First-principles study of the stability and diffusion properties of hydrogen in zirconium carbide

Xiao-Yong Yang [a], Yong Lu [a, b], Ping Zhang [a, *]

[a] Institute of Applied Physics and Computational Mathematics, Beijing 100088, People's Republic of China
[b] Beijing Computational Science Research Center, Beijing 100084, People's Republic of China

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ABSTRACT

The stability and diffusion properties of interstitial hydrogen atom in bulk ZrC have been investigated by first-principles calculations. In energy, hydrogen atoms prefer to occupy the carbon substitutional site (C-SS) with a negative formation energy, consistent with the experimental observations. In the C-SS, the hydrogen atom obtains 0.702 electrons from its 1 NN Zr atoms, tending to achieve the most stable $1s^2$ electronic state. Two hydrogen atoms in the same tetrahedral interstitial site are able to form a pairing cluster along the $\langle 110 \rangle$ direction with the H–H pair equilibrium distance of 1.30 Å, nearly twice the length of H_2 bond, suggesting a relatively weak interaction between the H–H pair. The diffusion energy barriers of hydrogen in pure and vacancy pre-existing ZrC matrix are calculated. It is found that the presence of native vacancies will capture the hydrogen atoms due to the large energy barrier to jump out the vacancy. Furthermore, the temperature-dependent diffusion coefficients of interstitial hydrogen, deuterium, and tritium in ZrC are predicted using the transition state theory.

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1. Introduction

Zirconium carbide (ZrC) is one of the well-known hard refractory ceramic materials due to its high melting point (~3540 °C), high thermal conductivity, good chemical stability, and superior mechanical properties at elevated temperatures, which has been widely used in machining tools, hard-coating industry, and electronic devices [1–7]. ZrC is also a promising coating material for fuel particles in future Generation-IV nuclear reactors, since it has remarkable low neutron absorption cross-section and high resistance to corrosion by fission products [3–9]. It is well known that hydrogen isotopes produced from water by thermo-chemical processes are a critical issue to develop the Generation-IV nuclear reactors [10]. These isotopes could penetrate and diffuse in materials, and most nuclear materials are susceptible to hydrogen damage including hydrogen embrittlement and corrosion. As a coating material for thermonuclear reactors, ZrC will be inevitably exposed to the environment full of radioactive isotopes. To guarantee the performance of the material, it is necessary to understand the solubility, permeability, and diffusivity of hydrogen isotopes in ZrC matrix.

In the previous studies, the behaviors of hydrogen isotopes in substoichiometric carbohydrides (ZrC_xH_{1-x}) and cabodeuterides (ZrC_xD_{1-x}) have been examined by X-ray and neutron diffraction techniques [11–13]. It is found that hydrogen isotopes tend to occupy the carbon sites in the ZrC matrix, and the concentration of absorbed hydrogen roughly corresponds to the amount of carbon vacancy. For instance, $ZrC_{0.64}$ and $ZrC_{0.81}$ absorbed hydrogen up to $ZrC_{0.64}H_{0.31}$ and $ZrC_{0.81}H_{0.12}$, respectively. These observations indicate that carbon vacancies act as the dissolution sites for hydrogen atoms [14]. The interaction between hydrogen isotopes and ZrC powder was examined by Hatano et al. at 873 K [15]. They observed a reversible absorption and release of hydrogen isotopes in ZrC powder, and evaluated the diffusion coefficient of deuterium to be 3×10^{-16} m^2 s^{-1} by fitting the absorption curves, where the ZrC powder were supposed as spherical particles with diameters of 1 μm.

On the theoretical side, although numerous studies have been performed on the elastic properties [16,17], lattice dynamics [18], the anharmonic properties [19], and the thermal properties [20,21] of ZrC, as well as the adsorption and dissociation of H_2 on the (001) surface of ZrC and Au_4/ZrC [22], the behaviors of hydrogen isotopes in ZrC matrix are still lacking in the literatures. As well, the incoherent experimental data of hydrogen isotopes in ZrC is not enough to establish the diffusion diagram and draw the decisive conclusion. Thus, a systematical study on the stability and diffusion properties

of hydrogen isotopes in bulk ZrC is necessary and urgent. Furthermore, the first-principles calculations based on the density functional theory have been widely used in the study of solid-state diffusion [23—25], which can help us to investigate the microscopic diffusion processes and derive specific quantitative values, such as solution and migration energies of impurity. All of these motivate us to perform the present study to systematically investigate the stability and diffusion properties of hydrogen isotopes in bulk ZrC, and obtain the solution energies, migration energy barriers, vibrational free energies, and diffusion coefficients quantitatively based on the first-principles calculations. The computational method is briefly introduced in Section 2. The calculated results are presented and discussed in Section 3. Finally, a summary of this study is given in Section 4.

2. Computational method

The formation energy of a interstitial hydrogen (H) atom in intrinsic ZrC is defined as

$$H_{int}^f = E(ZrC, H) - E(ZrC) - \frac{1}{2}E(H_2), \tag{1}$$

where $E(ZrC,H)$ is the total energy of the ZrC supercell containing single hydrogen atom at the tetrahedron interstitial site (T-IS), $E(ZrC)$ is the reference energy of the ideal ZrC supercell, $E(H_2)$ is the energy of a H_2 molecule, which is -6.76 eV according to the present calculation.

