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First-principle studies of radioactive fission productions of Cs/Sr/Ag/I adsorption on silicon carbide in HTGR

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ABSTRACT

Silicon carbide (SiC) is one of the important fuel-element materials in high-temperature gas-cooled reactors (HTGRs), and learning the adsorption behavior of radioactive fission products on the SiC surface is essential for source-term analysis in HTGR. In this study, the adsorption behavior of cesium, strontium, silver, and iodine on β-SiC is investigated using first-principle calculations. We find that the interactions between the adatoms and SiC substrate are strong for all four types of nuclides with binding energy of approximately 1–3 eV. These results are confirmed again by analysis of the charge density difference and density of state. Furthermore, the adsorption rates of the four nuclides are obtained, and we explain that these nuclides display significant adsorption rate on the SiC surface but are not easily desorbed, which shows that the solid fission products have difficulty penetrating through the SiC. These results demonstrate that in HTGR, intact SiC could effectively obstruct the diffusion of fission products from the uranium dioxide in tri-isotropic (TRISO) particles to the primary circuit, which are first obtained in a micro perspective.

1. Introduction

In a high-temperature reactor–pebblebed modules (HTR-PM), helium is used as coolant in the primary circuit, and large amount of spherical fuel elements filled with fuel particles piled up in the reactor core (International Atomic Energy Agency, 1997). The fuel particles used in high-temperature gas-cooled reactors (HTGRs) are tri-isotropic (TRISO) coated ones. Let us consider an HTR-PM as an example. The TRISO consists of five parts: (1) low-enriched uranium dioxide (UO_2) kernels surrounded by subsequent layers, (2) porous pyrolytic carbon (PyC) (buffer layer), (3) dense inner PyC, (4) silicon carbide (SiC), and (5) outer PyC. The SiC layer with a thickness of approximately 35 μm is mainly used to prevent diffusion of fission products in the TRISO. The particles, whose number is approximately 11,000, are homogeneously distributed in a graphite matrix with the fuel element sealed by a graphite shell, as shown in Fig. 1 (International Atomic Energy Agency, 1997).

A large amount of nuclides such as cesium, strontium, silver, iodine, and tritium compose the main radioactive products of the fission reaction in an HTR-PM. These radioactive nuclides leak into the primary circuit through defects such as vacancies, voids, and cracks in the sealed TRISO. SiC is the most important and effective barrier during this process (Yang et al., 2014). From the experiment, the primary conclusion is that SiC provides a blocking effect on the fission products, but the microscopic mechanism of this effect remains unclear. The microscopic mechanism of this blocking effect is related to the adsorption and desorption interaction between the nuclides and SiC. Therefore, studying such adsorption and desorption behavior from the micro level is important and necessary (Liu and Cao, 2002).

The first-principle calculation provides a method of studying the above issue. Since the 1980s, many scientists have studied adsorption on the substrate (Mark Riffe et al., 1990; Persson and Ishida, 1990; Horn et al., 1988; Lamble and Brooks, 1988). After 30 years of continuous development, researchers can now perform further and deeper investigation into the problem of adsorption using more advanced facilities, including more powerful computers and more precise experimental apparatus. The first-principle calculation is based on the density functional theory (DFT) (Kohn et al., 1965), and it is implemented in the Vienna ab initio

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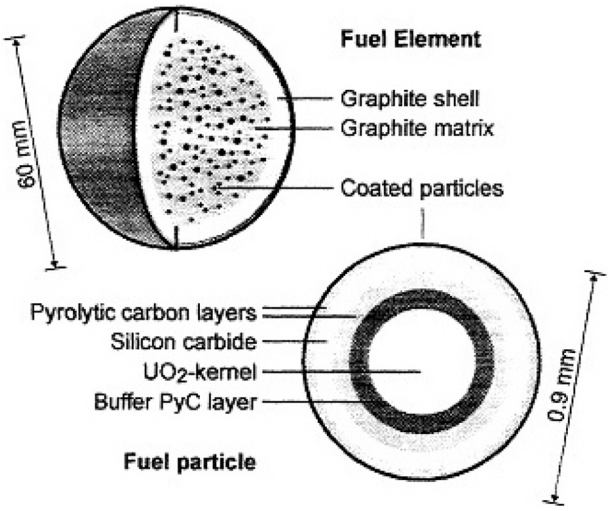

Fig. 1. Configuration of the fuel particle and element used in HTR-PM (International Atomic Energy Agency, 1997).

simulation package (VASP) by the group of Kresse and Furthmüller (Kresse and Furthmüller, 1996a, 1996b; Kresse and Hafner, 1993).

