Journal of Nuclear Materials 446 (2014) 172–177

Contents lists available at ScienceDirect

Journal of Nuclear Materials

journal homepage: www.elsevier.com/locate/jnucmat

# First-principles study of the stability and migration of Kr, I and Xe in $ZrO_2$

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ARTICLE INFO

*Article history:*
Received 24 May 2013
Accepted 28 November 2013
Available online 6 December 2013

ABSTRACT

The stability and migration of Kr, I and Xe in bulk $ZrO_2$ and on the $ZrO_2$ (111) surface have been studied by standard density functional theory (DFT) and the DFT-D2 method that corrects for the van der Waals interaction. Both methods show that Kr and Xe prefer to incorporate in the bulk phase rather than adsorb on the surface, and Xe is very mobile in the bulk state. For Kr and Xe adsorption on the surface, van der Waals interaction dominates, causing the weak interaction between the adsorbate and substrate. Iodine is found to have comparable stability in both phases and forms ⟨I–O⟩ bonds with strong covalency. It exhibits higher mobility on the surface than in the bulk $ZrO_2$, and diffusion from bulk-like state to surface state is an exothermic process. The fission product behavior in $ZrO_2$ is shown to be a complicated synergetic effect of fission product atomic size, electron negativity, occupation site and phase structure of the host.



## 1. Introduction

In nuclear reactor systems, the chemical compatibility between the fuel and cladding is extremely important for safe operation of a reactor [1]. One of the important factors that affect the compatibility is the distribution of the fission products (FPs) generated within the fuel. Fission gases, such as krypton (Kr) and xenon (Xe), and volatile corrosive fission products, e.g., iodine (I) and cesium (Cs), are produced during and after the irradiation of nuclear fuel. These fission products undergo transport towards the periphery of the fuel pin and then are released into the fuel-cladding gap. The build-up of Kr, Xe, I and Cs concentrations at the cladding interface can result in thermal conductivity deterioration, matrix swelling, development of microcracks and voids, degradation of mechanical properties, brittle fracture and stress corrosion cracking of the cladding [2,3]. Investigating the stability and migration of fission products in nuclear materials is thus of significant importance for predicting the behavior of the nuclear fuel/cladding assembly and evaluating fuel performance.

Fission product behavior in fluorite-structured oxides has been an active area of research for many years. A large number of experimental and theoretical studies have focused on urania ($UO_2$) nuclear fuel [1,4–11], whereas FP trapping and diffusion in cubic zirconia ($ZrO_2$) are scantily reported [12]. Because zirconia possesses high chemical durability, excellent radiation tolerance and good corrosion resistance, and actinides are readily incorporated in the structure, this high temperature refractory material has been considered as both a nonfertile inert matrix nuclear fuel [13–15] and a surrogate fuel material to gain fundamental understanding of urania, plutonia ($PuO_2$) and thoria ($ThO_2$). Among the various polytypes of zirconia that are formed as a function of temperature, i.e., high temperature cubic phase at 2640–2950 K, intermediate tetragonal phase at 1440–2640 K, and low temperature monoclinic phase below 1420 K [13], the cubic phase is of particular interest because it is isostructural with nuclear fuels urania, plutonia and thoria [16,17].

A crucial issue for the application of cubic $ZrO_2$ as inert matrix fuel is its ability to confine the fission products [18]. The distribution of FPs in the fuel depends on a number of factors, including the solubility in the fuel, the mobility, the chemical affinity with other reactive surface, etc. [4]. Up to now, numerous efforts have devoted to understand FP solubility and diffusion in the bulk $UO_2$, while FP surface diffusion through mechanical structural imperfection, such as nano-pores or nano-cracks, has not gained much attention. In our previous work on near-surface and bulk behavior of Ag in SiC [19], a combined *ab initio* total energy and ion beam irradiation study suggested that surface diffusion is a possible mechanism for Ag release from the SiC in the nuclear reactor. Liu et al. studied fission product incorporation and segregation in bulk and at interfaces of oxides [20]. They found the thermodynamic driving force of segregation for Xe and Cs from bulk MgO to the MgO/fluorite interface is strong. To effectively reduce or control FP production and transport for safe and economic operation of nuclear reactors, it is important to develop a fundamental understanding of FP behavior in both bulk and surface of matrix fuel.

