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Theoretical study of the interaction between metallic fission products and defective graphite

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ABSTRACT

The adsorption and diffusion behaviors of the metallic fission products of Cs, Sr, Ag on the defective graphite surface with double vacancy and Stone–Wales defect are theoretically studied by using density functional theory. Our results show that the Cs, Sr and Ag adatoms are adsorbed preferably at the defect areas of graphite surface. Electronic structure analysis indicates that the defects enhance the adsorption of metallic fission products. Further study on the diffusion properties also proves that the adatoms prefer to diffuse toward the defective area. These processes can readily occur due to zero or ignorable diffusion energy barriers of different kinds of point defects, indicating that point defects can serve as the trap sites for the metallic fission products.

1. Introduction

Tristructural-isotropic (TRISO) coated fuel particles, which are designed to effectively retain and contain fission products during normal operation as well as postulated accident conditions [1,2], are used in the high temperature gas-cooled reactor (HTGR) and the fluoride salt-cooled high temperature reactor (FHR). In the TRISO particle, there are two layers of pyrolytic carbon that cooperate with the silicon carbide layer to prevent the release of nuclear fuel or fission products. However, recent studies have shown that metallic fission products, e.g. Ag, Cs, and Sr, can be released from fuel particles at extreme condition [3]. The metallic fission products diffused from the TRISO particle will be adsorbed in the carbon matrix of pebble fuel or in the carbon dust, which leads to radioactive pollution in cooling loop of the reactor [4–6]. Therefore, it is of critical importance to understand the behaviors of metallic fission products on graphite and to evaluate the release of radioactive nuclides during the operation of nuclear reactor.

Both experimental and theoretical studies have been carried out to investigate the behaviors of fission products on carbon structures. The experimental studies report that the binding energy of Cs adatom on graphite substrate depends on the particular substrate structure [7], especially at the vacancy area of the graphite [8]. The theoretical studies by using density functional theory (DFT) suggest that the van *der* Waals interaction between graphite layers has a little influence on the adsorption state of adatoms on defective graphite [9]. Cs and Sr have a tendency to form stronger bonds with the sp^3 defects than the perfect sp^2 C on the graphite surface [10]. Up until now, the adsorption behaviors of several fission products have been reported in various carbon structures, e.g. graphite, graphite surface with single vacancy (SV), amorphous carbon structures, etc. These studies help to clarify the initial adsorption behaviors of different fission products on the graphite. However, there are many types of point defects in carbon structures, e.g. double vacancy (DV) and Stone–Wales (S–W) defect, which have not been fully understood yet. The diffusion behaviors of fission products on the graphite surface, especially on the defective graphite surfaces, is also rarely touched.

The point defects including SV, DV, S–W defect, etc., which are the basic units of larger defects such as grain boundaries, defect clusters, void, can be generated by irradiation damage in graphite [11–13]. Clarifying the interaction between fission products and point defect in graphite is important to understand the diffusion process of fission products during reactor operation. In this work, the interaction between metallic fission products, e.g. Cs, Sr and Ag, on the graphite surface with DV and S–W defect are studied based on the first-principles calculations. The adsorption energies

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of fission products on these substrates are calculated and compared to the previous studies. Detailed projected density of states (PDOS) and Charge Density Difference (CDD) of the adsorption system are analyzed to elucidate their preferable adsorption. Moreover, the diffusion behaviors for fission products migrating on the graphite surface with or without point defects are studied and the corresponding energy barriers are evaluated to get a deep understanding for the adsorption behaviors. Our results of fission products on graphite may further help to illustrate the diffusion properties of fission products on larger defect areas such as grain boundaries, vacancy clusters and voids.

2. Theoretical details

All of the calculations are performed by using DFT method [14] implemented in the Vienna *Ab Initio* Simulation Package (VASP) [15–17]. The exchange correlation interaction is treated in the generalized gradient approximation (GGA) with the parameterization of PW91 [18]. The projector augmented wave (PAW) pseudo-potential [19] is employed to describe the electron–ion interaction. The energy cut-off for the plane wave basis is set to 400 eV to ensure a good convergence. The geometry optimization is performed using conjugate gradient scheme with force convergence criterion of 0.01 eV/Å. The diffusion energy barriers are estimated by using climbing image nudged elastic band (CI-NEB) method [20–22]. To describe the diffusion behaviors of fission products on graphite, a 6×6 hexagonal supercell containing 72 carbon atoms is used to model the one layer graphite surface, as shown in Fig. 1a. Periodic boundary conditions are adopted in all three directions and the size of supercell in z axis is set to be 20 Å. The Brillouin zone (BZ) is sampled with a Gamma-centered grid $4 \times 4 \times 1$ k-points. The lattice constant of optimized graphite surface is 2.467 Å, which agrees well with the experimental values ($a = b = 2.464 \pm 0.002$ Å) [23].

