Journal of Nuclear Materials 385 (2009) 510–516

Contents lists available at ScienceDirect

Journal of Nuclear Materials

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

Theory of He trapping, diffusion, and clustering in UO_2

Younsuk Yun *, Olle Eriksson, Peter M. Oppeneer

Department of Physics and Materials Science, Uppsala University, Box 530, S-751 21 Uppsala, Sweden

ARTICLE INFO

Article history:
Received 19 November 2008
Accepted 15 December 2008

PACS:
66.30.Jt
61.72.−y
61.72.Ji

ABSTRACT

We have performed *ab initio* total energy calculations to investigate the behavior of helium and its diffusion properties in uranium dioxide (UO_2). Our investigations are based on the density functional theory within the generalized gradient approximation (GGA). The trapping behavior of He in UO_2 has been modeled with a supercell containing 96-atoms as well as uranium and oxygen vacancy trapping sites. The calculated incorporation energies show that for He a uranium vacancy is more stable than an oxygen vacancy or an octahedral interstitial site (OIS). Interstitial site hopping is found to be the rate-determining mechanism of the He diffusion process and the corresponding migration energy is computed as 2.79 eV at 0 K (with the spin-orbit coupling (SOC) included), and as 2.09 eV by using the thermally expanded lattice parameter of UO_2 at 1200 K, which is relatively close to the experimental value of 2.0 eV. The lattice expansion coefficient of He-induced swelling of UO_2 is calculated as 9×10^{-2}. For two He atoms, we have found that they form a dumbbell configuration if they are close enough to each other, and that the lattice expansion induced by a dumbbell is larger than by two distant interstitial He atoms. The clustering tendency of He has been studied for small clusters of up to six He atoms. We find that He strongly tends to cluster in the vicinity of an OIS, and that the collective action of the He atoms is sufficient to spontaneously create additional point defects around the He cluster in the UO_2 lattice.

1. Introduction

Many fission products (Xe, Kr, I, etc.) as well as α-particles (He) are produced during and after the irradiation of fuel in nuclear reactors. The presence of the fission products and He atoms can lead to the formation of bubbles and to a possible swelling of the fuel material, mostly UO_2 or mixed oxides, because of their low solubility in the fuel lattice [1–3]. Especially, a large concentration of He is created during the long-term storage of spent fuel which affects the mechanical properties of the burned-up fuel material with possible consequences for the long-term storage process [4].

For those reasons, the behavior of He has been experimentally investigated to improve the performance and stability of the nuclear fuel [5]. Several experimental studies have been carried out to determine the most favorable location as well as diffusion coefficient of He in UO_2 [6–8]. The formation of He bubbles has been investigated as a function of temperature and implantation conditions in UO_2 [9]. Theoretical studies have contributed also to understanding the behavior of He trapped at various defects and the variation of the lattice parameter of UO_2 induced by He [10–13]. Despite the amount of work already done, some open questions do remain. For instance, the stability of He trapped at a vacancy or an interstitial site has been debated so far. Petit et al. [11] and Crocombette [12] suggested that the most stable trap site for He is a uranium vacancy (V_U) while two other theoretical groups predicted that the occupancy of interstitial sites would be more probable [10,13]. In addition, theoretical investigations of the migration behavior of He are lacking and little is known about diffusion properties of He in UO_2. Most of all, a precise investigation of He bubble nucleation has not been performed for the UO_2 fuel matrix by an *ab initio* approach so far.

The purpose of this study is to investigate in detail the diffusion properties of He and its site stability in UO_2 by carrying out energetic calculations based on the density functional theory (DFT). First, we have determined the most stable location of He from the calculated incorporation energy, using generalized gradient approximation (GGA) [14] calculations. We have performed nudged elastic band (NEB) [15,16] calculations, to clarify the site stability from the energy path of He between two trap sites. In order to understand the diffusion mechanism of He, the migration energy has been calculated by taking into account spin-polarization (SP), spin-orbit coupling (SOC), and finite temperature effects. Next, we have calculated the lattice expansion coefficient of UO_2 due to interstitial He. We have also investigated the structure and behavior of two He atoms in the UO_2 matrix calculating the total energy of possible configurations of two He atoms and the lattice expansion induced by them. Lastly, the clustering behavior of He has been investigated more precisely, by increasing the number of He atoms in the supercell and letting all atomic positions relax

---

* Corresponding author. Tel.: +46 18 471 7308; fax: +46 18 471 3524.
E-mail address: younsuk.yun@fysik.uu.se (Y. Yun).

0022-3115/$ - see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.jnucmat.2008.12.311

until the minimum energy configuration is obtained. The employed computational methodology is briefly presented in the next section. In Section 3 our results are presented, compared to previous studies and discussed in detail.