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0022-3115/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jnucmat.2013.11.044

In the present study, *ab initio* methods based on density functional theory, with and without considering van der Waals correction, are employed to study the stability and migration of Kr, I and Xe in $ZrO_2$. Cs is not included in this study because van der Waals correction is not available for this chemical element. Both bulk $ZrO_2$ and $ZrO_2$ (1 1 1) are considered for comparison to future experimental studies. The occupation site, geometrical configuration, interaction energies, and energy barriers for migration are all determined. The migration pathway for FPs in both bulk and surface $ZrO_2$ are also identified. It is shown that FP behavior in $ZrO_2$ is significantly dependent on the atomic size and electronic configuration of the FPs, as well as the phase state of the host. The results from this study provide important information for advancing the current understanding of fission product transport and release in fluorite-structured oxides like $UO_2$ and $PuO_2$.

## 2. Computational details

All the calculations were carried out using the Vienna *Ab Initio* Simulation Package (VASP) [21]. The exchange–correlation effects were treated using the general gradient approximation [22] with spin-polarized effects considered. For bulk $ZrO_2$, a supercell consisting of 96 atoms was used, and three trapping sites for FPs are considered: Zr vacancy ($V_{Zr}$), O vacancy ($V_O$) and octahedral interstitial (Octa., as shown in Fig. 1(a)) sites. The O-terminated $ZrO_2$ (1 1 1) surface was simulated by a repeated slab model [23,24], in which one slab consists of six zirconium layers (four Zr atoms per layer) and eleven oxygen layers (four O atoms per layer), and a vacuum region of 15 Å separating the repeated slabs was used. A $(2 \times 2)$ surface unit cell was considered. The structural model and the considered five adsorption sites, including the surface vacant Zr ($SV_{Zr}$) and O sites ($SV_O$), and Hol1, Hol2 and Top sites, are shown in Fig. 1(b). Adsorbates were introduced only on one side of the slab. The adsorbate and the atoms in the top eight layers were allowed to relax, while the others were fixed at the bulk truncated positions. A plane-wave cutoff energy of 500 eV was used throughout our calculations. The geometric structure was optimized using the conjugated-gradient technique. A $4 \times 4 \times 4$ and a $2 \times 2 \times 1$ k-point sampling in Brillouin zone were employed for bulk and surface calculations, respectively. Because the standard DFT are unable to describe correctly van der Waals interactions in systems like Kr and Xe, the DFT-D2 method, which was proposed by Grimme [25] to correct the interaction, was also employed for comparison. The calculated lattice constants and cohesive energies of bulk Kr, I, Xe and $ZrO_2$ obtained by DFT and DFT-D2 methods are presented in Table 1. For bulk Kr and Xe (fcc structure), it is clear that the structural and energetic properties from DFT-D2 calculations are in much better agreement with experiments [26–29] than standard DFT results. In the case of bulk I (orthorhombic structure), the DFT-D2 method describes better overall the lattice structures, whereas the cohesive energy obtained from standard DFT agrees well with the experimental value [29]. For bulk $ZrO_2$, both methods present relatively similar results.