3. Results and discussion

3.1. Adsorption behaviors of fission products

The adsorption energies (E_{ad}) of Cs, Sr and Ag on graphite surface with point defects are calculated to understand their corresponding adsorption states. The adsorption energy is defined as: $E_{ad} = E_{sub} + E_{atom} - E_{atom\text{-}sub}$, where E_{sub}, E_{atom}, $E_{atom\text{-}sub}$ are the energies of graphite surface, fission product atom, and the adatom–graphite system, respectively.

As a benchmark calculation, three adsorption sites with high symmetry on pristine graphite surface are firstly considered, labeled as top (T) site, bridge (B) site, hollow (H) site, respectively, as shown in Fig. 1a. The adsorption energies for the fission products such as Cs, Sr and Ag on different graphite substrates are shown in Table 1. It shows that the most favorable adsorption site on pristine graphite surface for fission products Cs and Sr is the hollow site with adsorption energies of 1.45 eV and 0.66 eV, respectively, which agrees well with the results of Luo et al. [9]. It shows Cs binds stronger than Sr on the hollow site.

The schematic diagrams for adsorption sites on graphite surface with defects are shown in Fig. 1b–f. Herein, several kinds of defective graphite surfaces are considered, including SV, DV5-8-5, DV555-777, DV5555-6-7777 and S–W defect. Their corresponding formation energies are 7.79 eV, 7.52 eV, 6.19 eV, 7.23 eV and 4.94 eV, respectively, which agree well with the previous results [24–27]. The graphite surface of SV or DV is planar while S–W defect is the "sinelike" structure from the side view of Fig. 1f [26]. Among the three kinds of DV, the configuration of DV5-8-5 containing two pentagons and one octagon can be obtained by structural optimization. The DV555-777 and DV5555-6-7777 can be obtained by rotating the marked bond in sequentially (see Fig. 1c–e). Several adsorption sites on graphite surface are considered and the red dots indicate unstable adsorption sites. The fission products adsorbed on the unstable sites of graphite surface with SV diffuse to H_0 site after structural optimization. For the graphite surface with S–W defect, the fission products of Cs, Sr and Ag adsorbed on these sites also diffuse to the neighboring stable sites.

Here, we also identify whether the interlayer interaction affects the adsorption. The adsorption of Cs on the bilayer graphite with fixed interlayer distance 3.4 Å is calculated and compared with the one on monolayer graphite. It shows that the adsorption energy of Cs adsorbed on the H_0 site of bilayer graphite with a SV is 2.47 eV, which is 0.02 eV higher than the one on monolayer graphite. The difference almost can be ignored and monolayer graphite is suitable to be used as the substrate for metallic fission product adsorption. The results agree well with Luo's result [9].

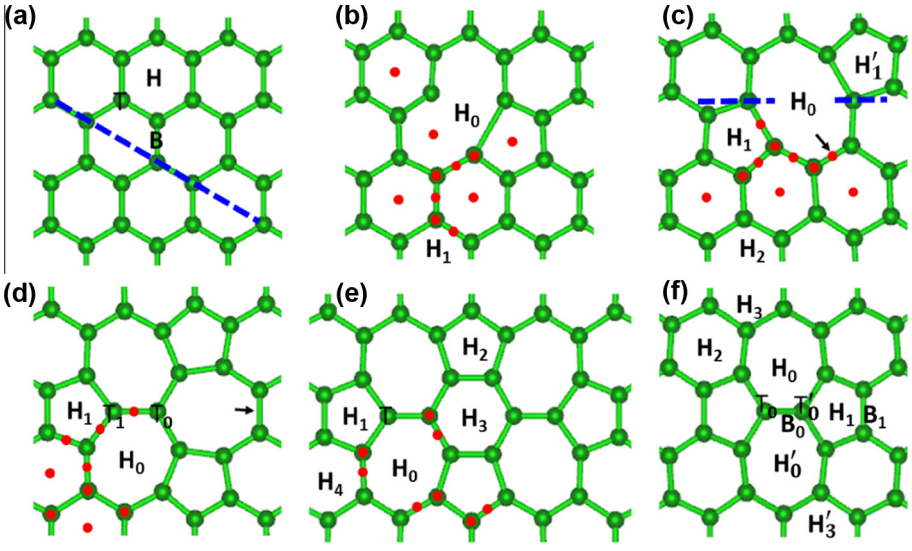

Fig. 1. Schematic diagram for different adsorption sites on (a) pristine graphite surface; optimized graphite surface with (b) single vacancy; (c) double vacancy DV5-8-5; (d) DV555-777 obtained by rotating the marked bond in (c); (e) DV5555-6-7777 obtained by rotating the marked bond in (d); and (f) Stone–Wales defect. The dash blue lines correspond to the cross-sectional lines of Charge Density Difference. The red dots indicate the unstable adsorption sites for the fission products. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)