2. Computational methodology

The present study has been performed using the Vienna *ab initio* Simulation Package (VASP) [17–19]. To investigate the electronic structure of UO_2, the projector-augmented wave (PAW) [20] method has been used, together with the GGA [14] approaches for the exchange-correlation functional. For all defect energy calculations, we have adopted the conventional GGA approach, first, because first-principles calculations without Hubbard U correction to the GGA approximation showed that it can give almost correct energy information for UO_2, regardless of the fact that a wrong electronic band structure was predicted [21–24]. In a previous study [25] it was shown that formation and migration energies of defects in UO_2 computed using the spin-polarized GGA method give energy values that agree well with experimental data. Second, the use of the GGA + U method to large supercells as we investigate is non-trivial, because non-global energy minima can occur in GGA + U calculations. Amadon et al. reports the difficulty to determine the ground states of a system with in GGA + U calculations due to the increase of metastable states [26].

In this study, large supercells containing up to 96-atoms have been employed to reduce any artificial error due to the use of a small supercell. Fig. 1(a) shows the oxygen sublattice in a 96-atom supercell, where the oxygen atoms are at the corners of the grey as well as transparent cubes. The uranium atoms occupy the center of the alternating grey cubes and the center of transparent cubes is a so-called octahedral interstitial site (OIS) in the FCC structure, as indicated in Fig. 1(b).

The incorporation energy is calculated as the energy difference between two systems, where He is trapped at an OIS and at a vacancy [25], respectively, and can be written as follows:

$$E^{In}_{He_X} = \left(E^{N}_{perfect} + E^{N}_{He_X}\right) - \left(E^{N+1}_{He_{OIS}} + E^{N-1}_{V_X}\right) \quad (1)$$

where V_X is a vacancy of element X, which is either a uranium or an oxygen atom and He_{OIS} and He_X indicate that He is trapped at an OIS and at a vacancy of an X-element, respectively. N is the number of atoms in the supercell, which is 96 in this study, and $E^{N}_{perfect}$ is the total energy of a defect-free supercell. In this study, we assume that vacancy defects pre-exist, thus we do not explicitly consider the vacancy formation energy, which is possible as we focus on the relative incorporation energy between a vacancy and an OIS. We have also investigated the He behavior at other locations including off-diagonal positions, and found that He always moves to the OIS during atomic relaxation in a defect-free UO_2. For defect structures with a vacancy, He moves from any interstitial positions to a vacancy due to the strain energy. From these calculations, we found that there are two kinds of stable sites of He, which are an OIS and a vacancy, in UO_2. Therefore, we concentrate in the following on an OIS, a uranium vacancy, and an oxygen vacancy. In Fig. 1(b) and (c), we shows the various He positions investigated.

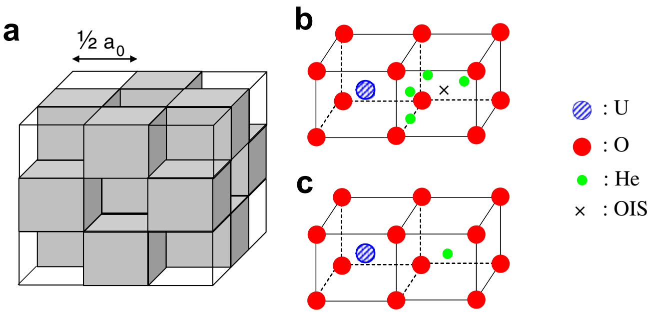

Fig. 1. The lattice structure of UO_2. (a): The oxygen sublattice in a 2 × 2 × 2 supercell containing 96-atoms. The oxygen atoms are at the corners of the cubes; the uranium atoms occupy the center of alternating grey cubes. The center of the transparent cubes indicates an octahedral interstitial site (OIS) of the FCC structure. Panels (b), and (c) show the modeling of possible locations of He at different interstitial sites, with specifically, (b) at the face center of the cube, the edge center between two oxygen atoms, and two other possible interstitial sites and (c) at an OIS.

To investigate the movement of He, the energy barrier has been calculated at the saddle point in its diffusion pathways between two adjacent OISs. All the energy values have been obtained using the VASP code within the PAW [20]–GGA [14] method. The cutoff energy of the plane-wave expansion was used up to 400 eV, and the electron charge density was computed using a 2 × 2 × 2 k-points grid in the Brillouin zone. All the calculations were done at constant volume while fully relaxing the atomic positions, and the force acting on each ion was relaxed until less than 0.01 eV/Å. As the number of He atoms in the supercell is increased, we have calculated the corresponding lattice parameter that gives the lowest total energy, and then we compared the calculated results with the values without He to obtain the lattice expansion induced by He.

3. Results and discussion

3.1. Trapping of a He atom

We first investigated the trap sites of He in UO_2. In a defect-free UO_2 matrix, there can potentially be three interstitial trap sites. As shown in Fig. 1(a–c), the interstitial He can be in the face-centered position, an axis centered position, or an octahedral interstitial position, respectively. We found that the only stable interstitial location of He is an OIS. We tested this by performing atomic relaxations with He initially in various interstitial positions. Always the He atomic position relaxes until it finally reaches the OIS.

