

First-principle studies of radioactive fission productions Cs/Sr/Ag/I adsorption on chrome–molybdenum steel in Chinese 200 MW HTR-PM

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Abstract Chrome–molybdenum steel (2·1/4Cr1Mo) is one of the main products of steam generation. The adsorption behaviors of radioactive fission products on 2·1/4Cr1Mo surface are critical in the analysis of HTR-PM. Here, the adsorption behavior of cesium, strontium, silver and iodine on 2·1/4Cr1Mo was investigated with first-principle calculations that the Ag and I atoms prefer to be adsorbed at the square hollow site of the face-centered cubic iron cell with a binding energy of about 1 and 3 eV, respectively. In contrast, Cs and Sr atoms are not adsorbed on the surface of the 2·1/4Cr1Mo. These results are again confirmed via analysis of charge density differences and the densities of state. Furthermore, the adsorption rates of these fission products show that only I and Ag have significant adsorption on the metal substrate. These adsorption results explain the amount of adsorbed radionuclides for an evaluation of nuclear safety in HTR-PM. These micro-pictures of the interaction between fission products and materials are a new and useful way to analyze the source term.

Keywords First-principle calculation · Fission product · Adsorption behavior · HTR-PM

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1 Introduction

High Temperature Reactor-Pebble Bed Modules (HTR-PM) are a typical high-temperature gas-cooled reactor (HTGR) [1]. In the HTR-PM, helium is used as the coolant to the primary circuit, and the fission products are released from fuel elements for separation in helium [2]. The adsorption of solid fission products (cesium, strontium, silver, iodine and etc.) on the pipeline and steam generator is essential and considerable. These adsorptive radionuclides have an important contribution to the entire source term in the HTR-PM [3]. One of the main metal materials in this pipeline and steam generator is chrome–molybdenum steel (2·1/4Cr1Mo). There are few studies on the adsorption behaviors of fission products on 2·1/4 Cr1Mo especially at the micro-level. Thus, it is difficult to comprehensively analyze the source terms in HTR-PM.

The first-principle calculation supplies a method to study this issue. From the 1980s on, many scientists began to study the adsorption on the substrate [4–7]. After thirty years of continuous development, the 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. The first-principle calculation is based on the density-functional theory (DFT) [8], and this is implemented in the Vienna Ab initio Simulation Package (VSAP) by Kresse and Furthmüller [9–11]. There are many theoretical approaches into research of metal materials via first-principle calculations especially for steel. Yu et al. [12] have studied the surface properties of bcc-Fe (body-centered cubic iron), fcc-Fe (face-centered cubic iron) and AISI-304 stainless steel. Wun et al. [13] have studied the structure and stability of Fe₃C-cementite surfaces crystal diffusion.

Toshiharu et al. have researched the vacancy–solute element interactions in body-centered cubic iron [14], etc. [15–18]. The minimum surface energy needed for bcc-Fe, fcc-Fe and AISI-304 stainless steel corresponds to the 110, 111 and 100 surfaces, respectively. Based on these few studies, the behaviors of the radioactive fission products adsorbed on the metal substrates are not yet fully understood.

In addition, there are relatively few experimental studies of the adsorption behavior of solid fission products in HTGR. A High Temperature Helium Experimental Loop (HTHEL) in the 10 MW High Temperature Gas-cooled Test Reactor (HTR-10) has been designed and studied by Fang et al. [2]. The experimental loop in the Chinese 200 MW HTR-PM has also been studied. When experimental data are accumulated, the theoretical results can be validated by comparing these data.

In this paper, the behavior of Cs, Sr, Ag and I adsorption on 2-1/4Cr1Mo was investigated with first-principle calculations using DFT. The electron transfer between the adatom and metal was analyzed by the charge density difference (CDD) and the density of states (DOS) of the adsorption system. Furthermore, the adsorption rates of these fission products were also studied. The Ag and I atoms can be adsorbed on the square hollow site of 2-1/4Cr1Mo, but Cs and Sr atoms are not adsorbed on the surface of the metal substrate.

2 Calculation model of fission products adsorption on 2-1/4 Cr1Mo on the micro-level

2.1 The construction of 2-1/4 Cr1Mo micro-model

The first-principle calculations were performed using DFT as implemented in VASP code and using the projector augmented wave (PAW) pseudo-potential [19] to describe the electron–ion interaction. The electron exchange and correlation energy are mostly treated in the generalized gradient approximation (GGA) parameterized by Perdew, Burke and Enzelhof [20].

To perform the first-principle calculation, the microstructure of 2-1/4Cr1Mo was determined in the first step. There are many kinds of alloy steel based on different dopants. These alloys have many different lattice structures. The 2-1/4Cr1Mo used in HTR-PM is a face-centered cubic structure. The strong interaction between the two adjacent layers of metal crystal and the multilayer structure should be considered. According to the manufacturing data, the chrome–molybdenum steel is composed of Fe, Cr and Mo with a weight fraction of 95.81, 2.24 and 0.95%, respectively [21]. The numerical ratio of these three elements is about 171:4.3:1. The Cr and Mo have the similar

chemical properties [22], and they have nearly the same effect as the doping element in our study. These two elements could be unified and simplified with a ratio of iron and chromium of 33:1. This ratio is similar to the replacement of one iron atom with a chromium atom at each $3 \times 3 \times 1$ ideal primitive cells of face-centered cubic iron. This significantly simplifies the calculation. Finally, the super-cells consisting of an adatom on the four layers of Cr-doped body-centered cubic iron with $3 \times 3 \times 2$ primitive cells (Fig. 1) are employed to calculate the adsorption energy using a-point of $4 \times 4 \times 1$. The vacuum thickness is set to 10.0 Å, and the kinetic energy cutoff is set to 500 eV [19].

