Journal of Nuclear Materials 385 (2009) 72–74

Contents lists available at ScienceDirect

Journal of Nuclear Materials

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

First-principles modeling of He-clusters 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

PACS:
61.72.Ji
66.30.Jt

ABSTRACT

We have investigated the behavior of He in UO_2, using the projector–augmented–wave (PAW) method and the generalized gradient approximation (GGA) based on the density functional theory. Total energy calculations with atomic relaxation included have been performed in a 96-atom large supercell. We have found that He has a strong tendency to form a cluster in vicinity of an octahedral interstitial site (OIS) in the UO_2 matrix. In addition, the strain energy produced by a He-cluster was found to be sufficient to create point defects of the host atoms in UO_2. Our study suggests that He-clusters and He-induced point defects play an important role for the local mechanical properties of UO_2.

1. Introduction

The atomic transport processes in UO_2 are of great interest for understanding the performance of UO_2 as a nuclear fuel. He, which is produced by α-decay, (n,α) reactions on oxygen, and ternary fission, tends to precipitate, form bubbles, or to be released from the UO_2 matrix due to their low solubility [1]. At lower temperatures below 500 °C, He release is not likely to occur due to lowered He mobility and He bubbles can form in UO_2 [2,3]. The presence of He is known to gives rise to fuel swelling and degrade mechanical properties of UO_2 [4–12]. Despite the large amount of research on He behavior, there are still many unknowns, specially regarding the microscopic understanding of the precipitation and bubble formation in the UO_2 matrix. In this study, we have investigated the migration and clustering behavior of He in UO_2. Considering possible configurations of He atoms, we have performed atomic relaxation in a supercell containing 96 atoms of UO_2. In order to understand the effect of strain energy produced by He, we have calculated the displacement of all atomic positions in the supercell. On the basis of the calculated results, we present an atomistic modeling picture of He nucleation in the UO_2 matrix.

2. Calculation details

The density functional calculations have been performed by using the PAW [13] and the GGA [14] method as implemented in the VASP code [15–17]. Regardless of the fact that the GGA method without Hubbard U predicts a wrong electronic band structure for UO_2 [18,19], the energetics of UO_2 is almost correctly obtained by the conventional GGA method [20,21]. In our previous studies, we also have reported that the calculated migration energies of point defects with the GGA method agree well with the experimental data [23,24]. Furthermore, it has been reported that the GGA + U method increases metastable states and causes the difficulty to determine the ground states of a system [22]. The cutoff energy of the plane–wave expansion was used up to 500 eV and the electron charge density was computed using a $2 \times 2 \times 2$ k-point grid within the Brillouin zone. In this study, a $2 \times 2 \times 2$ supercell of UO_2 containing 96 atoms has been employed to model the UO_2 matrix containing He atoms. For all considered structures, atomic relaxation was performed, and all atoms in the supercell were relaxed with the constant volume until the Hellman–Feynman forces derived from the total energy are smaller than than 0.01 eV/Å. The influence of He on the UO_2 volume was investigated recently [24]. The energy needed to incorporate a free He atom at an octahedral interstitial site (OIS) in UO_2 is calculated from:

$$E^{I}_{\mathrm{He_{OIS}}} = E_{\mathrm{He_{OIS}}} - \left(E_{\mathrm{perfect}} + E_{\mathrm{He_{free}}}\right), \tag{1}$$

where $E_{\mathrm{He_{OIS}}}$ is the total energy of a supercell containing He trapped at an OIS, and E_{perfect} is the energy of a defect-free supercell. $E_{\mathrm{He_{free}}}$ is the energy of free He atom.

3. Results and discussion

UO_2 has the cubic fluorite (CaF_2) structure as shown in Fig. 1(a). Fig. 1(b) shows a $2 \times 2 \times 2$ supercell of UO_2 used in this study.