After having confirmed that the OIS is the only stable interstitial site for He, we consider this together with other defects. In a defect structure, e.g., with O or U vacancies, we calculated the incorporation energy of He for different defects in UO_2 and compared with those obtained in previous theoretical studies, as shown in Table 1. As mentioned earlier, the incorporation energies are given relative to the value obtained for an OIS as follows:

$$\Delta E_{In}(V_X - OIS) = E^{In}_{V_X} - E^{In}_{OIS} \quad (2)$$

where X is a uranium or oxygen atom. A negative value for $\Delta E_{In}(V_U\text{–}OIS)$ indicates an energy decrease of the system when He moves from an OIS to an V_U. Conversely, positive value for $\Delta E_{In}(V_O\text{–}OIS)$ means that energy has to be provided to incorporate He at a V_O. We found that the favorable He-incorporation site in a UO_2 matrix that contains O and U vacancies is the U vacancy site, while He-incorporation in a defect-free UO_2 crystal favors the OIS site.

Table 1
Incorporation energy (unit in eV) of He calculated for different sites in the UO_2 lattice; OIS is a octahedral interstitial site, V_U and V_O are uranium and oxygen vacancies, respectively.

	Favorable site	$\Delta E_{In}(V_U\text{–}OIS)$	$\Delta E_{In}(V_O\text{–}OIS)$
Grimes et al. [10]	OIS	0.08	0.01
Freyss et al. [13]	OIS	0.50	2.50
Petit et al. [11]	V_U	−8.70	0.09
Crocombette [12]	V_U	−1.20	1.60
This study	V_U	−0.70	0.67

In the literature there exists a controversy over the site stability of He at an OIS and a V_U [10–13]. As seen in Table 1, Grimes et al. [10] and Freyss et al. [13] report that an OIS is more stable for He than a V_U while He results of Petit et al. [11] and Crocombette [12] are consistent with our findings that V_U is more stable. In addition, while three theoretical studies in Table 1 report that V_O is more unstable than V_U, Grimes et al. [10] obtained that the V_O is more stable for He than V_U, because the ΔE_{In} is smaller at V_O than V_U. In this study, to clarify better the issue, we performed nudged elastic band (NEB) [14,15] calculations, which is an efficient method for finding the energy saddle point between a given initial and final state of a transition, to understand the energy path of He diffusion between an OIS and a V_U. When an OIS and a V_U are located at the nearest lattice sites of one another, a diffusion path of He from one position to the other can be investigated. Fig. 2(a) and (b) shows the two configurations where He is located at an OIS or a V_U, respectively. Our total energy calculations showed the configuration of He at a V_U to be energetically favorable (Fig. 2(b)). In addition, the NEB calculations showed that there is no energy barrier in the energy path of He between an OIS and V_U, and, consequently, He moves spontaneously from an OIS to a V_U if, in the calculation, it is shifted from the center of the OIS. Fig. 2(c) shows four positions of He on the path between OIS and V_U where we performed the NEB calculations. These are indexed ①, ②, ③, and ④; the He moves through theses positions into a V_U during relaxations.

An interpretation of our results can be that He is expected to be found in OISs when a low concentration of vacancies is present in the UO_2 matrix. Although a V_U may not necessarily constitute the majority site available to He, our calculations nevertheless suggest that a V_U is an energetically more stable site for He than an OIS. We also carried out similar calculations for defect configurations where a V_O exists instead of a V_U (as shown in Fig. 2(a) and (b)) and obtained that in this case an OIS is a more stable site than an V_O. In order to clarify further our results, we have calculated the electron charge density of He when it occupies an OIS, V_U, or V_O, respectively. The lowest charge density was obtained at a V_U as summarized in Table 2. This finding explains why a V_U is the most stable for He among OIS, V_U, and V_O, because, it is well known [27] that a He atom prefers to occupy the site with the low electron density because of its filled-shell electronic configuration.

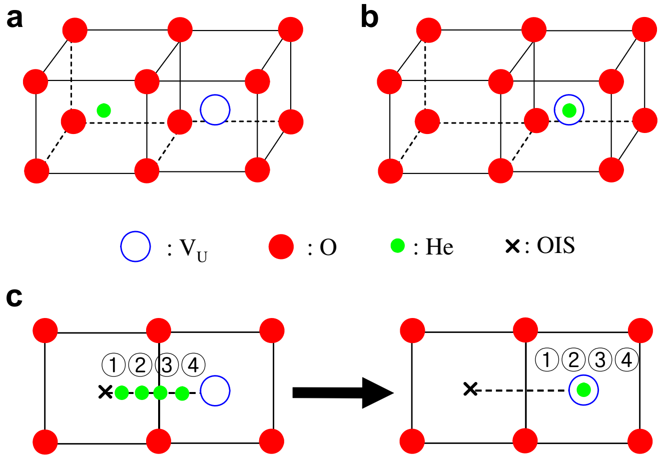

Fig. 2. Configuration of He and diffusion path of He between an OIS and a V_U. (a) He is located at an OIS, (b) located at the nearest V_U, and (c) movement of He from any positions, which are between an OIS and a V_U, into a V_U during ionic relaxation.

Table 2
Calculated electron charge density of He at an OIS, a V_U, or a V_o.

