

## First-Principles Study on Thermodynamic Stability of $\text{UO}_2$ with He Gas Incorporation via Alpha-Decay

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**Abstract** – Using first principles calculations we investigated the thermomechanical stability of spent nuclear fuels (SNF), especially how mechanical properties of  $\text{UO}_2$ , such as, bulk, shear and Young's moduli and Poisson's ratio vary through alpha-decay of U into Th with generation of He gas. Our results indicate that substitution of U by Th through alpha decay ( $\text{U}_{1-x}\text{Th}_x\text{O}_2$ ) does not significantly affect the stability of the grain in a fuel matrix. In addition, we studied the transport properties of He in and boundaries of the  $\text{U}_{1-x}\text{Th}_x\text{O}_2$  grain. Helium preferentially resides at the grain boundaries through diffusion. Our study can contribute to substantial reduction of environmental risk and enhancement of our sustainability by safe control of radioactive materials.

**Key words:** First-principles, Uranium dioxide, Alpha decay, Thermodynamic stability, Helium gas

### 1. Introduction

Uranium dioxide ( $\text{UO}_2$ ) has been a key nuclear fuel, yet in spite of many benefits of nuclear energy, the safe and economic, disposal of radioactive waste is global concern [1,2]. Especially, highly radioactive spent nuclear fuels (SNFs) are the central materials for the handling [3]. Recently, reducing the radioactivity and volume through pyroprocessing technology was studied, but still long-term storage or permanent disposal of SNFs in deep earth is the major way.

In the disposed SNFs, a large quantity of helium (He) gas can be generated and coalesced into bubbles in the fuel matrix, which may lead to swelling of the materials [4]. To improve the safety level, there have been many experimental or theoretical studies on the behavior of He in the fuel matrix [5-7]. For example, the stability of He was evaluated by calculating its incorporation energy in the grain [8,9]. It was reported that He thermodynamically does not stay in the interstitial sites of bulk  $\text{UO}_2$  since the incorporation energy is very high (0.72~0.89 eV per He atom). In addition, activation energies of He for diffusion in bulk  $\text{UO}_2$  were calculated as 2.2~4.15 eV [5,8] and measured as 1.87~2.23 eV [9,10] meaning the process is, in fact, difficult.

Since an alpha decay of U into Th is of importance for the production of He [11], a pure  $\text{UO}_2$  may not be a relevant model system for studying SNF stability. In this study, we calculated moduli and

Poisson's ratio of  $\text{U}_{1-x}\text{Th}_x\text{O}_2$  to identify variation of the mechanical strength as a function of Th composition. Using first-principles calculations the incorporation energy and diffusion energy barrier of He in the  $\text{U}_{1-x}\text{Th}_x\text{O}_2$  at  $x = 0.0, 0.13$  and  $0.25$  were predicted. Since  $\text{UO}_2$  pellet is a poly-crystalline [12], we set up a  $\Sigma 3(111)$  tilt grain boundary model, which is one of common grain boundaries [13,14] to investigate stability of SNF.

### 2. Computational Details

All calculations in this study were carried out as density functional theory calculations as implemented in Vienna ab initio simulation package (VASP) [15]. The generalized gradient approximation (GGA) with Perdew-Burke-Ernzerhof (PBE) [16,17] was used for exchange correlation functional, and the projected augmented wave (PAW) potentials [18] were used to substitute core electrons of U, Th, O and He. Convergence criteria for ionic relaxation for all calculations were energy difference less than  $10^{-5}$  eV compared to the right before step. For bulk properties, such as incorporation energies and mechanical properties, the k-points sampling was conducted on a  $4 \times 4 \times 4$ , while for grain boundaries  $5 \times 5 \times 3$  mesh was used. We performed calculations including the effective Hubbard correction in the GGA+U approximation to correct the localized f electrons of uranium, using  $U_{\text{eff}} = 3.96$  eV [14,19] with U-ramping scheme [20,21] to optimize ground state of  $\text{UO}_2$ .

### 3. Results and Discussion

#### 3-1. Stability of fuels in a grain of $\text{U}_{1-x}\text{Th}_x\text{O}_2$

As both  $\text{UO}_2$  and  $\text{ThO}_2$  have cubic fluorite structures ( $a = 5.47$  for

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‡This article is dedicated to Prof. Yong-Gun Shul on the occasion of his retirement from Yonsei University.