In contrast to pure substrates, an adatom on the Cr-doped face-centered cubic iron has more adsorptive sites. As shown in Fig. 2, there are five and three adsorptive sites for Cr atoms in the top and bottom layers, respectively. In this work, all eight adsorptive sites are considered to obtain more comprehensive information about the different adsorption geometries that affect the adsorption energy and adsorption properties.

2.2 The theory of adsorption energy, Fermi energy, CDD and DOS in the system of fission products and 2-1/4 Cr1Mo

The adsorption energy is defined as

$$E_{\text{ad}} = E_{\text{metal}} + E_{\text{atom}} - E_{\text{atom-metal}}, \quad (1)$$

where E_{ad} , E_{metal} , E_{atom} and $E_{\text{atom-metal}}$ are the energies of the adsorption, metal, a single atom and the adatom–metal system, respectively. The numerical values of E_{metal} , E_{atom} and $E_{\text{atom-metal}}$ can be determined by the first-principle calculations directly, and E_{ad} is obtained from Eq. (1). This is one of the most important parameters in determining the adsorption rate.

The Fermi level E_F is usually defined as the position of highest energy that is filled with the free electrons at 0 K. For example, for the isolated I atom, the position of the 5p orbit will be the Fermi level. When the atom is adsorbed on the metal surface, the E_F will have a shift for both adatom and substrate.

The charge density difference (CDD) is one of the most important parameters in the calculation because it can display the visual image of electron transfer that enables us to see the interaction between nuclide and substrate intuitively. Another important parameter is density of state (DOS), which is used to calculate the distributions of electrons in each energy level. Detailed information of electron transfer will be seen in the DOS analysis. Both of these methods are used here.

Of note, even the energies in Eq. (1) are calculated at 0 K because the energy of an electron is insensitive to

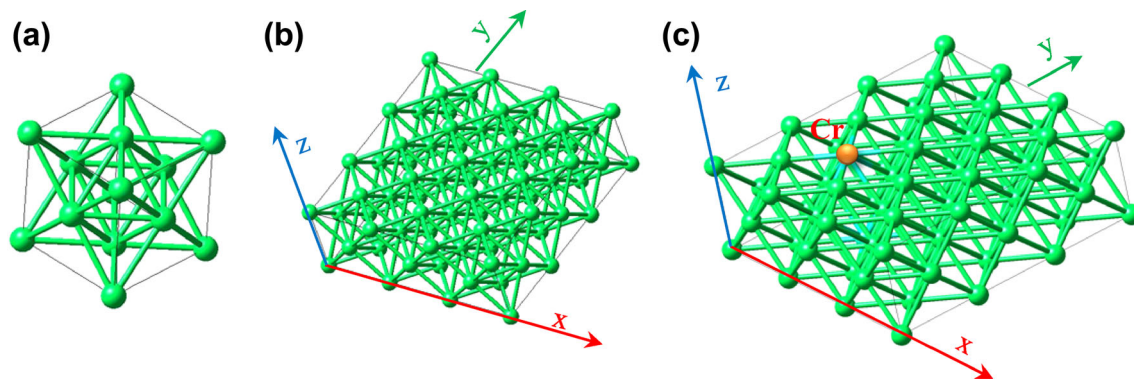
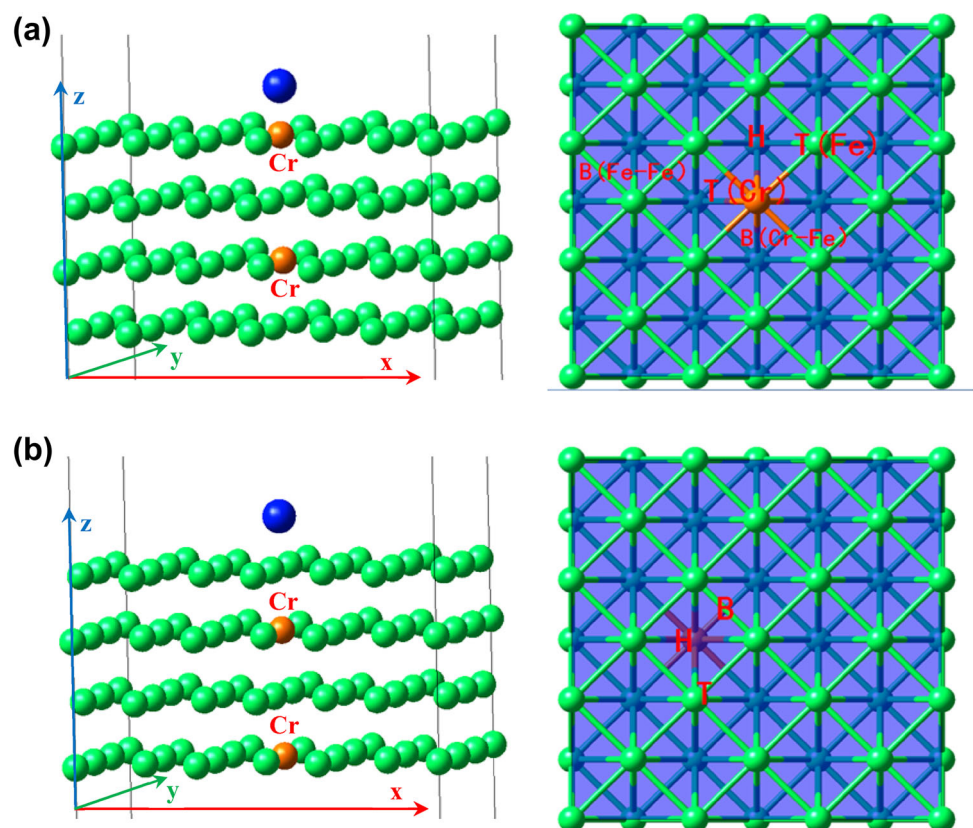


