First principles study of point defect effects on iodine diffusion in zirconium

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ABSTRACT

The formation energies, diffusion barriers, and vibration frequencies of complex iodine defects in zirconium are calculated with first principles calculations and nudged elastic band method. The effective diffusion rates of these complex defects are evaluated in the temperature range from 300 K to 2000 K. The iodine interstitial diffusion and the iodine diffusion via $I_{Zr} - V_{Zr}$ are the dominant diffusion mechanisms. The vacancies may be traps for iodine diffusion and they can slow down the diffusion of iodine atoms. For the zirconium cladding materials in light water reactors, various point defects may be generated. Our calculated effective diffusion coefficients agree with the experimental data well and it indicates that bulk diffusion may be a main diffusion mechanism for the iodine diffusion in zirconium alloy.

1. Introduction

The fuel cladding material in the light water reactor (LWR) is an important safety barrier which is used to prevent the radioactive fuel products from releasing to the cooling water [1]. How radioactive fuel products release from the cladding materials is of great interests to engineers and researchers to develop high quality cladding materials [2].

One important fission product in LWR is radioactive iodine. For example, iodine isotopes ^{129}I ($T_{1/2} = 15.7 \times 10^6$ years) and ^{131}I ($T_{1/2} = 8$ days) in the thyroid gland is harmful to human body [3,4]. In light water reactors, iodine induced stress corrosion cracking (ISCC) occurs on the inner side of the zirconium fuel cladding [5–7]. As a result, the diffusion of iodine in zirconium alloy is an interesting topic. Diffusion of various fission products in cladding materials have been studied with experimental methods [8–14]. For example, ion implantation method is used to generate iodine impurity in cladding materials, and following high temperature annealing is used to activate the diffusion process, then, Rutherford back scattering spectrometry (RBS) is used to detect the concentration and analyze the diffusion for the iodine diffusion in Zr [8] and SiC [10–12].

Computational simulations are also used to study the iodine in cladding materials [15–21]. They provide insights for material design and overcome the limitation of the experimental study. For example, irradiation facilities are expensive and the accuracy of the detection method is limited. Diffusion of Cs, Ag, and B in silicon carbide have

been studied by Morgan et al. [22–27]. Trinkle and his co-authors studied oxygen diffusion in various *hcp* metals, including zirconium [28,29]. Interstitial iodine diffusion in a stoichiometric SiC sample is calculated and compared with the diffusion of iodine interstitial in zirconium by first principles calculation and nudged elastic band methods [30]. Since neutron irradiation will generate various point defects in the cladding material, defect effects on iodine diffusion in zirconium is an important topic [31–34].

In this paper, first-principles calculations [15,35] and nudged elastic band (NEB) method [36–38] are used to study the formation energies, migration energy barriers, and attempt-to-diffuse rates of various iodine defects in bulk zirconium material. Effective energy barriers and attempt-to-diffuse rates can be used to analyze the differences among different diffusion mechanism [22,23] and they are calculated for iodine diffusion via different point defects.

2. Calculation methods

2.1. Density functional theory calculations

In the diffusion calculations, density functional theory (DFT) calculations [15,35] are performed to calculate the system energies with Vienna *ab initio* Simulation Package(VASP) code [39–41]. Projected augmented wave (PAW) method [42,43] is used to deal with the wave functions near the core region of atoms and the exchange correlation functional within the generalized gradient approximation (GGA)

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parameterized by Perdew, Burke, and Enzerof (PBE) [44,45] is used in the calculations. The cutoff of the plane-wave kinetic energy is 350 eV. The spin polarization is used in all calculations. The residual minimization method with direct inversion in the iterative subspace (RMM-DIIS) [46,47] is used in the electronic relaxation and the energy convergence criterion is 10^{-4} eV. Conjugate gradient method is used to minimize the Hellmann–Feynman forces in the ionic relaxations and the force stopping criterion is 0.05 eV/Å. A $6 \times 6 \times 3$ super cell with 216 Zr atoms is fully relaxed and then it is used for the formation energy calculation. During the defect formation energy calculations, the box size is fixed and the atoms inside are relaxed. The summations over the Brillouin zone are performed with a $2 \times 2 \times 2$ Monkhorst–Pack k-point mesh.

2.2. Formation energy of a point defect

Since point defect may affect the diffusion of iodine atom in bulk zirconium, various point defects are generated in the zirconium super cell. The formation energy (F) of certain point defect in a zirconium super cell is defined as the following equation [48],

$$
\begin{aligned}
F &= E^r - E_{pure} + \Sigma dn_s E_s \\
&= E^r - E_{pure} + dn_{Zr}E_{Zr} - E_I.
\end{aligned}
\tag{1}
$$

Here, F represents the formation energy of certain point defect; E^r represents the energy of a structure which contains certain defect; E_{pure} is the system energy of the zirconium super cell without any defect; E_s represents for the energy of certain single atom or the cohesive energy per atom of certain bulk material, for example, E_I is the energy of an iodine atom inside a box with same shape and volume as the zirconium super cell and E_{Zr} is the cohesive energy per atom of bulk zirconium; dn_s is the corresponding atom number change for the species s inside the super cell after the doping process.