The solution energy, defined as the energy gain by adding a impurity atom to a vacancy site, of a substitutional hydrogen at an intrinsic vacancy in ZrC is expressed as

$$E_{sub}^s = E(V_X, H) - E(V_X) - \frac{1}{2}E(H_2), \quad (X = Zr, C), \tag{2}$$

and the formation energy of a substitutional hydrogen in ZrC is defined as

$$H_{sub}^f = E(V_X, H) - E(V_X) - \frac{1}{2}E(H_2) + H_{V_X}^f, \tag{3}$$

where $E(V_X,H)$ is the total energy of the supercell with a single hydrogen atom at the Zr substitutional site (Zr-SS) or the C substitutional site (C-SS), $E(V_X)$ is the energy of the supercell with one vacancy (V_{Zr} or V_C). The vacancy formation energy is written as

$$H_{V_X}^f = E(V_X) - \frac{N-1}{N}E(ZrC), \tag{4}$$

where N is the number of atoms in defect-free ZrC supercell.

The binding energy of two hydrogen atoms in intrinsic ZrC is defined as

$$E_b(H_1, H_2) = [E(H_1) + E(H_2)] - \left[E(H_1 + H_2) + E_{ref}\right], \tag{5}$$

where $E(H_1)$ [respectively $E(H_2)$] is the energy of the supercell with H_1 (respectively H_2) atom only, $E(H_1 + H_2)$ is the energy of the supercell containing the interaction between H_1 and H_2, and E_{ref} is the energy of the corresponding supercell without H_1 and H_2 atoms. With such a scheme a negative value of binding energy indicates repulsion between the entities, while positive one denotes attraction.

The diffusivity can be calculated from the energy barrier along migration path using the transition state theory (TST). For a system with non-interacting interstitial particles, the diffusion coefficient is expressed as

$$D = D_0 e^{-Q/kT}, \tag{6}$$

where Q is the activation energy along the diffusion path, corresponding to a particular saddle-point. D_0 is a pre-factor, and k is the Boltzmann's constant. Following the Wert and Zener [26], the diffusion coefficient can be written as

$$D = n\beta d^2 \Gamma, \tag{7}$$

where n is the number of available nearest-neighbor stable sites for the diffusing interstitial atom, β is the jump probability in the direction of diffusion, d is the migration distance, Γ is the rate of jump between adjacent sites of the diffusing atom. According to the transition state theory [27,28], the jump rate Γ can be expressed as

$$\Gamma = \frac{kT}{h} \frac{\prod_{i=1}^{3N}\left[2\sinh\left(\frac{h\nu_i^0}{2kT}\right)\right]}{\prod_{i=1}^{3N-1}\left[2\sinh\left(\frac{h\nu_i^{TS}}{2kT}\right)\right]} e^{-\triangle H_m/kT}, \tag{8}$$

where ν_i^0 and ν_i^{TS} are the vibrational frequencies at the ground state and the transition state, respectively. Using the expression of the phonon free energy

$$F_{vib} = -kT \ln Z_{vib} = kT \int_0^\infty g(\nu)\ln\left[2\sinh\left(\frac{h\nu}{2kT}\right)\right]d\nu, \tag{9}$$

the jump rate can be written as

$$\Gamma = \frac{kT}{h} e^{-(\Delta F_{vib} + \Delta H_m)/kT} \tag{10}$$

where the zero-point energy (ZPE) is included in the F_{vib} term.

The first-principles calculations have been performed using the projector-augmented-wave (PAW) potential method [29,30] as implemented in the Vienna Ab-initio Simulation Package (VASP) [29,31] based on the density functional theory (DFT). The exchange and correlation effects are described by the GGA in the Perdew-Burke-Ernzerhof (PBE) form [32]. The plane wave energy cutoff is set to be 500 eV. The Brillouin zone is represented by Monkhorst-Pack special k-points mesh [33] of $3 \times 3 \times 3$. The total energy changes during the optimization process are finally converged to 1.0×10^{-4} eV/cell and the forces are reduced to 0.01 eV/Å. The atomic positions and the cell parameter are first fully optimized from the relaxation cycle for the perfect ZrC matrix in the $2 \times 2 \times 2$ supercell configuration. Then, during the supercell calculations for hydrogen in ZrC matrix, the shape and size of the supercell are fixed while the fractional atomic coordinates are relaxed. Twelve electrons ($4s^2 4p^6 4d^2 5s^2$) for zirconium (Zr), four electrons ($2s^2 2p^2$) for carbon (C), and one electron ($1s^1$) for hydrogen (H) are taken into account as valence electrons, respectively. The saddle-point structure and associated energy barrier of diffusion path are calculated by employing the climbing image nudged elastic band (CINEB) method [34]. The vibrational frequencies are calculated using the density functional perturbation theory with the help of PHONOPY package [35].

3. Results and discussion

3.1. Stability of a single hydrogen atom in ZrC matrix

The stability of hydrogen atom in bulk ZrC will influence the