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Influences of Zr, Ce and Ba fission products on the surface properties of UO_2: Atomistic simulations

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ABSTRACT

Molecular dynamics (MD) simulations with a shell-core model have been carried out to investigate the influences of Zr, Ce and Ba fission products on the surface properties of UO_2. Simulation results indicate that (i) the presence of these fission products will change the surface energy of three low-index surfaces in UO_2; (ii) the individual addition of Ce has no significant effect on the surface energy, while the individual addition of Ba will dramatically decrease the surface energy of UO_2 by approximately 18% on (100) surface, 7% on (110) surface and 9% on (111) surface with the Ba contents ranging from 0 to 12.5 mol% at 300 K, which is obviously contrary to the Zr; (iii) the combined additions of Zr, Ce and Ba fission products will continuously increase the surface energy of UO_2 (100), (110) and (111) surfaces; (iv) the structures of the three low-index surfaces in pure UO_2 as well as $U_{0.8}(Zr, Ce, Ba)_{0.2}O_2$ are dramatically disturbed after the free relaxation; (v) The nearest O atoms move towards the Zr and Ce atoms center by about 0.21 Å and 0.12 Å but move away from the Ba atom center by about 0.27 Å.

1. Introduction

As one of the most widely used materials for nuclear fuel, uranium dioxide (UO_2) has been the subject of numerous experimental as well as theoretical studies in the past few decades. In nuclear reactors, the fissile isotopes ^{235}U and ^{239}Pu in UO_2 fuel fission, thus yielding a number of different fission products. The fission products can be classified as solid fission products (e.g., Zr, Ce, Ba, Mo, Ru, Rh, Pd, Nb, Y, La, Sm, Pm) and gaseous fission products (e.g., Xe, Kr, I, Cs, Br, Te) according to their state in the fuel matrix. The presence of these fission products, especially the solid fission products in UO_2 fuel matrix, can drastically change the structures, mechanical properties and thermophysical properties of UO_2, which can lead to a series of serious consequences for the safety of nuclear devices [1–3].

The solubility, trap site and diffusion of solid fission products in UO_2 matrix has been investigated by the density functional theory (DFT) and molecular statics calculations in the past few decades [3–14], and the existing studies show that most of the solid fission products, such as Zr, Ce, Ba, Sr, Y, Sm, Rb, Nb, La, are soluble in UO_2. Additionally, solid fission products occupy preferentially the single uranium vacancy trap sites for stoichiometric and all nonstoichiometric UO_2. This is in contrast with the large fission gas atoms such as Xe and Kr, which majorly occupy divacancy or trivacancy trap sites in stoichiometric UO_2 [15–17]. Apart from Ru, the solid fission products in UO_2 all exhibit higher activation energy than the fission gas Xe and the most solid fission products diffuse with rates similar to the U self-diffusion.

However, to the best of our knowledge, there are still few studies on the influences of the solid fission products on the surface properties of UO_2 are available. It should be noted that the knowledge of the surface properties of a nuclear fuel, such as surface energy and surface structure, is very important for understanding and predicting of the crystal growth rates, cleavage, crystal morphologies, sintering, strength, fracture behavior and the gas absorption [19–24]. Moreover, the surface energy is a significant parameter in the modeling of the fission gas behavior in UO_2 fuel during irradiation [25,26]. Thus the fuel performance analysis code requires the surface energy of fuel matrix as an essential input parameter.

Therefore, the present study aims to investigate the influence of solid fission products (individually and in combination) on the surface properties of UO_2, using the MD simulation with a shell-core model. The major three solid fission products, Zr, Ce and Ba are considered as the dopants in UO_2 in this work. The surface energies and atomic structures of the doped and pure UO_2 (100), (110) and (111) low miller index surfaces are calculated with different solid fission products contents and temperatures. This study will help for the understanding and predicting of the surface properties of UO_2 fuel during irradiation.

2. Simulation methodology

As with any MD simulation, the accuracy and reliability of the simulation results depend ultimately on the quality of the interatomic

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Table 1
Potential parameters of $U_{1-y}M_yO_2$ (M = Zr or/and Ce, Ba).

Species	A(eV)	ρ(Å)	C(eV Å^6)	Y(e)	k(eV Å^{-2})	Reference
U^{4+}-O^{2-}	1761.780	0.3582	12.3	—	—	[33]
O^{2-} O^{2-}	9547.960	0.2192	32.0	—	—	[33]
$Zr^{4+}-O^{2-}$	1502.110	0.3477	5.1	—	—	[34]
$Ce^{4+}-O^{2-}$	1809.680	0.3547	20.4	—	—	[35]
$Ba^{2+}-O^{2-}$	4818.416	0.3067	0.0	—	—	[36]
U^{4+}	—	—	—	−0.10	160.00	[33]
O^{2-}	—	—	—	−2.04	6.30	[33]
Zr^{4+}	—	—	—	−0.05	189.70	[34]
Ce^{4+}	—	—	—	−0.20	177.84	[35]
Ba^{2+}	—	—	—	0.169	34.05	[36]

potentials employed. In this study, the classical Buckingham potentials were used to describe the short range interaction between ions,

$$U(r) = A\exp\left(-\frac{r}{\rho}\right) - \frac{C}{r^6} \quad (1)$$

where A, ρ, and C are the adjustable parameters and r is the atom distance. The polarizability of the ions is realized through the shell-core model [27]. In this model, the polarizable ion is assigned two charges: one charge (Y) on the massive core and the other charge (X) on a displaceable massless spherical shell which is linked to the core through an isotropic harmonic spring with a force constant k. The shells and cores in the shell-core model are allowed to relax independently during the simulation process and the short-range potential acts between shells. Although lots of shell model potentials are appropriate for the investigation of the surface properties of UO_2 [28–32], we have chosen the parameters which are listed in Table 1 since they are a consistent set that includes the Zr, Ce and Ba fission products cations. The potential parameters for each pair of ions used in this work have been proved to be able to correctly reproduce the elastic constants, lattice parameter, dielectric constants and defect formation energies for UO_2, ZrO_2, CeO_2 and BaO. The details of the potential parameters have been discussed elsewhere [33–36].