Many theoretical approaches are available for researching SiC materials using the first-principle calculations, especially on SiC nanotubes or nanowires. Rosso et al. studied the properties of Fe atom adsorbed on the surface of planar SiC nanotubes (Rosso and Baierle, 2014). Song et al. developed a new template for Li and Ca decoration and hydrogen adsorption on graphene-like SiC (Song et al., 2015). Shi et al. studied the structural and electronic properties of SiC nanotubes filled with Cu nanowires (Shi et al., 2013), etc. (Wang, 2012; Bui et al., 2012; Masumian et al., 2014; Simsek and Aydin, 2011). In addition, many experimental approaches were carried out by the post-irradiation examination (PIE) of the US advanced gas-cooled reactor (AGR), and the results are very helpful in understanding the detailed diffusion behavior of fission products through the SiC shell [2016 American Nuclear Society (ANS) winter meeting, paper numbers 18447, 18560, 18574, and so on]. According to a few studies, the behavior of radioactive fission products adsorbed on the crystal SiC substrates has not been fully understood yet.

In the present study, the adsorption behavior of Cs, Sr, Ag, and I on SiC is studied by first-principle calculations using DFT. The electron transfer between the adatom and SiC is analyzed using the charge density difference (CDD) and density of state (DOS) of the adsorption system. Furthermore, the adsorption rates of the above-mentioned fission products are studied. We find that the interactions between the adatoms and SiC substrate for all four types of nuclides are strong.

2. Calculation model of fission product adsorption on SiC at micro level

2.1. Construction of the SiC micro model

First-principle calculations were performed based on DFT as implemented in the VASP code, and we employed the projector-augmented wave pseudo-potential (Kresse and Joubert, 1999) to describe the electron–ion interaction. Electron exchange and correlation energy are mostly treated in the generalized gradient approximation parameterized by Perdew, Burke, and Enzelhof (Perdew et al., 1996).

To perform the first-principle calculation, the SiC micro structure was determined in the first step. According to the manufacturer data, β-SiC has a typical diamond cubic crystal structure. In contrast to pure diamond, each carbon atom is surrounded by four Si atoms in the SiC crystal. Because of the strong interactions between two adjacent atoms in the atomic crystal, the crystal structure of SiC is very stable. This property ensures that the crystal lattice of SiC does not easily deform when it interacts with the nuclides. Therefore, SiC can effectively block the diffusion of radioactive fission products from the fuel particle.

Finally, a super surface, which consists of an adatom on eight layers of SiC lattice with $3 \times 3 \times 1$ primitive cells [Fig. 2(a)], was employed to calculate the adsorption energy using a $4 \times 4 \times 1$ k-point. The vacuum thickness was set to 10.0 Å, and the kinetic energy cutoff was set to 500 eV (Kresse and Joubert, 1999). Four types of adsorptive sites were considered, including the top (T), bridge (B), hcp-hollow (hH), and fcc-hollow (fH), as shown in Fig. 2(b).

2.2. Theories of adsorption energy, Fermi energy, CDD, and DOS in the system of fission products and SiC

The adsorption energy is defined as

$$E_{ad} = E_{SiC} + E_{atom} - E_{atom-SiC} \quad (1)$$

where E_{ad}, E_{SiC}, E_{atom}, and $E_{atom-SiC}$ are the energy expressions of the adsorption, SiC, a single atom, and the adatom–metal system, respectively. The numerical values of E_{SiC}, E_{atom}, and $E_{atom-SiC}$ can be directly determined from the first-principle calculations, and E_{ad}, which is obtained from Eq. (1), is one of the important parameters to determine the adsorption rate. According to the different adsorptive geometries (such as adsorptive sites and height), the value of E_{ad} varies, and the maximum value corresponds to the most stable adsorptive geometry.

Fermi level E_F is usually defined as the position of the highest energy that is filled with free electrons at a temperature of 0 K (e.g., for the isolated I atom, the position of the 5p orbit is the Fermi level), and when an atom is adsorbed on the metal surface, E_F will experience a shift for both the adatom and substrate.

CDD is one of the most important obtained parameters from the calculation because it can display a visual image of the electron transfer, which enables us to intuitively observe the interaction between the nuclide and substrate. Another important obtained parameter is DOS, which is used to calculate the distributions of electrons in each energy level. The detailed information of the electron transfer is revealed through the DOS analysis. In this study, both the two above-mentioned methods are performed.

We need to point out that even if the energy expressed in Eq. (1) are calculated at 0 K temperature, because the energy of the electron is insensitive to the temperature at the range of $T \sim 10^3$ K (Fang and Lu, 1980) and the maximum temperature of the fuel elements is approximately 1200 K (Fang et al., 2012), the results can be applied to real scenarios of HTR-PM.

2.3. Calculation methods of adsorption rate with equilibrium statistical physics

In the TRISO core, the radioactive fission products released from the UO_2 form a layer of ideal gas on the inside surface of the SiC with a concentration of approximately $n = 1 \times 10^{24} m^{-3}$ (Fang et al., 2012). On the basis of the approach used in the literature (Fang et al., 2012; Luo et al., 2012), the grand canonical ensemble model is introduced to describe this system and to evaluate the balanced adsorption rate of the nuclide on the metal. In this model, the metal-adsorbing nuclide atoms are considered as an open