Fig. 1 (Color online) The crystal structure of Cr-doped body-centered cubic iron: **a** ideal primitive cell, **b** ideal $3 \times 3 \times 1$ primitive cells and **c** one Cr-doped $3 \times 3 \times 1$ primitive cells

Fig. 2 (Color online) The adsorptive sites: **a** Cr at the top layer and **b** Cr at the bottom layer



temperature $<10^3$ K [23], and the 2-1/4 Cr1Mo is mainly used for preheating, evaporating and low overheating section. This ensures that the temperature is below 10^3 K [24], and the results can be used for real scenarios in HTR-PM.

2.3 The calculation methods of adsorption rate with equilibrium statistical physics

In the primary circuit, the radioactive fission products used a coolant gas from the fuel elements. Some of them

will be adsorbed on the metal. For a normal operating reactor, the adsorbed and separate nuclide atoms will have a dynamic equilibrium system. In following the literature approach [24, 25], the grand canonical ensemble model has described this system and evaluated the balanced adsorption rate of the nuclide on the metal. In this model, the metal-adsorbing nuclide atoms are considered to be an open system, and the separate nuclide atoms in the coolant gas are treated as a particle and heat source. We define $\bar{N}$ and N_0 to represent the number of adsorbed nuclide atoms and the total adsorptive centers, respectively, and the

relationship between $\bar{N}$ and N_0 is given by the theory of the statistic physics as follows:

$$\bar{N} = \frac{N_0}{1 + e^{-(E_{\text{ad}} + \mu)/K_b T}}, \quad (2)$$

Here μ is the chemical potential of nuclide atoms, K_b is the Boltzmann's constant, and T is the temperature of the circumstance. The adsorption rate θ is determined by $\bar{N}/N_0$.

Because the density of fission products is very small (less than 10^{12} m^{-3} in HTR-PM [24]), the ideal gas model can be used to deal with the nuclide gas source. When the reactor achieves an equilibrium state, the chemical potentials of the nuclide atoms in the open system are identical to those of the gas source. According to the theory of the ideal gas model, the chemical potential of the nuclide can be written as follows,

$$\mu = K_b T \ln \left[n \left(\frac{h^2}{2\pi m K_b T} \right)^{3/2} \right], \quad (3)$$

Here n is the concentration of the nuclide in the primary circuit, h is the Planck constant, and m is the atomic mass of the nuclide atom.

By multiplying Eqs. (2) and (3), one can easily obtain the adsorption rate,

$$\theta = \frac{1}{1 + \frac{1}{n} \left(\frac{2\pi m K_b T}{h^2} \right)^{3/2} e^{-\frac{E_{\text{ad}}}{K_b T}}}. \quad (4)$$

Equation (4) shows that the adsorption rate depends on three parameters: n , T and E_{ad} . The value of n and T in HTR-PM can be determined by either experimental measurements or reactor physics calculations, while E_{ad} can be obtained through the first-principle calculations using Eq. (1). This grand canonical ensemble model provides a new way to understand the microscopic-level behavior of nuclides adsorbed on the substrate.

3 Results and discussion

3.1 Adsorption energy

The variations in the adsorption energy with different adsorptive sites were first studied. This was used to obtain

the most stable sites. The adsorption energies at different adsorptive sites are listed in Tables 1 and 2. This shows that the adsorption energies of the hollow site are significantly higher than other sites regardless of the Cr atom on the top or bottom layer. Therefore, the most stable adsorption sites are hollow site for all four adatoms.

In this result, it is necessary to highlight that the negative values appear in the adsorption energy indicating that the adsorption behavior for this site is physical adsorption or non-absorption. This point will be more clearly seen in the discussion of adsorption rate below. The appearance of the large negative numbers on the top site is likely because these adsorptive sites are quite unstable for the adatom–metal system [26]. Tables 1 and 2 indicate that the adsorption behavior of cesium and strontium tends to be physical adsorption or non-adsorption, and the adsorption of silver and iodine is chemisorption, qualitatively.

3.2 Analysis of electronic structure

Next, we studied the electronic structure of the adatom–metal system to identify the underlying physical nature of the adsorptive behavior. The charge density difference of the adatom–metal system is shown in Figs. 3 and 4 using the VESTA software [27]. Note that the yellow areas represent the increases in charge density, and the blue areas represent the decreases in charge density. With Cr at the top layer, there is no change in electronic cloud between Cs and substrate. The same image appears for Sr. This indicates that Cs and Sr can not be directly adsorbed on the metal.

