Study of interaction between radioactive nuclides and graphite surface by the first-principles and statistic physics

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ABSTRACT

The adsorption and desorption of four kinds of main radioactive productions (cesium, iodine, strontium and silver) on graphite surface in high temperature gas cooled reactors (HTGRs) have been studied. Using the first-principles density-functional theory, adsorptive geometry, energy and electron structure on the perfect and defective graphite surfaces have been calculated. It turns out that the adsorption of Cs, I and Sr atoms belongs to chemisorption while the adsorption of Ag is a pure physisorption. When introducing a vacancy in graphite surface, nuclide adatoms will be trapped by the vacancy and form chemical bonds with three nearest neighbor carbon atoms, leading to significant increase of the adsorption energy. In addition, a model of grand canonical ensemble is employed to deduce the adsorption rate as a function of temperature and partial pressure of nuclides produced. The transition temperate from adsorption to desorption of nuclides on graphite surface is defined as the inflexion point of the adsorption rate and its variation with nuclide density is obtained.

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1. Introduction

In the high temperature gas cooled reactors (HTGRs), helium gas, as cooling medium, fills up and circulates in the whole primary circuit. The reactor core is piled up with large amount of spherical fuel elements filled with fuel particles. Sealed with graphite shell, the fuel element contains TRISO-coated fuel particles with a quantity of about 12000 homogeneously distributed in graphite matrix [1]. In the fission reaction of UO_2, a large amount of nuclides such as cesium, strontium, silver and iodine are the main radioactive products in the HTGRs. These radioactive nuclides will leak into the primary circuit through defects, such as vacancies, voids and cracks, of the sealed graphite shells, which may be induced in the making process of the fuel particles and elements and have been producing on service due to radiation. On the other hand, during the circulation progress, a large amount of graphite spherical particles are also formed by friction of fuel element spheres in the primary circuit. Thus, the interactions between these nuclides and graphite (including the graphite matrix, graphite reflector and graphite

carbon brick) are continuous [2]. When analyzing the source terms in HTGRs, it is important and necessary to know the amount of nuclides adsorbed on the graphite, so the thorough investigation of adsorption behaviors of nuclide atoms on the graphite surface is inevitable. As a first step to understand the interaction between nuclide atoms and graphite, the present work will focus on adsorption of these nuclides on the graphite surface with or without vacancies.

From the 1980s on, many scientists began to study the adsorption on the substrate to answer two questions which were then the topic of lively debate [3–6]: (1) what is the nature of the bond between the adatom and the substrate, chemisorption or physisorption? (2) At which level of coverage the adatom and the substrate is the most compatible? The studies have been being continuous, and researchers can now do further and deeper investigation on the problem of adsorption with more advanced facilities including more powerful computers and more precise experimental apparatus. Researches have been performed using experiments and theoretical calculations with various methods to study about adsorption on graphite [7–11]. The graphite has semimetallic properties with the low density of states at the Fermi level. If using the graphite as the substrate, the excitation spectrum of the substrate will be especially sensitive to charge transfer from

the adatom [10]. In experimental studies, therefore, many people use high-resolution low-energy electron diffraction (LEED) to perform structural characterization, and high-resolution electron-energy-loss spectroscopy (EELS) to investigate the nature of the adsorption by determining the excitation spectra [10,12–14]. In the theoretical approaches, the simplified tight-binding model [15], first-principles total-energy calculations [16], a full-potential slab method [17] etc. are applied to get the details of adsorption. The following assumption is often taken to simplify the calculations, i.e. a 2D graphene layer, instead of 3D graphite, as the substrate is used in adsorption calculations, for the influence on adsorption energy by successive graphite planes is very small owing to weak interaction between graphite planes.

In the present work, one of our pursuing aims is to reveal the origin of adsorption, i.e. electron transfer and structure of the adsorption system by the first-principles. We compare our results with some previous works reported in the literature. In the Case of Cs/graphite, Michael Gleeson et al. have used EELS to study plasmon excitations in pristine and alkali metal dosed highly oriented pyrolytic graphite in the temperature range 85–400 K [12]. The adsorption of iodine diatomic molecules (I_2) on graphene has been investigated using density functional theory with taking into account nonlocal correlation effects by means of van der Waals density functional approach by A.N. Rudenko et al. [18] However in the HTGRs, the concentration of nuclide is very small leading to a majority of adsorption in the form of single atom on graphite surface. There is few direct data on the adsorption of Sr on graphite. Martin Amft et al. [19] performed a systematic density functional (DF) study of the adsorption of Ag adatoms on pristine graphene, with considering van der Waals (vdW) interactions by the vdW-DF [20] and PBE + D2 [21] methods. Another aim of our study is to obtain adsorption rate as a function of temperature and nuclide's partial pressure, which is used to obtain the release amount of radioactive nuclides for the nuclear safety evaluation in the supposed accident of HTGRs. A model of grand canonical ensemble is employed to determine the adsorption rate of nuclides on graphite at any circumstance temperature and nuclide's partial pressure with the adsorption energies calculated from the first-principles. The transition temperate from adsorption to desorption of nuclides on graphite surface defined as the inflexion point of the adsorption rate is presented.