	OIS	V_U	V_O
Electron charge density	2.06	2.03	2.12

From all these results, we insist that a V_U is the most favorable site for He in UO_2, among the single vacancies and OIS.

3.2. Diffusion property of a He atom

To understand the diffusion mechanism of He in UO_2, we calculated its migration energy between two adjacent incorporation sites. The migration energy is given as the energy barrier which is the energy difference between the saddle point along the migration pathway and the highest in energy initial or final states. The energy barrier was obtained to be 2.97 eV between two OISs in a defect-free lattice, as summarized in Table 3. This energy value is much lower than that calculated by Grimes et al. [28] using an empirical potential, but it is still relatively-high compared to the energy value of 2.0 eV[6] obtained experimentally, which Roudil et al. performed He implantation on UO_2 matrix and determined the migration energy from the Arrhenius relation on the diffusion coefficient of He. We note that it is not straightforward to compare the current and the previous results with experimental values, because the simulation techniques used are based on different theoretical approaches. However, the migration energy is calculated the relative energy difference between an initial and saddle configurations in a diffusion pathway. Even though an absolute energy value of each configuration can not be comparable with other calculated results using different approaches, the relative energy difference between configurations should be comparable each other. In addition, it is important to compare the trends of the calculated energy barriers for different diffusion pathways. Table 3 shows that the energy barriers of He are remarkably decreased when He hops through a V_U or V_O site. The energy barrier is a little lower for V_U than V_O, and this result is considered to be associated with the relative incorporation energy of He compared to an OIS as shown in Table 1. The smaller energy difference between OIS and V_U incorporation energies implies that a lower energy barrier is needed when He hops through a V_U than a V_O from one OIS to another OIS. These results indicate that the vacancy-assisted diffusion of He is considerably more efficient than He diffusion by the interstitial mechanism only. Grimes et al. also reported the lower energy barrier of He for the vacancy-assisted diffusion as shown in Table 3, however, the energy needed to hop through V_O is lower than V_U in contrast with the current results. Nevertheless, this discrepancy is considered to be connected with the different results for the relative incorporation energies that the energy difference is smaller for V_O than V_U in the calculations of Grimes et al. [10] as shown in Table 1. Although the interstitial mechanism is regarded [29] as the rate-determining diffusion process of He in UO_2, the computed migration energy of He is somewhat higher than the experimental data. To investigate the origin of this discrepancy and obtain an improved result, we have calculated the energy barrier considering the effects of SP and SOC. First, we have calculated the new equilibrium lattice constant of UO_2 including SP and SOC

Table 3
Calculated energy barrier for migration of He between two OISs. The path of the He in the UO_2 matrix is listed as well as the computational conditions.

Initial and final position	Grimes et al. [28]	This study
OIS–OIS	3.80	2.97
OIS–V_U–OIS (hopping via V_U)	0.24	0.79
OIS–V_O–OIS (hopping via V_O)	0.38	0.41
OIS–OIS (SOC)	–	2.79
OIS–OIS (1200 K)	–	2.09

Experiment [6] = 2.0 eV.

using the equation of states and found that the lattice constant is larger by 0.02 Å and the unitcell volume by 8×10^{-6} Å^3. We have calculated the energy barrier using the new lattice constant. Considering the SOC effect in the energy calculations we found that the computed energy barrier is reduced by 0.18 eV, as shown in Table 3. SP calculations, on the other hand, do not lead to a notable energy difference. This may be because He is a non-magnetic atom and the SP of UO_2 does not affect its movement.

The reduction of 0.18 eV of the barrier obtained with SOC suggests that the SOC effect should not be ignored in energy calculations of UO_2. We also examined the finite temperature effect, because the energy barrier is expected to be lower at high temperatures due to the expansion of the lattice parameter. We calculated the energy barrier using the temperature-expanded lattice parameter (i.e. larger) experimentally determined at 1200 K, 5.53 Å [29]. The energy barrier value corresponding to a temperature of 1200 K is calculated to be 2.09 eV, which agrees well with the experimental migration energy of 2.0 eV obtained in the temperature range of 1123–1273 K [6]. The calculated results in Table 3 imply that the presence of uranium and oxygen vacancies nearby He is very important for He diffusion, because the energy barrier of He is largely decreased for a diffusion pathway with vacancies. In a previous study, the diffusion of vacancies in UO_2 was investigated and the migration energies of a oxygen and a uranium vacancy was calculated as 0.63 eV and 2.19 eV, respectively [25]. Although the diffusion processes by the vacancy-assisted mechanism hardly occur at normal operating temperatures due to the low concentration and the limited migration of vacancies, defects will be continuously provided by radiation damage, and then the vacancy-assisted diffusion of He could occur readily in UO_2 under long-term storage conditions.

3.3. He-induced swelling of UO_2

We further investigated the variation of the lattice parameter of UO_2 induced by He atoms. We did two kinds of calculations to determine the lattice parameter. First, we considered one He atom in 12-, 24-, 48-, and 96-atoms supercells and computed the new equilibrium lattice parameters. The obtained results are indicated by the colored symbols in Fig. 3. The relative lattice expansion $\Delta a/a_0$ can be seen to increase linearly with the He concentration.