For Ag, there is slight electron transfer between the adatom and substrate, and this is considered to be physical

Table 2 The adsorption energies (in eV) at different adsorptive sites for the Cs, Sr, Ag and I adatoms with a substrate bottom layer of Cr

Nuclides	Hollow	Bridge	Top
Cs	−1.356	−4.901	−24.282
Sr	+0.276	−1.025	−12.732
Ag	+1.261	−1.923	−10.324
I	+3.351	−0.829	−14.351

Table 1 The adsorption energies (in eV) for different adsorptive sites for the Cs, Sr, Ag and I adatoms with a substrate top layer of Cr

Nuclides	Hollow	Cr–Fe bridge	Fe–Fe bridge	Cr top	Fe top
Cs	−1.990	−7.539	−6.209	−37.079	−31.258
Sr	−0.413	−2.587	−1.669	−23.243	−16.614
Ag	+0.806	−3.349	−2.684	−12.402	−12.440
I	+2.762	−3.342	−1.926	−21.262	−17.591

Fig. 3 (Color online) The charge density difference with Cr at the top layer: **a** Cs, **b** Sr, **c** Ag and **d** I

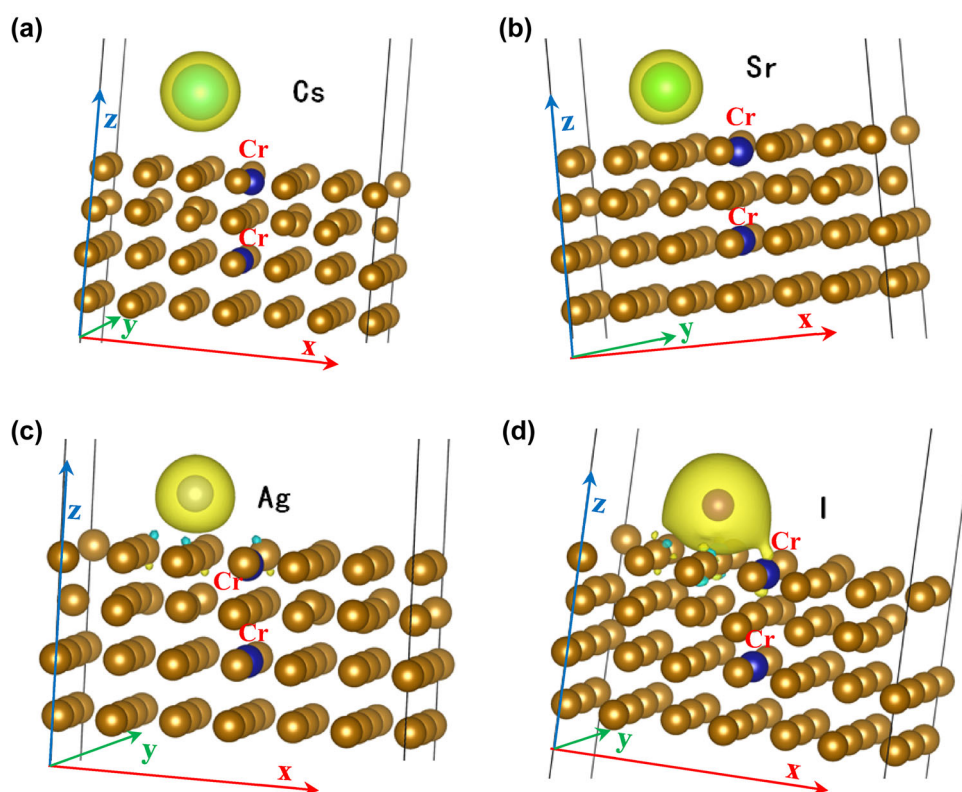
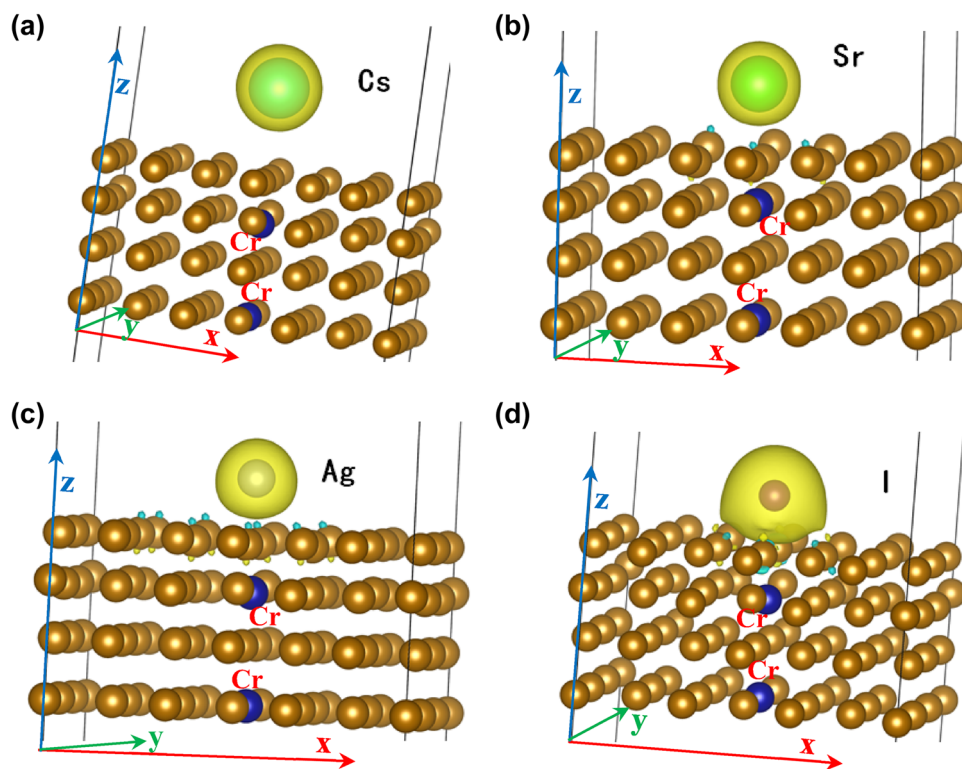


Fig. 4 (Color online) The charge density difference with Cr at the bottom layer: **a** Cs, **b** Sr, **c** Ag and **d** I



adsorption. I has a strong electron transfer from the metal to the iodine atom, which indicated that the adsorption between I and the metal is chemisorption. For the bottom

layer of Cr (Fig. 4), the results are somewhat different from the previous data. Sr has physical adsorption, and the case three other nuclides are the same.