2. Method of calculation

2.1. First-principle calculation

Ab initio calculations have been performed within the density functional theory (DFT) [22] that is implemented in the "Vienna ab initio simulation package" (VASP) code [23–25]. The projector augmented wave (PAW) pseudo potential [26] is employed to describe the electron–ion interaction, using the generalized gradient approximation (GGA) [27] for the exchange–correlation term together with the Vosko–Wilk–Nusair [28] interpolation. Supercells consisting of a monolayer of ideal graphite with 3×3, 4×4, 5×5, 6×6, 7×7, 8×8 and 9×9 primitive cells are employed to calculate adsorption energy of an adatom on the perfect surface of graphite with a k-point of $6 \times 6 \times 1$. Supercells containing a graphite monolayer of 6×6 primitive cells and a bilayer of 4×4 primitive cells with a vacancy on surface are used to calculate the trapping energy of a surface vacancy to a nuclide adatom, using a k-point of $6 \times 6 \times 1$ and $6 \times 6 \times 3$, respectively. Periodic boundary conditions are adopted in all three directions and the size of supercells in *z* axis is set to be 2 nm, large enough to avoid interaction between graphite monolayer and its mirror image. The energy cutoff for the plane wave basis is set to 400 eV.
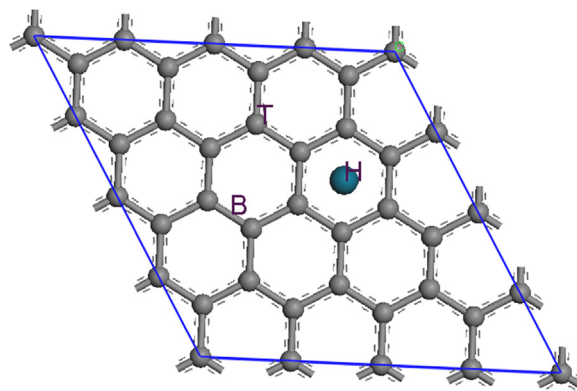

Fig. 1. The adsorptive sites on the graphite surface, where H, B and T represent the hollow, bridge and top positions of hexagonal cell of carbon. The figure shows one adatom on graphite surface with 4×4 primitive cells.

In order to search the most compatible adsorptive state, three influencing factors are considered: 1. the adsorptive sites, 2. the height between the adatom and substrate, 3. the coverage of adatoms on graphite. The sketch diagram showing different adsorptive sites on graphite surface is given in Fig. 1. The surface coverage is defined as the fraction of the adsorption sites occupied. For a hexagonal cell in Fig. 1, there is one H site, three B sites and two types of T sites above the vertex of hexagonal cell because of the reverse spins of the nearest neighbor carbon atoms. The calculation results show that the adsorption energy at two types of T sites is almost identical. Thus, we don't distinguish them and consider two T sites in one hexagonal cell. Accordingly, one adatom on 3×3, 5×5, 7×7, and 9×9 primitive cells corresponds to the coverage of 1/9, 1/25, 1/49, and 1/81, respectively, for H site. The corresponding coverage for T and B sites is half, and one third, of that for H site, respectively.

The most stable adsorptive state with the maximum adsorption energy is searched by the following method. First, we obtain the optimum structure of graphene by relaxing lattice shape and volume as well as carbon atoms. It gives the lattice parameters of graphene $a = b = 2.464$ Å, in good agreement with experimental results ($a = b = 2.464 \pm 0.002$ Å) [29]. Second, for a given coverage of adatom, calculate the adsorption energy at different heights for H, B, T adsorptive sites. To facilitate fast calculation, we do not relax the atoms of the adatom-graphite system in this step. Third, at the height corresponding to the largest E_{ad} for each adsorptive site, totally relax system to obtain the value of adsorption energy, and thus obtain the optimum adsorptive site and height. Finally, at the different coverage of adatom, repeat the calculations of the above two steps to reveal the influence of coverage on the adsorption energy.

As for the defective graphite, we first perform our calculation with a supercell (namely, an adatom and a 6×6 graphene with a vacancy). The vacancy is produced by removing a carbon atom in the center region of graphene. The adatom is placed right above the vacancy and the heights are set the same with optimum ones obtained on the ideal graphite. Of course, we totally relax the system. To see whether the other graphite layer has an influence on the adsorption of adatom on a defective surface, we then calculate the adsorption energy again introducing another ideal layer of graphite below the defective one. The height between the bilayer is set to be 3.4 Å which is the same with graphite crystal. The primitive cells of 4×4 and the k-point of $6 \times 6 \times 3$ are used in the supercell with graphite bilayer.

The adsorption energy is defined as:

$$E_{ad} = E_{gra} + E_{atom} - E_{atom-gra} \tag{1}$$