Next, we calculated the variation when the number of He atoms is increased in a 96-atom supercell. The black circles in Fig. 3 show that the lattice parameter linearly increases with the number of He atoms. These results were obtained on the assumption that all He atoms are located at distant OISs in the supercell. Fig. 3 shows that He in a 96-atom unitcell (black circles) and He in smaller unitcells (colored squares) have somewhat different expansion values for the same concentration of He. This is understandable because the configurations of the He atoms are different for each sizes of supercell. However, we expect that the results obtained with a 96-atom supercell, which are shown as the black circles in Fig. 3, are more accurate than those obtained by using smaller supercells, which are shown as the colored squares. In a 96-atom supercell, He atoms have more distant locations to each other than they have in a smaller cell, taking the periodic boundary condition into account. The expansion of the lattice parameter of UO_2 due to He defects can be written as

$$\frac{\Delta a}{a_0} = \alpha \times C + \beta \qquad (3)$$

where C is the concentration of He and α is the expansion coefficient. β indicates the variation of the lattice parameter at the zero-concentration of He; we obtained $\beta \approx 0$ at $T = 0$, as expected. By fitting the two data sets shown in Fig. 3, we obtained the expansion coefficient α as 9×10^{-2} for the 96-atom supercell and 7×10^{-2} for the smaller supercells, respectively. Although He in UO_2 has been investigated experimentally, there does apparently not exist an experimental value for α pertaining to He in defect-free UO_2 in the literature. The fission process which generates He also generates other defects in the crystal lattice. Theses defects are extended defects which are expected to give rise to a substantial change in lattice parameter [30]. Hence, the calculated change in lattice constant, shown in Fig. 3, is only partially responsible for any observed change in a real material.

3.4. Behavior of two He atoms

To understand which configuration of He atoms is energetically favored we compared the total energies of possible configurations of two He atoms in UO_2 as shown in Fig. 4(a–d).

Fig. 4(a) and (b) shows two He atoms which are initially located at two OISs; our calculations show that both He atoms would then remain in the same positions during a self-consistent relaxation.

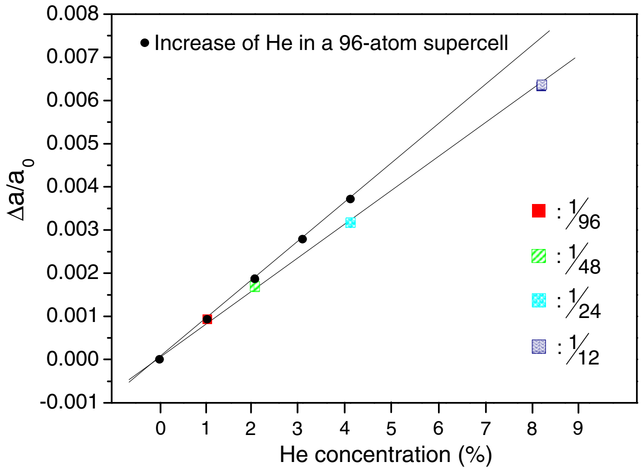

Fig. 3. Computed relative expansion of lattice parameter of UO_2 induced by He atoms. The four kinds of color points are the computed values induced by one He atom per a 12-, 24-, 48-, and 96-atom supercell, respectively, and the black circles indicate the relative lattice expansion obtained when the number of He atoms in a 96-atom supercell is increased.

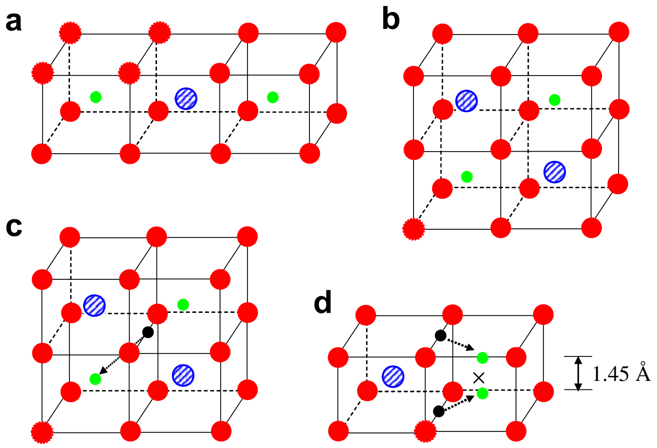

Fig. 4. Possible configurations of two He atoms in UO_2. Panels (a) and (b) : both of the He atoms are located at two OISs; (c) one is at an OIS and the other one is in the middle of the axis connecting two oxygen atoms, and (d) both of them are in the middle of two oxygen atoms. Black circles indicate their initial positions and green ones are the finial positions determined from atomic relaxations.