The DOS should be calculated to discuss details of electron transfer. Figures 5, 6, 7, 8 and 9 show the DOS for single adatom, metal substrate and the adatom–metal system. Because there is no adsorption interaction between Cs and metal substrate for both top and bottom Cr, the DOS analysis will not contain Cs. The abscissa values in the figures are represented by the energies of states relative to the Fermi level, and this is applied to all Figs. 5, 6, 7, 8 and 9.

Figure 5 gives the total DOS for the isolated I atom, the isolated metal substrate, the I adatom–metal system, and a comparison of the partial DOS of the I atom between an isolated atom and I on the metal surface. Figure 5b shows that for an isolated I atom, the peak of the 5s state is below E_F , and the 5p state lies in E_F , which is the same as the electron configuration of $[\text{Kr}]4d^{10}5s^25p^7$. When I atom is adsorbed on the metal surface, the densities of the 5s and 5p states have been broadened due to adsorption

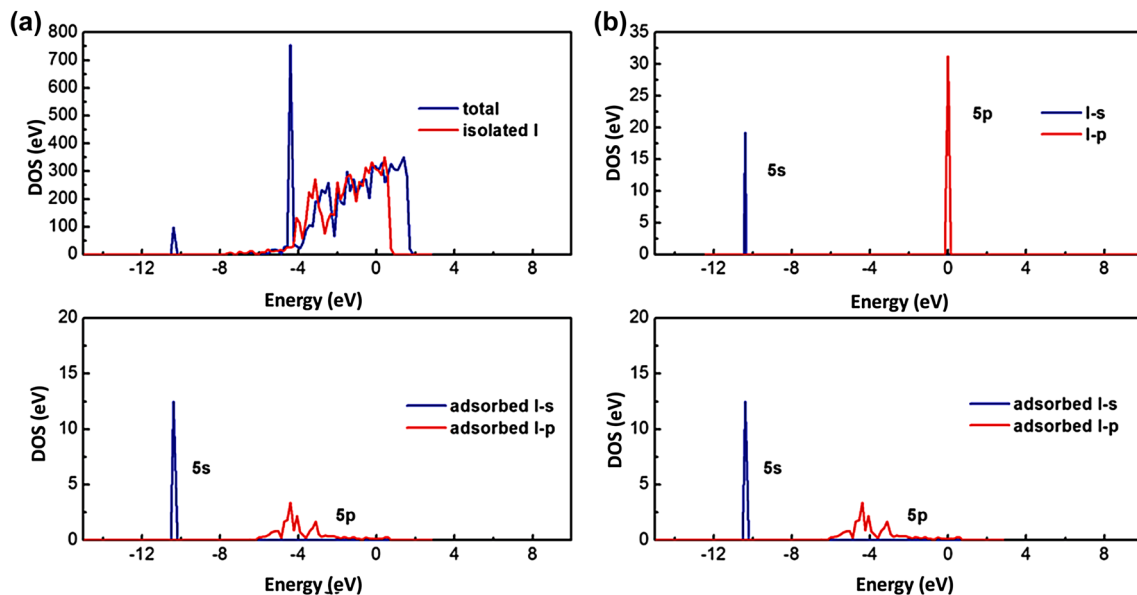


Fig. 5 (Color online) A comparison of DOS with top site Cr: **a** for the I adsorption system, the isolated metal substrate and the I adatom on the metal, and **b** between the isolated I atom and I adatom on the

metal. The energy is relative to the Fermi level E_F , which is indicated by the dashed line at $E = 0$ eV