2.3. Diffusion rate calculations

Climb image nudged elastic band (CI-NEB) method [36–38] is used to search the minimal energy paths and calculate the diffusion energy barriers of an iodine atom diffusion inside zirconium with certain point defect. VTST code [49] coupled with VASP package are employed to perform the NEB calculations. There are four or more images between the initial and the final configurations for the NEB calculations. The fictitious spring constant is 5.0 eV/Å^2 and the force convergence criteria is 0.05 eV/Å. The volume is fixed in NEB calculation since the volume change can be ignored during diffusion process.

The frequency of diffusion follows the Arrhenius law [50],

$$
\Gamma = \Gamma_0 exp\left(-\frac{\Delta E}{k_B T}\right),
\tag{2}
$$

where ΔE represents the diffusion energy barrier and Γ_0 is the attempt-to-diffuse frequency. Considering the transition state theory (TST) [51,52] and the classical harmonic approximation, the attempt-to-diffuse frequency is $\Gamma_0 = n\nu$, where n is the number of equivalent diffusion paths and ν is,

$$
\nu = \frac{\Pi_{i=1}^{3N}\nu_i}{\Pi_{i=1}^{3N-1}\nu_i'},
\tag{3}
$$

ν_i and ν_i' represent the normal vibration models of initial state and transition state. There are $3N - 1$ normal models at transition state because one of the frequencies is imaginary. N is the atom number.

Since NEB calculations need more computer resource, balancing the computing time and the accuracy, a $4 \times 4 \times 2$ super cell with 64 Zr atoms is used for the NEB calculations.

2.4. Effective diffusion coefficient

The effective diffusion coefficient corrected by defect's concentration ratio can be used to describe iodine diffusion in zirconium with various defect types [48,53]. Iodine diffusion in zirconium had been investigated with ion implantation and Rutherford back scattering spectrometry (RBS) analysis [8]. The ion implantation is used to generate iodine impurity in various types. After ion implantation, high temperature annealing are used to activate the diffusion process and RBS is used to detect the concentration of iodine in Zr. If there are vacancies near the iodine impurities, local quasi-chemical equilibrium will be established between the vacancies and iodine atoms quickly [54,55]. With this equilibrium assumption, the effective diffusion coefficient can be written as [48,53],

$$
D_i^{eff} = D_i^{int}\frac{c_i}{\sum c_i}.
\tag{4}
$$

D_i^{eff} and D_i^{int} in Eq. (4) represent the effective and intrinsic diffusivity of certain diffusion mechanism via specified defect. The c_i represents the concentration of certain point defect in the zirconium sample. The diffusion coefficient obeys the Arrhenius relationship,

$$
D = D_0 exp\left(-\frac{\Delta E}{k_B T}\right),
\tag{5}
$$

and the diffusivity D_0 can be written as [48],

$$
D_0 = d^2\Gamma_0 = d^2 n\nu.
\tag{6}
$$

Here, d represents the diffusion length. Γ_0 is the attempt-to-diffuse frequency of certain diffusion mechanism and it is defined in Eqs. (2) and (3).

The denominator of the concentration part in Eq. (4) is the summation of the concentrations of all types of defects. This concentration part represents the probability of an iodine atom passing through certain type of defect. The concentration of certain type of defect can be estimated by the formation energy of this type of defect,

$$
c_i = A_0 exp\left(-\frac{F_i}{k_B T}\right).
\tag{7}
$$

F_i is the formation energy of the defect type i.

Then we substitute Eqs. (5)–(7) into Eq. (4). Since the pre-factor A_0 in numerator and denominator of the concentration component are canceled, we get the following result,

$$
\nu_i^{eff} exp\left(-\frac{\Delta E_i^{eff}}{k_B T}\right) = \nu_i^{int} exp\left(-\frac{\Delta E_i^{int}}{k_B T}\right)\frac{exp\left(-\frac{F_i}{k_B T}\right)}{\Sigma exp\left(-\frac{F_i}{k_B T}\right)}
\tag{8}
$$

The formation energies F_i, intrinsic vibration models ν_i^{int}, and the diffusion energy barriers E_i^{int} can be calculated from *ab initio* simulations and NEB method. Then the effective vibration model ν_i^{eff} and diffusion energy barrier E_i^{eff} of certain defect can be evaluated via Eq. (8) within certain temperature range. E_i^{eff} is linear proportional to $E_i^{int} + F_i$.

3. Results and discussion

3.1. Formation energies of iodine defects

As a cladding material, various point defects are generated in zirconium by irradiation effects. The fission product iodine may diffuse into the cladding tube via pellet cladding interaction (PCI). Point defect effect may affect the diffusion rate of iodine in zirconium. In this work, four types of point defects associated with iodine impurities in zirconium are studied. They are iodine interstitial, substitutional interstitial, substitutions, and substitutions with vacancies. The schematics of these four types of point defects are shown in Fig. 1.

The schematic of an iodine interstitial is shown in Fig. 1(a). For the