoms fill the octahedral interstitial sites coordinated by Zr atoms, as shown in Fig. 1. The obtained equilibrium lattice parameter a_0 for stoichiometric ZrC is 4.72 Å, which is in fair agreement with experimental values of 4.698 Å [30] and 4.68 Å [31], as shown in Table 1. Some other bulk properties are tabulated in Table 1, which all agree well with the experimental and previous theoretical results. The calculated formation energy of −0.84 eV/atom is in good agreement with previous theoretical values ranging from Ref. −0.82 to −0.91 eV/atom [4,11,15]. While they are all somewhat lower than the experimentally measured values −1.04 ± 0.03 eV/atom [35], as presented in Table 1.
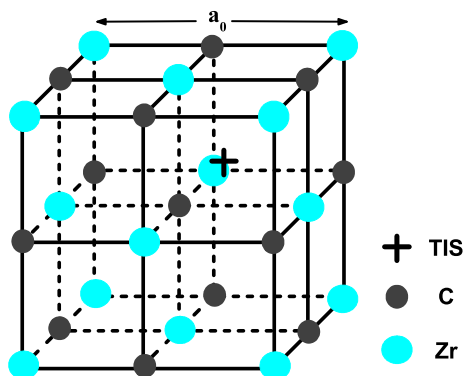

Fig. 1. Conventional unit cell of ZrC. Zr atoms are located in the 4a (0,0,0) Wyckoff positions and C atoms are located in the 4b (0.5, 0.5, 0.5). + indicates the tetrahedron interstitial site (TIS) in the lattice.

Table 1
Calculated equilibrium lattice parameter a_0 (Å), bulk modulus B_0 (GPa), cohesive energy E_{coh} (eV), and formation energy $\triangle H_f$ (eV/atom) of rocksalt ZrC at the ground state. For comparison, previous experimental and theoretical values are also listed.

Parameter	Present work	Previous calculations	Experiments
a_0 (Å)	4.72	4.689[a], 4.72[b]	4.698[c], 4.68[d]
B_0 (GPa)	230.5	237[b], 229[e]	223[f], 230[g]
E_{coh} (eV)	−15.90	−16.01[i]	–
$\triangle H_f$ (eV/atom)	−0.84	−0.82[h], −0.86[i], −0.91[j]	−1.04 ± 0.03[k]

[a] Ref. [28].
[b] Ref. [29].
[c] Ref. [30].
[d] Ref. [31].
[e] Ref. [32].
[f] Ref. [33].
[g] Ref. [34].
[h] Ref. [4].
[i] Ref. [11].
[j] Ref. [15].
[k] Ref. [35].

3.2. Stability of intrinsic point defects

In this subsection, the potential point defects are explicitly studied in the calculation of the formation energies as follows: vacancies, i.e., V_C (C vacancy) and V_{Zr} (Zr vacancy), interstitials at the tetrahedron interstitial site (TIS), i.e., C_i (C interstitial) and Zr_i (Zr interstitial), Frenkel pairs, and Schottky defect, where "V" stands for a vacancy and "i" stands for an interstitial.

Generally, the interaction of a point defect in a too small supercell with its image in the nearest supercell could wrongly contribute to the calculated formation energy due to the periodic boundary condition [36]. Thus, to test the convergence of defect formation energies versus supercell size, we carefully considered supercells representing repetition of conventional cell as following repetition patterns: $1 \times 1 \times 1$ (8 atoms), $2 \times 1 \times 1$ (16 atoms), $2 \times 2 \times 1$ (32 atoms), $2 \times 2 \times 2$ (64 atoms), $2 \times 2 \times 3$ (96 atoms), and $3 \times 3 \times 3$ (216 atoms).

In the present work, the formation energy of a point defect X is calculated as follows. Formation energy of a vacancy, $E_f^{V_x}$, is

$$E_f^{V_x} = E_{def}(X) - E(\text{ZrC}) + \left(E_X^{\text{bulk}} + \Delta\mu_X \right) \quad (X = Zr, C), \tag{1}$$

where the entropic contribution and pressure volume terms are supposed to be inconsequential in order that the total energies can be directly calculated from DFT. $E_{def}(X)$ is the total energy derived from the defected supercell calculation, $E(\text{ZrC})$ is the total energy of the equivalent defect-free supercell, E_X^{bulk} is the energy per atom of each chemical species in its standard zero energy reference state (X = Zr or C). The reference states are chosen as the ground state of hexagonal closed-packed (hcp) structure of zirconium and the graphite phase of carbon. The modification value $\triangle\mu_X$ is the deviation of the actual chemical potential from the energy per atom of each chemical species because of the stability limit of ZrC. Here, the formation energy of bulk ZrC is defined as

$$\Delta H_f(\text{ZrC}) = E(\text{ZrC}) - \sum_X n_X E_X^{\text{bulk}}, \tag{2}$$

where n_X denotes the number of atoms of species X. The calculated result is collected in Table 1. Under stoichiometric equilibrium growth condition, $\triangle\mu_X$ and $\triangle H_f(\text{ZrC})$ satisfy the condition

$$\Delta\mu_{Zr} + \Delta\mu_C = \Delta H_f(\text{ZrC}). \tag{3}$$

So the modification chemical potentials for Zr (C) are