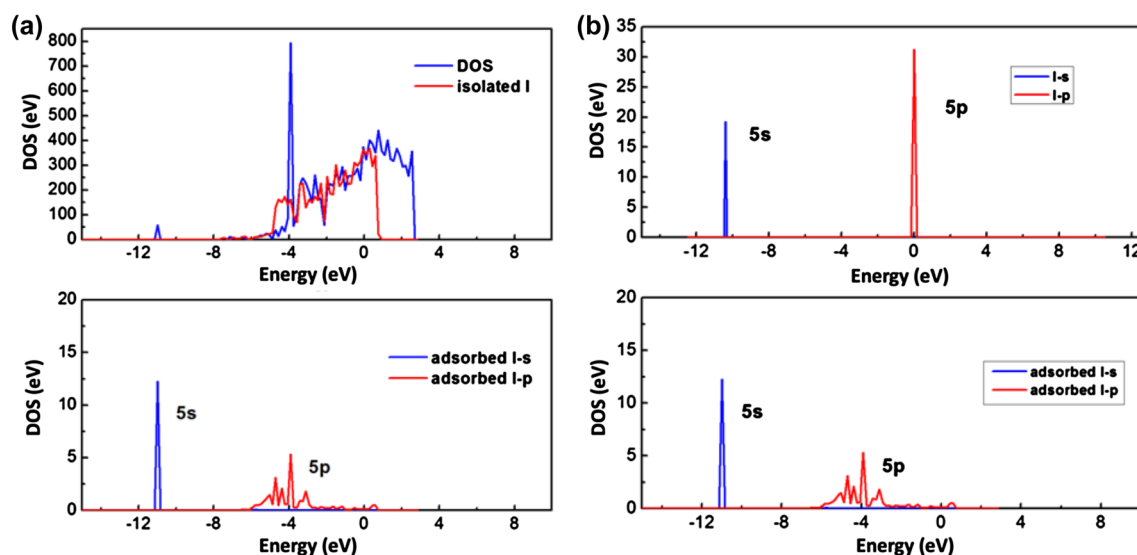


Fig. 6 (Color online) A comparison of DOS with bottom site Cr: **a** for the I adsorption system, the isolated metal substrate and the isolated I atom, and **b** between the isolated I atom and I adatom on the metal

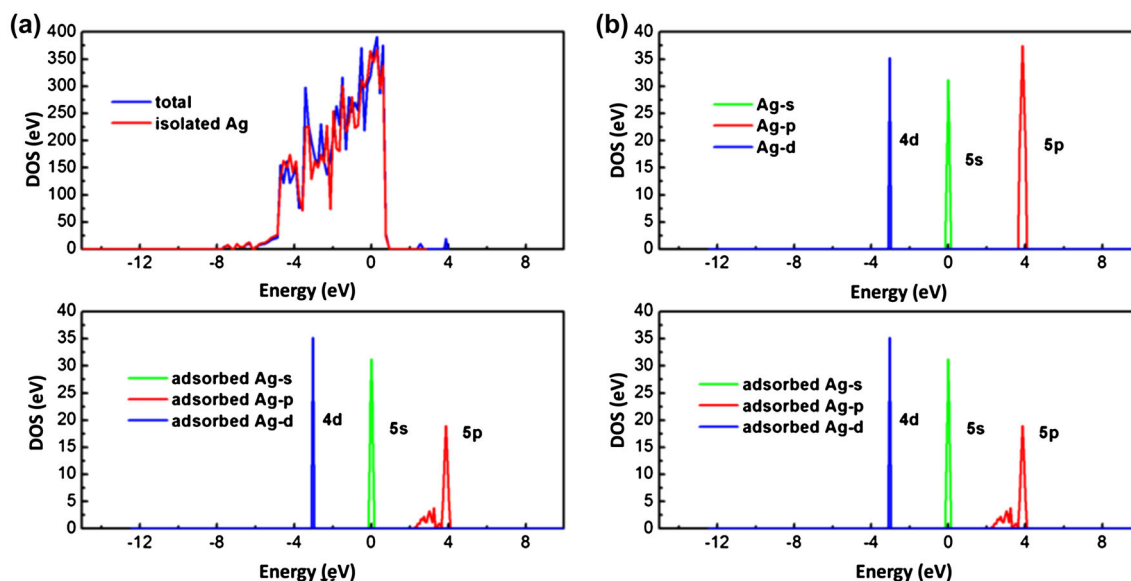


Fig. 7 (Color online) A comparison of DOS with top site Cr: **a** for the Ag adsorption system, the isolated metal substrate and the Ag adatom on the metal, and **b** between the isolated Ag atom and Ag adatom on the metal

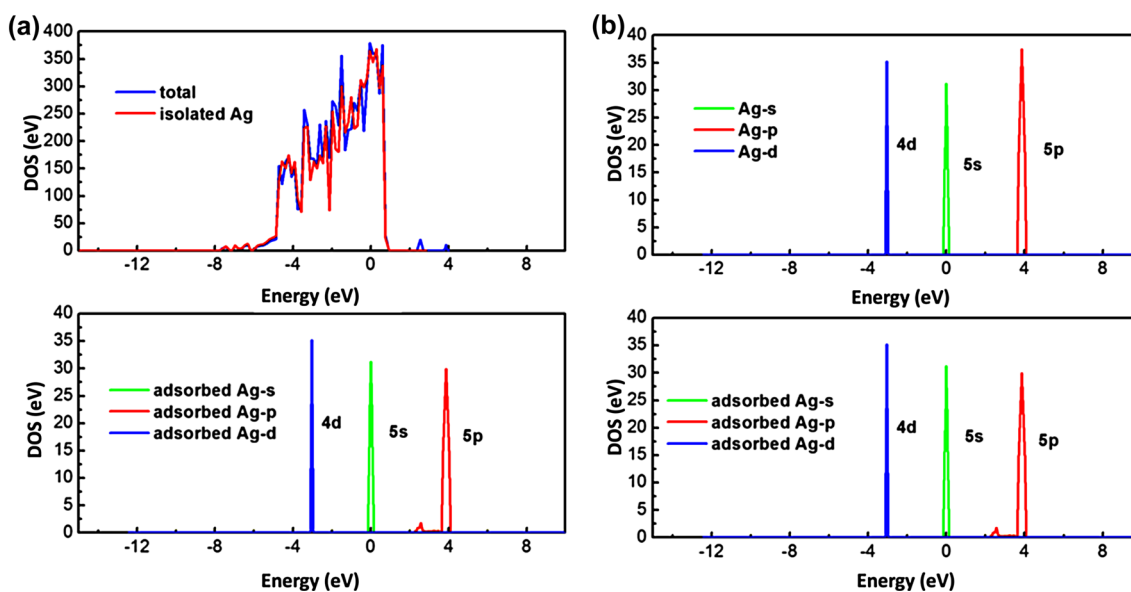


Fig. 8 (Color online) A comparison of DOS with bottom site Cr: **c** for the Ag adsorption system, the isolated metal substrate and the isolated Ag atom, and **d** between the isolated Ag atom and Ag adatom on the metal