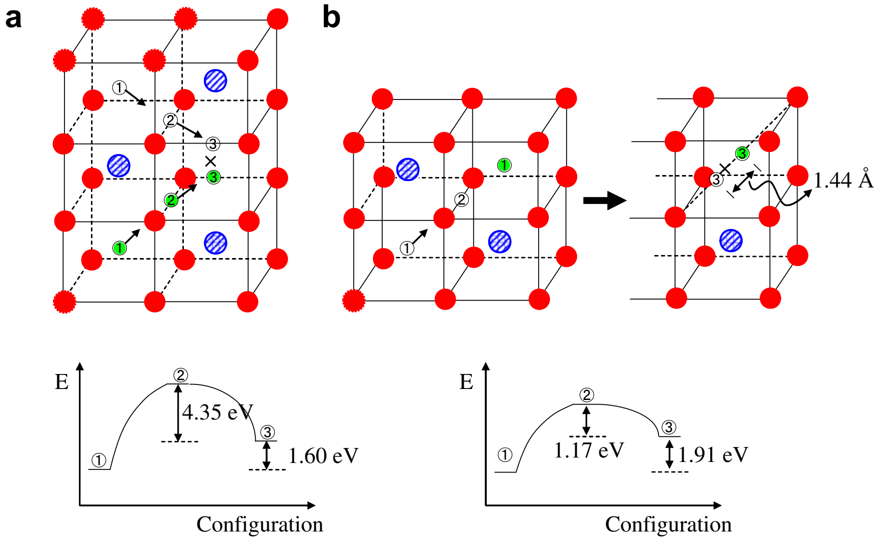

Fig. 5. Energy barrier between two configurations when two He atoms move from different OISs and form a dumbbell. (a) Two He atoms move simultaneously to the nearest empty OIS, and (b) one He moves to the other He trapped at an OIS.

The configuration of Fig. 4(c) indicates a configuration where one of the two He atoms, which is initially located in between two oxygen atoms, moves to a nearest empty OIS during atomic relaxation by the strain energy. After self-consistent relaxation the two He atoms finally occupy the two nearest OISs as shown by the two green circles.[1] We considered another possible configuration of two He atoms, which are close to each other but do not occupy OISs as shown in Fig. 4(d). In this case, both He atoms simultaneously moved to the direction of their nearest OIS, and formed a dumbbell configuration with a He–He distance of 1.45 Å. However, we find that the calculated total energy of the configuration (d) is higher than (a–c), respectively. This result implies that two He atoms are energetically more stable at distant OISs than at the dumbbell configuration, but they are likely to form a dumbbell if they are close to each other.

Fig. 5(a) and (b) shows schematically the energy barriers for the process where two He atoms form a dumbbell from being located at two different OISs (see Fig. 4(a) and (b)). The green and white circles with number 1 indicate that two He atoms are initially located at two OISs. One of the possible migration pathways when forming a dumbbell is shown in Fig. 5(a), where the two He atoms migrate simultaneously along the saddle point, which is depicted by the number 2 circles, placed between their initial positions 1 and the final positions 3. The energy barrier values at the saddle points are calculated to be 5.95 eV (4.35 + 1.60) and 2.98 eV (1.17 + 1.91), respectively.

The dumbbell configuration is more unstable than the configurations of He trapped at two OISs, and the energies of the configurations are 1.60–1.91 eV higher for the dumbbell than for the others. The relatively-high energy barriers in Fig. 5(a) and (b) imply that it seems to be improbable for He to form dumbbells through thermally activated processes. However, if the He concentration is increased by α-decay and He atoms are close to each other, the dumbbell is expected to be formed through the migration pathway in Fig. 5(b) with the lower energy barrier of 2.98 eV. Furthermore, we have calculated the variation of the lattice parameter and found that the lattice parameter is increased more at the dumbbell configuration than at the OISs, as shown in Table 4 (See Fig. 3). If He atoms accumulate in UO_2 lattice by α-decay, it is predicted that the structural stability of UO_2 will be decreased by expansion of the lattice parameter.

Table 4
Variation of the lattice parameter of a 96-atom supercell containing two He atoms in different configurations.

Two He atoms	OISs	Dumbbell
$\Delta a/a_0$	0.00186	0.00279

3.5. He-clustering in UO_2

As presented in the previous section, two He atoms form a dumbbell if they are close to each other. This result suggests that He atoms tend to cluster themselves in UO_2 matrix. We have investigated the clustering behavior of He atoms in more detail, by increasing the number of He atoms in the supercell. To start with, we have placed several He atoms at various positions and performed full atomic relaxations. Fig. 6(a) and (b) shows the initial and obtained final configuration of three He atoms in the supercell in a process of self-consistent atomic relaxation. We initially placed each of the three He atoms at the center of the axis between two oxygen atoms as shown in Fig. 6(a), because the axis between oxygen atoms was found to be the position of the energy barrier between two adjacent OISs (see Fig 4). Fig. 6(b) shows their finial configurations in which they have formed a small cluster after the process of self-consistent atomic relaxations. Finally, the three He atoms are located closely at an OIS. If we use other He starting positions, where the He atoms are farther apart, then they prefer to migrate to distant OIS positions.