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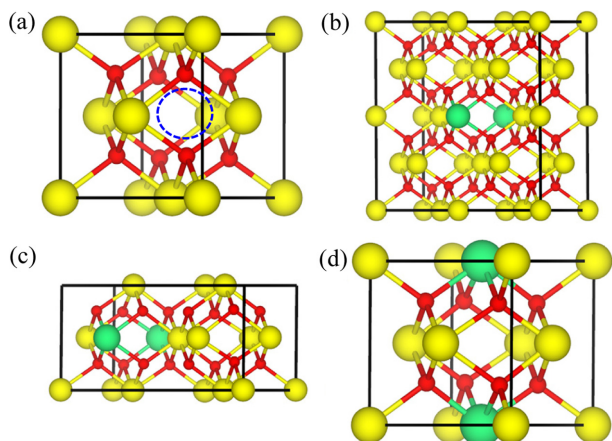


Fig. 1. Model systems of (a)  $\text{UO}_2$  (b)  $\text{U}_{0.94}\text{Th}_{0.06}\text{O}_2$  (c)  $\text{U}_{0.87}\text{Th}_{0.13}\text{O}_2$  and (d)  $\text{U}_{0.75}\text{Th}_{0.25}\text{O}_2$  to calculate incorporation energies. Yellow, green and red atoms indicate U, Th and O, respectively. The blue circle in (a) indicates OIS.

$\text{UO}_2$ ,  $a = 5.60$  for  $\text{ThO}_2$ ) [22],  $1 \times 1 \times 1$  unit cells of  $\text{U}_{1-x}\text{Th}_x\text{O}_2$  were employed to model  $\text{U}_{1-x}\text{Th}_x\text{O}_2$  matrix. An octahedral interstitial site (OIS) [23,24] was considered for He atom in the matrix as shown in Fig. 1. Supercells of  $2 \times 1 \times 1$  and  $2 \times 2 \times 1$  of  $\text{UO}_2$  were used, and in each supercell a U atom was replaced by Th atom to describe  $\text{U}_{0.87}\text{Th}_{0.13}\text{O}_2$  and  $\text{U}_{0.94}\text{Th}_{0.06}\text{O}_2$ , respectively, via alpha decay.

The incorporation energy was defined as Eq. (1),

$$E_{\text{inc}} = E_{\text{bulk+He}} - (E_{\text{bulk}} + E_{\text{He}}) \quad (1)$$

$E_{\text{inc}}$  represents incorporation energy,  $E_{\text{bulk+He}}$  is total energy of the model  $\text{U}_{1-x}\text{Th}_x\text{O}_2$  with He at the OIS,  $E_{\text{bulk}}$  is the total energy of the  $\text{U}_{1-x}\text{Th}_x\text{O}_2$  without He and  $E_{\text{He}}$  is the energy of non-interacting He atom.

Incorporation energies of  $\text{U}_x\text{Th}_{1-x}\text{O}_2$  were 0.89, 0.85, 0.91 and 0.90 eV at  $x = 0.0, 0.06, 0.13$  and  $0.25$  as shown in Fig. 2(a), and activation barriers of He in  $\text{UO}_2$  and  $\text{U}_{0.03}\text{Th}_{0.97}\text{O}_2$  obtained by nudged elastic band (NEB) method [9,10] are illustrated in Fig. 2(b). Since  $E_{\text{inc}}$  in  $\text{U}_{1-x}\text{Th}_x\text{O}_2$  are positive He is thermodynamically unstable in  $\text{U}_{1-x}\text{Th}_x\text{O}_2$ . It implies that He prefers diffusing out of the grain and

into grain boundary or more open space. Diffusion activation barriers of He between OIS in  $\text{UO}_2$  and  $\text{U}_{0.97}\text{Th}_{0.03}\text{O}_2$  were estimated as 2.39 eV and 2.40 eV, respectively, as shown in Fig. 2(b). These values are similar because bond strength Th-O are stronger than U-O. In the diffusion process in  $\text{UO}_2$  the diffusing He only elongates U-O bond length from 2.39 to 2.52 Å, while Th-O bond length remains the same. This feature is the same in  $\text{U}_{0.97}\text{Th}_{0.03}\text{O}_2$  even when He moves beside Th.