interaction, and the $5p$ state shifts left toward less energy than E_F . This indicates that I atoms gained partial electrons from the metal and their energy could be reduced. These partial metal electrons occupy the $5p$ state of I, and this reflects the resonance between the $5p$ state of I atom and metal surface. In other words, the I and the metal formed a chemical bond through orbital hybridization, and thus, the adsorptive behavior between I and metal is chemisorption.

Figure 5a also shows that the total DOS of the I-metal system shifts right versus the isolated metal substrate. The appearance of more states above E_F suggests that the metal

loses its partial electrons to form chemical bonds. On the other hand, an electrochemical view is that the electronegativity of I is much larger than Fe and Cr. This causes I to gain partial electrons from metal when they interact with each other. For the bottom layer of Cr, the results are similar to Fig. 5a, b but with a more significant right shift of total I-metal system. Figure 6a, b presents the case for bottom Cr, and the results are similar to Fig. 5a, b with a more significant right shift of total I-metal system DOS.

The DOS for Ag and Sr are also shown in Figs. 7, 8 and 9. There is no obvious change in total DOS of adatom-

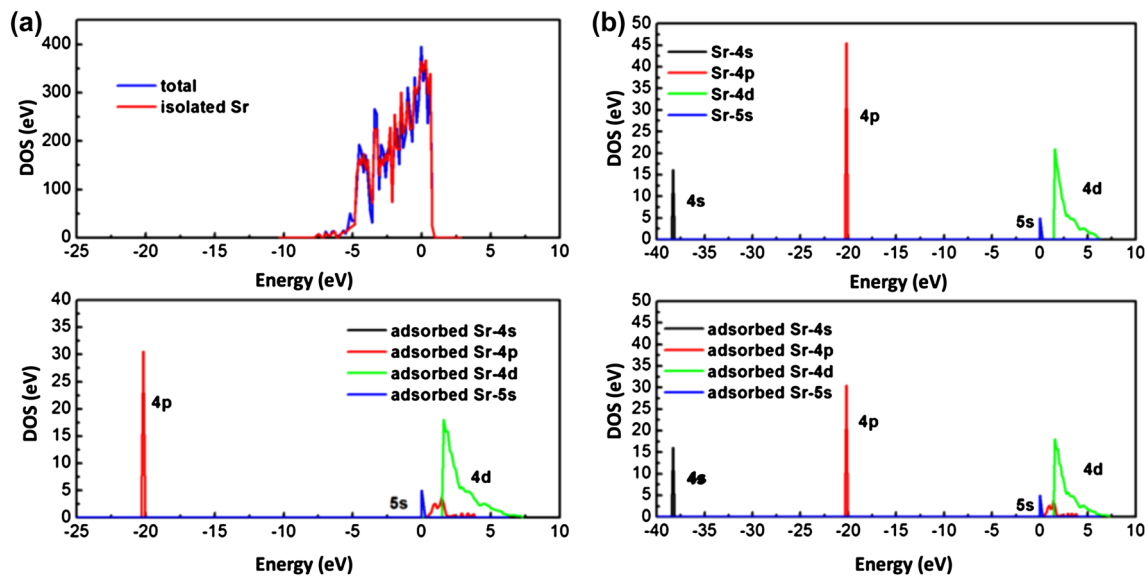


Fig. 9 (Color online) A comparison of DOS with bottom site Cr: **a** for the Sr adsorption system, the isolated metal substrate and the Sr adatom on the metal, and **b** between the isolated Sr atom and Sr adatom on the metal

metal system, and we conclude that the adsorptive behavior of these two nuclides is both physisorption. However, Fig. 6b shows that the $5p$ state of Ag broadens toward low energy. For Sr, Fig. 7b indicates that few of new states appear above the Fermi level when adatom due to adsorptive interactions between adatoms and metal substrate. These results reveal that there is a weak interaction between adatoms and metal. We also analyzed these phenomena concerning different electronegativity values. As we know, the Ag atom with an electron configuration of $[Kr]4d^{10}5s^1$ is stable, and its electronegativity is larger than Fe and Cr. This leads the Ag atoms to gain partial electrons from metal when they interact. In contrast, the electronegativity of Sr is smaller than Fe and Cr, and the Sr atoms will share their outer most electrons during the interaction.

We note that the electronic structure of Cs, Sr, Ag and I adsorbed on the metal substrate is quite different from when these nuclides are adsorbed on graphite. The Cs and Sr have positive adsorption energies that are larger than Ag and I on graphite [25, 28–30]. These results for the two substrates illustrate that in HTR-PM, the main solid radioactive fission productions Cs, Sr, Ag and I have different adsorption and deposition behavior. Elements with strong metallic character like Cs and Sr tend to be adsorbed on the graphite first, and this is then deposited on the metal together. However, elements with strong nonmetallic character like Ag and I prefer to be adsorbed on the metal directly.