From further calculations for four and five He atoms, we have found that the OIS plays the role of a nucleation center for He cluster formation when other defects are not introduced in the UO_2 lattice.

In particular, if the number of He atoms exceeds five, we have found that the collective action of these He atoms is sufficient to create a small He bubble surrounded by additional point defects. Fig. 7(a) and 7(b) show the original starting and final configuration of the simulation with 6 He atoms. As the He atoms cluster, they push the nearest uranium and oxygen atoms from their normal equilibrium lattice sites, forming a void in the lattice to capture

---

[1] For interpretation of color in Figs. 1–6, the reader is referred to the web version of this article.

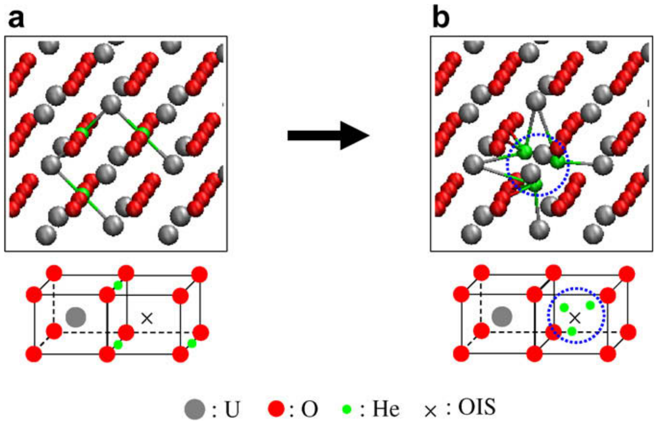

Fig. 6. (a) Three He atoms are initially located each between two oxygen atoms, and (b) during self-consistent relaxation, they move to the closest OIS and form a small He-cluster.

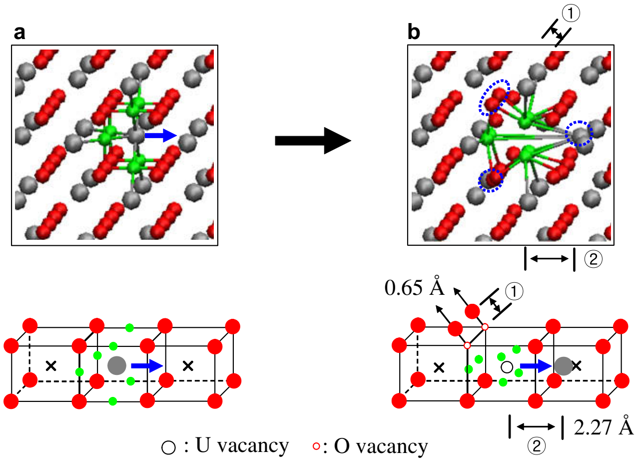

Fig. 7. (a) Six He atoms are initially located at the middle of two oxygen atoms, and (b) when these He atoms form a He cluster, point defects of U and O atoms are created through the cluster formation of the He atoms.

sufficient space for their nucleation. The nearest uranium and oxygen atoms are displaced by about 2.27 and 0.65 Å, respectively, in Fig. 7(b).

The displaced host atoms and the corresponding vacancies represent Frenkel pair defects. The introduction of further He atoms is expected to produce secondary Frenkel pairs in the shell of the next nearest neighboring atoms. It is well known that point defects contribute to swelling of materials by changing the lattice parameter of materials. Therefore, the strong agglomerating tendency of He could affect the local mechanical properties of UO_2 through the creation of He bubbles and additional point defects.

4. Conclusion

In this study, we have performed total energy calculations to investigate the trapping of He and diffusion properties of He in UO_2, using the PAW–GGA method. The incorporation energy and NEB calculations suggest that trapping of a He atom at a V_U is more stable than at a V_O or at an OIS. To investigate the diffusion mechanism of He, we calculated the migration energy of He between two adjacent lattice sites and found that the computed results are improved by considering SOC interaction as well as the thermally expanded lattice parameter. From the very small energy barrier by the vacancy-assisted diffusion, which is less than about 0.79 eV, it is expected that the diffusion of He will be accelerated as nuclear fission and radiation damage are increased. From the calculations on the He-induced expansion of the lattice parameter, we found that the variation of the lattice parameter of UO_2 depends somewhat on the supercell size because of the different ordering distances of the He atoms in supercells of different size. A theoretical expansion coefficient of 9×10^{-2} has been obtained for He in pure UO_2 crystal. We found that the energetically favored configuration of two He atoms is to occupy two distant OISs. Meanwhile, two He atoms form a dumbbell, if they are very close to each other. The calculated lattice expansion induced by He dumbbell is larger than that induced by two He atoms at two OISs, and the larger lattice expansion implies that He dumbbell formation will affect the local mechanical properties of UO_2 more.