### 3-2. Mechanical strength of $\text{U}_x\text{Th}_{1-x}\text{O}_2$

For a cubic crystal, three independent elastic constants ( $C_{11}$ ,  $C_{12}$ , and  $C_{44}$ ) [25] are defined.  $C_{44}$  can be obtained from applying a monoclinic volume-conserving distortion matrix,  $\Delta_{\text{mono}}$  to a relaxed unit cell [25].

$$\Delta_{\text{mono}} = \begin{pmatrix} 1 & \delta/2 & 0 \\ \delta/2 & 1 & 0 \\ 0 & 0 & 4/(4-\delta^2) \end{pmatrix}$$

where  $\delta = -0.1, -0.05, 0.05$  and  $0.1$ . The energy increase per unit cell volume  $E(\delta)$  is given by Eq. (2),

$$E(\delta) = C_{44}\delta^2 + O(\delta^3) \quad (2)$$

Tetragonal shear constant  $C'$  [ $C' = ((C_{11}+C_{12})/2)$ ] can be obtained from applying a tetragonal volume-conserving distortion matrix,  $\Delta_{\text{tetra}}$  to a relaxed unit cell [25].

$$\Delta_{\text{tetra}} = \begin{pmatrix} 1+\delta & 0 & 0 \\ 0 & 1-\delta & 0 \\ 0 & 0 & 1/(1-\delta^2) \end{pmatrix}$$

where  $\delta = -0.1, -0.05, 0.05$  and  $0.1$ . The energy increase per unit cell volume  $E(\delta)$  is also related to the tetragonal shear constants as Eq. (3),

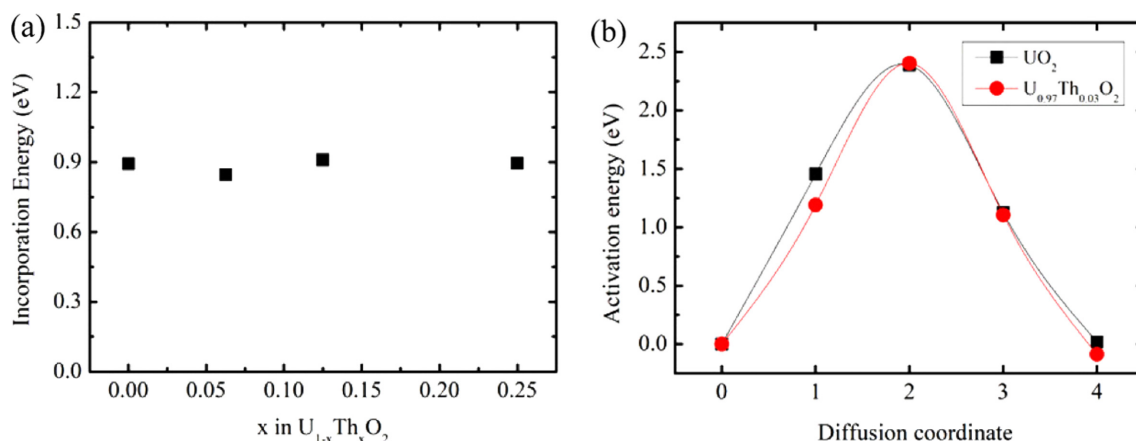


Fig. 2. (a) Incorporation energy of  $\text{U}_{1-x}\text{Th}_x\text{O}_2$  at  $x = 0.89, 0.85, 0.91$  and  $0.90$ . (b) Energy variations of  $\text{UO}_2$  and  $\text{U}_{0.97}\text{Th}_{0.03}\text{O}_2$  when He atom diffuses from OIS to another nearest OIS.

$$E(\delta) = C'\delta^2 + O(\delta^3) \quad (3)$$

Bulk modulus,  $B$ , can be similarly obtained from a volume-changing matrix to a relaxed unit cell. Here, we used the volume changes of -10 %, -5 %, 5 % and 10 % to the relaxed unit cell volume, respectively. From the tetragonal shear constant and bulk modulus,  $C_{11}$  and  $C_{12}$  were obtained [ $B = (C_{11} + 2C_{12})/3$ ].

From these elastic constants, we calculated shear moduli ( $G$ ) and Poisson's ratio ( $\nu$ ). The  $G$  can be calculated by the Hershey-Kröner averaging method relation [25,26] by which poly-crystalline effect is considered as shown in Eq. (4).

$$8G^3 + (9B + 4C')G^2 - 3C_{44}(B + 4C')G - 6BC_{44}C' = 0 \quad (4)$$

Young's modulus ( $E$ ) is obtained from the relation between bulk and shear moduli [25,27] as Eq. (5).

$$E = \frac{9BG}{3B + G} \quad (5)$$

Poisson's ratio  $\nu$  is obtained from bulk and Young's moduli [25] as Eq.(6).

$$\nu = \frac{3B - E}{6B} \quad (6)$$

We calculated elastic constants to obtain moduli and Poisson's ratio with respect to  $x$  in  $U_{1-x}Th_xO_2$ , where  $x$  is 0, 0.25, 0.5, 0.75 and 1.0, which are represented in Table 1.