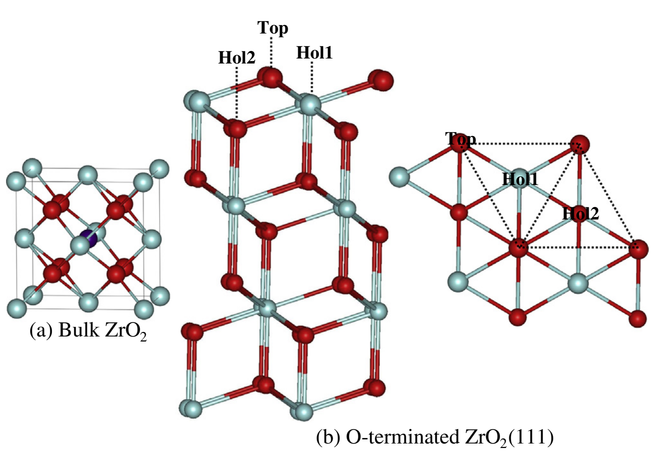


**Fig. 1.** (a) Schematic view of bulk $ZrO_2$. (b) Side and top view of O-terminated $ZrO_2$ (1 1 1) surface. Octa.: an octahedral interstitial site; Top: the site on top of a first-layer O atom; Hol1: the threefold hollow site of three first-layer O atoms that is also on the top of a second-layer Zr atom; Hol2: the threefold hollow site of three first-layer O atoms that is also on the top of a third-layer O atom.

## 3. Results and discussion

### 3.1. Trapping geometries and energies of fission products in bulk $ZrO_2$

To investigate the stability of Kr, I and Xe in bulk $ZrO_2$, the structure of fission products trapped in the $V_{Zr}$ and $V_O$, and octahedral interstitial sites are relaxed and the incorporation energies are calculated. The incorporation energy is the energy required to incorporate an atom in a pre-existing defect site: $E_{FP}^{XInc} = E_{FP}^{X} - E^{X} - E_{FP}$, where $E_{FP}^{X}$ and $E^{X}$ are the total energies of the system with and without incorporation of fission product in site *X*, and $E_{FP}$ is the total energy of an isolated fission product atom [3]. The calculated results are presented in Table 2, where the negative values indicate the fission product becomes more stable when it is incorporated in the corresponding site than its isolated state, and the positive values suggest that a certain amount of energy is needed to accommodate a fission product at the corresponding site. For I trapping, the energies are negative for incorporation in a Zr vacancy site and positive for other sites, indicating that the vacant Zr site is more favorable. In the case of Kr and Xe, the incorporation energies are positive for all the sites, and the energies for the vacant Zr site are the lowest. The results that iodine and noble gases occupation at $V_{Zr}$ sites are exothermic and endothermic, respectively, suggest that I is more easily to be trapped than the noble gases. This agrees well with our previous study of Br and Xe occupation in $ThO_2$ and $CeO_2$ [3], in which Br is more easily to be trapped than Xe. Our finding that the lowest incorporation energy corresponds to the cation vacancy site is found to be consistent with the incorporation of Br, Cs, and Xe in $ThO_2$ and $CeO_2$ [3], and Cs in $UO_2$ [4,6,30]. Comparing the incorporation energies obtained by DFT and DFT-D2 methods, we find that consideration of van der Waals correction changes the relative stability of Kr and Xe. Standard DFT predicts that Xe is more likely to be trapped than Kr, while DFT-D2 shows comparable stability of both noble gases. However, both methods predict the preference for Zr vacancy site occupation to other sites and the preference of I incorporation over Kr and Xe.

Table 3 illustrates the geometrical and electronic properties for fission product incorporation in the vacant Zr site of bulk zirconia. As compared with bulk $ZrO_2$ containing one Zr vacancy, fission product incorporation causes volume swelling, and the swelling caused by I trapping is the smallest, i.e., 0.34%. The ⟨I–O⟩ bond length of 2.27 Å is ∼0.09 Å shorter than the distance between other FPs and their neighboring oxygen atoms, indicative of stronger interaction between iodine and oxygen. This is consistent with the Bader charge analysis, which shows I shares the most electrons with the neighboring oxygen atoms. In order to reveal the nature of the bonding between the FPs and their neighboring atoms, we further analyze the charge density difference for FP trapping at the Zr vacant site of bulk $ZrO_2$, as presented in Fig. 2. In all cases, the bonding between the FPs and their first neighboring O atom exhibits covalent character, and the strongest covalency is found for ⟨I–O⟩. Although Kr and Xe are noble gases and historically were thought to be non-reactive, relatively stable compounds of both