The MD simulation program, Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) [37] is used to perform the simulations in this work. The simulations are implemented in a constant number of atoms, constant volume and constant temperature ensemble (NVT) with the temperature controlled by a Nose-Hoover thermostat method [38]. The simulation time step of integral is 1 fs. A visual molecular dynamics (VMD) program [39] was used for the visualizations.

In order to predict the influence of Zr, Ce and Ba fission products on the surface properties of UO_2, the standard slab model was employed. Surfaces were constructed by truncating single crystals of $U_{1-y}M_yO_2$ (M = Zr or/and Ce, Ba) parallel to the plane of interest. In the $U_{1-y}M_yO_2$ system, the desired number of Ze, Ce and Ba ions which

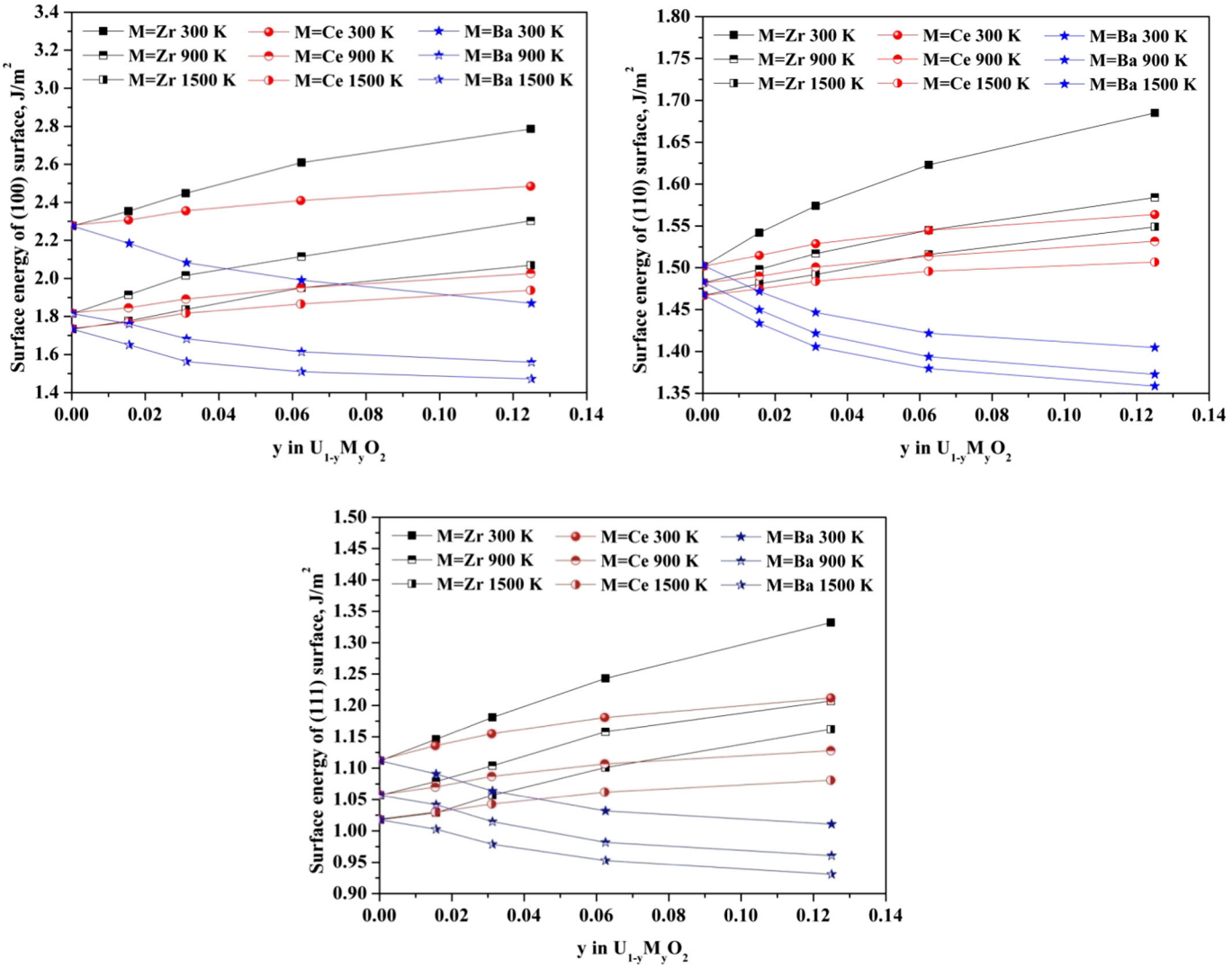

Fig. 1. Effects of individual additions of Zr, Ce and Ba on the surface energy of (100), (110) and (111) surfaces in UO_2 at three different temperatures.