Our calculations for Poisson ratios for  $UO_2$  (0.251) and  $ThO_2$  (0.220) are slightly smaller than experimentally measured ones (0.291~0.302 [28] and 0.279 [29], respectively). It can be ascribed to the anharmonicity in the moduli of the materials. From the results, the mechanical strength of  $UO_2$  does not significantly change when the substitutional defects of U ions to Th ions are generated.

### 3-3. Stability of He in the grain boundary

$\Sigma 3(111)$  tilt grain boundary is one of the most abundant coincident site lattice (CSL) boundaries [14]. This boundary consists of two (111) planes as shown in the Fig. 3. Grain boundary energy and surface energy are defined as Eq. (6-1) and (6-2).

$$E_{gb} = \frac{E_{tot}(gb) - N_{gb}E_{bulk}}{2A_{gb}} \quad (6-1)$$

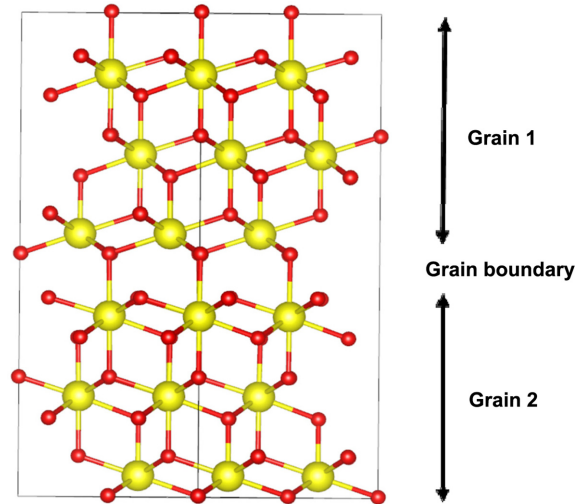


Fig. 3. Structure of  $\Sigma 3(111)/[110]$  tilt grain boundary and Position of a helium atom along the grains.

$$E_{surf} = \frac{E_{tot}(surf) - N_{surf}E_{bulk}}{2A_{surf}} \quad (6-2)$$

where  $E_{tot}(gb)$  and  $E_{tot}(surf)$  indicate total energy of grain boundary and surface of  $UO_2$ , respectively, and  $E_{bulk}$  does the energy of a pristine bulk  $UO_2$  per formula unit.  $N_x$  and  $A_x$  represent number of  $UO_2$  units in the system  $x$  and a cross-sectional area of the system  $x$ . If  $E_{gb} - 2E_{surf} < 0$  two grains with grain boundaries are more stable than two non-interacting grains with terminated by (111) surfaces. As we calculated grain boundary energy  $E_{gb} = 0.057 \text{ eV}/\text{\AA}^2$  and surface energy  $E_{surf} = 0.053 \text{ eV}/\text{\AA}^2$  the  $\Sigma 3(111)$  tilt grain boundary is more stable than two grains with terminated with (111) surfaces supporting experimental observation.

We calculated incorporation energies of a He atom for three different locations near the grain boundary shown in Fig. 3. The grain boundary incorporation energy of He was calculated as 0.85 eV, which is, in comparison with a pristine bulk, lower by 0.05 eV. It means He more easily resides at the more open grain boundary than inside bulk grain (the distance between two U atoms at the grain boundary increases from 3.17 Å to 3.30 Å. Therefore, we found that helium becomes more stable as helium migrates to the  $\Sigma 3(111)$  tilt grain boundary.

Table 1. Shear modulus, Young's modulus

Compound	B	G	E	$\nu$
$UO_2$	192.0	114.6	286.7	0.251
	192-240 [30]	80-105 [25]	-	0.30-0.34 [25]
	209-221 [31]	83 [31]	-	0.29-0.30 [28]
$U_{0.75}Th_{0.25}O_2$	190.1	138.6	334.6	0.206
$U_{0.50}Th_{0.50}O_2$	246.9	153.7	381.8	0.242
$U_{0.25}Th_{0.75}O_2$	193.9	121.4	301.3	0.241
$ThO_2$	189.1	129.7	316.7	0.220
	198 [22]	100 [32]	-	0.279 [29]

#### 4. Conclusion

We performed first-principles modeling to investigate the influence of Th and grain boundary on mechanical properties and stability of UO<sub>2</sub> nuclear fuels. By calculating incorporation energy of He and mechanical properties we concluded that Th does not affect the stability of SNFs significantly. Among the various grain boundaries, we chose  $\Sigma 3$  (111)/[110] tilt grain boundary to see stability of He. We found that this grain boundary is a more thermodynamically stable position for He than bulk grain.

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