Noble gas atoms prefer to occupy an OIS of the defect-free UO_2 matrix [23,24]. If He is initially located at any other interstitial sites, it moves spontaneously to an OIS during atomic relaxations. The incorporation energy of He for an OIS, $E^{I}_{\mathrm{He_{OIS}}}$, was calculated as 2.5 eV, and the positive value indicates the insolubility of He atom in the UO_2 matrix. The positive incorporation energy also agrees with the calculated result by Grimes et al. [25], which was reported

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

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doi:10.1016/j.jnucmat.2008.10.036

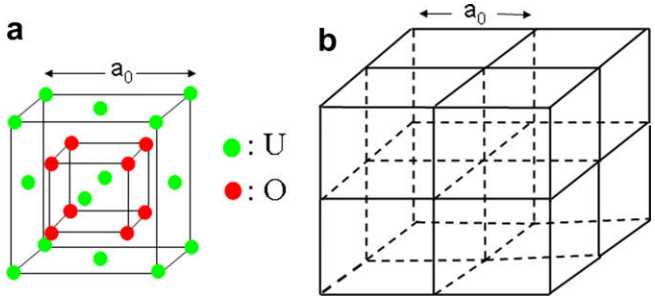

Fig. 1. (a) Conventional unitcell of UO_2 which crystalizes in the CaF_2 structure. The center of the unitcell is the OIS. (b) A $2 \times 2 \times 2$ supercell of UO_2 containing 96 atoms used in the present study.

as 1.5 eV. We recently calculated the relative incorporation energy of He, and reported that a uranium vacancy is a more stable site for He than an OIS and more stable than an oxygen vacancy [24]. Furthermore, the lowest electron charge density of He was obtained at a uranium vacancy. This result supports that a uranium vacancy is the most stable location for He. It is well known that a He atom prefers to occupy the site with the lowest electron density because of its filled-shell electronic configuration [26]. In the current study, we focus on the behavior of an increased number of He atoms in the near vicinity of an OIS. For two He atoms, we found that they energetically prefer to occupy distant OISs. However, if they are close to each other, they are likely to cluster and form a He-dumbbell. Fig. 2 illustrates how two He atoms form a dumbbell during atomic relaxation. If two He atoms are close until the center of the edge between two oxygen atoms (see the first schematic picture in Fig. 2), they both move to the center of an OIS and form a He-dumbbell.

The clustering of He was obtained for three and four He atoms as well. Fig. 3(a) and (b) show the initial configurations of three and four He atoms at the center of the edge between two oxygen atoms, respectively, and their finial configurations forming clusters after atomic relaxation. This *ab initio* obtained clustering behavior of the He atoms is considered to be closely associated with the experimentally observed precipitation of He in UO_2 matrix.

In addition, we found that the collective action of He atoms can create interstitial uranium and oxygen atoms. Fig. 4 shows that six He atoms push an uranium atom in their immediately surrounding off its lattice site, to capture sufficient space for their nucleation. As a result, the uranium atom was displaced by about 2.27 Å toward the direction of its nearest OIS.

This result implies, first, that He atoms have a strong tendency to agglomerate themselves and, second, that the strain energy induced by the He-cluster formation is sufficient to create an interstitial uranium atom. Besides the interstitial uranium atom, four

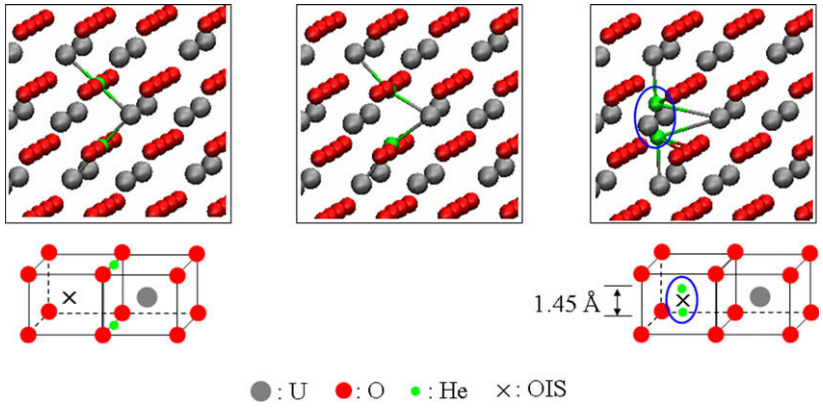

Fig. 2. A He-dumbbell is formed by the clustering behavior of two He atoms, with a distance of 1.45 Å between them.