He atoms has a strong tendency to form a cluster in UO_2, and the OIS is found to play the role of nucleation center for the clustering action in defect-free UO_2 lattice. Our calculations show that the clustering of six He atoms is sufficient to spontaneously push an uranium and four oxygen atoms off from their normal sites, thereby creating Frenkel pair defects. This clustering behavior of He atoms is considered to be closely associated with the experimentally observed precipitation of He in the UO_2 matrix. If He is increased in the UO_2 matrix by α-decay, the probability of He agglomeration is increased. The He-induced formation of a void in the UO_2 lattice and the creation of further point defect around it will degrade the mechanical properties of UO_2.

Acknowledgements

We gratefully acknowledge discussions with L. Werme. This work is supported by SKB, the Swedish Nuclear Fuel and Waste Management Company. Computer time granted by the Swedish National Infrastructure for Computing (SNIC) is acknowledged. This work was also supported by the Korea Research Foundation Grant (KRF-2007-35-D00283) funded by the Korean Government (MOEHRD).

References

[1] F. Rufeh, D.R. Olander, T.H. Pigford, Nucl. Sci. Eng. 233 (1965) 335.
[2] P. Sung, Equilibrium Solubility and Diffusivity of Helium in Single-Crystal Uranium Oxide, PhD Thesis, University of Washington, 1967.
[3] G. Sattony, F. Garrido, L. Thomé, Philos. Mag. Lett. 84 (2004) 115.
[4] Ian Farnan, Herman Cho, William J. Weber, Nature 445 (2007) 190.
[5] H.J. Matzke, T. Wiss, Radiation damage in nuclear material, ITU Annual Report, EUR 19812, 2000, p. 30.
[6] D. Roudil, X. Deschanels, P. Trocellier, C. Jegou, S. Peuget, J.-M. Bart, J. Nucl. Mater. 325 (2004) 148.
[7] F. Garrido, L. Nowicki, G. Sattonnay, T. Sauvage, L. Thomé, Nucl. Instr. Meth. Phys. Res. B 219&220 (2004) 196.
[8] C. Ronchi, J.P. Hiernaut, J. Nucl. Mater. 325 (2004) 1.
[9] G. Sattonnay, L. Vincent, F. Garrido, L. Thomé, J. Nucl. Mater. 355 (2006) 131.
[10] R.W. Grimes, in: S.E. Donnelly, J.H. Evans (Eds.), Fundamental Aspects of Inert Gases in Solids, Plenum, New York, 1991, p. 415.
[11] T. Petit, M. Freyss, P. Garcia, P. Martin, M. Ripert, J.-P. Crocombette, F. Jollet, J. Nucl. Mater. 320 (2003) 133.
[12] J.-M. Crocombette, J. Nucl. Mater. 305 (2002) 29.
[13] M. Freyss, N. Vergnet, T. Petit, J. Nucl. Mater. 352 (2006) 144.
[14] [a] J.P. Perdew, J.A. Chevary, S.H. Vosko, K.A. Jackson, M.R. Pederson, D.J. Singh, C. Fiolhais, Phys. Rev. B 46 (1992) 6671;
[b] J.P. Perdew, J.A. Chevary, S.H. Vosko, K.A. Jackson, M.R. Pederson, D.J. Singh, C. Fiolhais, Phys. Rev. B 48 (1993) 4978(E).
[15] G. Mills, H. Jónsson, Phys. Rev. Lett. 72 (1994) 1124.
[16] G. Mills, H. Jónsson, G. Schenter, Surf. Sci. 324 (1995) 305.
[17] G. Kresse, J. Hafner, Phys. Rev. B 47 (1993) 588 (ibid. 49 (1994) 14251).
[18] G. Kresse, J. Furthmüller, Comput. Mater. Sci. 6 (1996) 15.
[19] G. Kresse, J. Furthmüller, Phys. Rev. B 54 (1996) 11169.
[20] G. Kresse, D. Joubert, Phys. Rev. B 59 (1999) 1758.
[21] H.Y. Geng, Y. Chen, Y. Kaneta, M. Kinoshita, Phys. Rev. B 75 (2007) 054111.
[22] K.N. Kudin, G.E. Scuseria, R.L. Martin, Phys. Rev. Lett. 89 (2002) 266402.

[23] C.J. Pickard, B. Winkler, R.K. Chen, M.C. Payne, M.H. Lee, J.S. Lin, J.A. White, V. Milman, D. Vanderbilt, Phys. Rev. Lett. 85 (2000) 5122.
[24] M. Freyss, T. Petit, J.P. Crocombette, J. Nucl. Mater. 347 (2005) 44.
[25] Y. Yun, Hanchul Kim, Heemoon Kim, K. Park, J. Nucl. Mater. 378 (2008) 40.
[26] B. Amadon, F. Jollet, M. Torrent, Phys. Rev. B 77 (2008) 155104.
[27] M.J. Puska, R.M. Nieminen, Phys. Rev. B 43 (1991) 12221.
[28] R.W. Grimes, R.H. Miller, C.R.A. Catlow, J. Nucl. Mater. 172 (1990) 123.
[29] Kweon Ho Kang, Ho Jin Ryu, Kee Chan Song, Myung Seung Yang, J. Nucl. Mater. 301 (2002) 242.
[30] W.J. Weber, J. Nucl. Mater. 98 (1981) 206.