3.3 Adsorption rate

The adsorption rate is determined by n , T and E_{ad} as shown in Eq. (4). As an example, the density of nuclide has

been set to be $n = 1 \times 10^{12} \text{ m}^{-3}$ [24]. The adsorption energy E_{ad} is determined by the above first-principle calculations with the bottom site chromium shown in Table 2 to investigate the variation trend of adsorption rate with T . It is clear that if the value of E_{ad} is positive, then the adsorption rate of the nuclide will decrease exponentially with increasing temperature. On the other hand, when the value of E_{ad} is negative, the adsorption rate will always close to zero regardless of temperature. This is seen in the fact that the nuclide atom could not be adsorbed on the substrate with negative adsorption energy. Therefore, only I, Ag and Sr's curves appear in Fig. 10.

Figure 10 shows that for the nuclide density of $n = 1 \times 10^{12} \text{ m}^{-3}$, the adsorption rate decreases

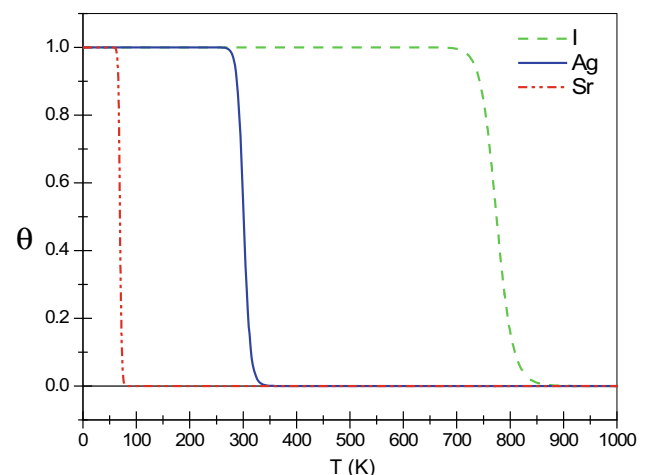


Fig. 10 (Color online) Variation of adsorption rate with temperature for I, Ag and Sr nuclides

Table 3 The parameters of the Cs, Sr, Ag and I in HTR-PM and adsorption rate

Nuclides	n (m^{-3})	m (10^{-25} kg)	θ ($T = 500$ K)	θ ($T = 750$ K)	θ ($T = 1000$ K)
Cs	9×10^{10}	2.29	6.1×10^{-37}	1.2×10^{-32}	1.4×10^{-30}
Sr	2×10^4	1.51	5.5×10^{-27}	3.6×10^{-28}	7.9×10^{-29}
Ag	9×10^8	1.84	1.8×10^{-12}	5.7×10^{-17}	2.9×10^{-19}
I	1×10^{11}	2.19	1	4.2×10^{-1}	1.1×10^{-6}

dramatically when the temperature is close to 800, 300 and 70 K for I, Ag and Sr, respectively. This indicates that when the temperature is higher than the corresponding value, the state of nuclide on the metal surface will have a transition from adsorption to desorption.

In addition, the real scenarios of HTR-PM are also been calculated here. The parameters and results are shown in Table 3, and the densities of the four nuclides are all less than $1 \times 10^{12} \text{ m}^{-3}$. The temperature range is about 500–1000 K. Table 3 shows that only I has a significant adsorption rate for the normal operating temperature in HTR-PM; Ag has a small adsorption rate at the cold end of HTR-PM, and Cs and Sr cannot be adsorbed on the metal directly.

The total amount of nuclides adsorbed on the metal in the primary circuit should be calculated to evaluate the release amount of radioactive nuclides in the supposed accident of HTR-PM for the nuclear safety evaluation [24]. This can be processed by calculating the total amount $\bar{N}$ of adsorbed radioactive nuclides through the sum of contributions from all parts in the first primary circuit according to temperature profile, nuclide concentration and the metal surface area. When $\bar{N} = N_0 \times \theta$, the present results of adsorption rate can be used to determine the amount of adsorbed radioactive nuclides for nuclear safety evaluation of HTR-PM.

4 Conclusion

In summary, the adsorption of four main solid radioactive fission productions (Cs, Sr, Ag and I) on 2-1/4 Cr1Mo surface in HTR-PM was studied with first-principle density-functional theory. We considered the adsorptive site of hollow, bridge and top with the bottom and top layer chromium-doping metal substrate influencing the adsorption energy. To understand more details of the adsorption behavior of the four nuclides, the electronic structure of the adsorption system was quantitatively analyzed by CDD and DOS. The CDD results suggest that the adsorption of I and Ag belongs to chemisorption and physisorption, respectively, and the adsorption of Sr and Cs are non-adsorption. The DOS calculations show that the $5p$ state of I atom gains electrons from the metal substrate, but there is no obvious electron transfer between Cs (Sr and Ag) atom

and metal substrate. The results of two analytical methods (CDD and DOS) coincide well with each other.

These results are quite different from the calculations of these nuclides adsorbed on graphite [25] indicating that when the coolant gas carried the fission products from the steam generator, I and Ag could be adsorbed on the metal directly, but Sr and Cs are adsorbed on the graphite first and then adsorbed on the steam generator with graphite. This insight can explain the adsorption behavior of the radionuclides more clearly and helps analyze the source term from the microscopic mechanism.

In addition, employing a model of grand canonical assembly and combining the adsorption energy determined by the first-principle calculation, the adsorption rate has been derived with different temperature and density of nuclides in HTR-PM. The results show that only I can have a significant adsorption rate for the normal operating temperature in HTR-PM, and the results can be used for nuclear safety evaluation of nuclide release during HTR-PM accidents.

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