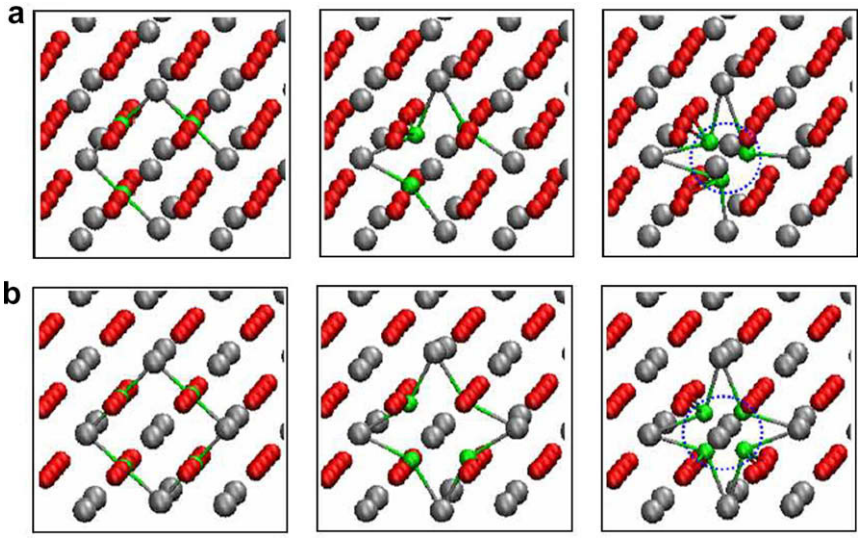

Fig. 3. Clustering processes of (a) three He atoms (b) four He atoms in the near vicinity of an OIS in the UO_2 matrix.

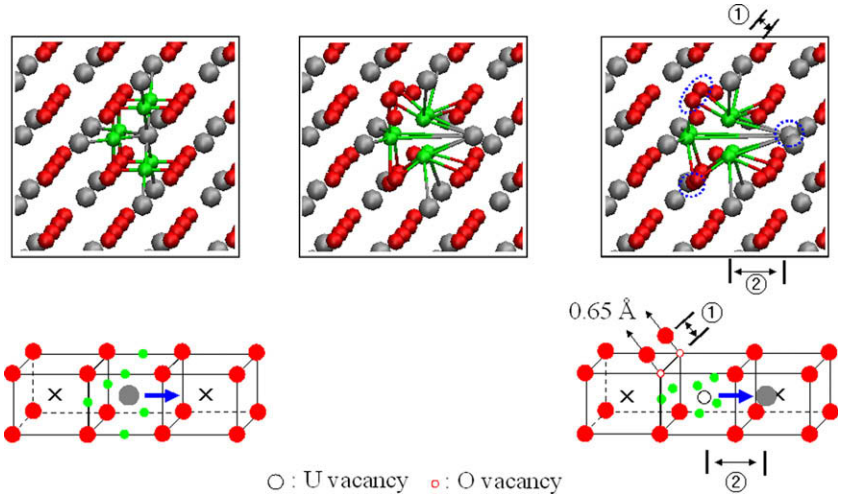

Fig. 4. Interstitial uranium and oxygen atoms are created during clustering processes of six He atoms. The displacement of the interstitial atoms from their original lattice sites are calculated as 2.27 Å for uranium and 0.65 Å for oxygen atoms.

interstitial oxygen atoms are created around the He-cluster, as shown in Fig. 4. The displacement distance of four oxygen atoms was calculated as 0.65 Å. These interstitial oxygen atoms and the corresponding oxygen vacancies represent oxygen Frenkel pair defects. From these results, we suggest that He nucleation play an important role for the local mechanical properties of UO_2 by creating point defects which are known to influence mechanical behavior of materials [27,28]. A system containing He bubble is energetically less stable than another one with distant He atoms trapped at OISs. However, He atoms kinematically are likely to agglomerate if they are close to each other. If the number of uranium or oxygen vacancies is increased by nuclear fission or thermally activated processes, He diffusion will be more activated, because of the fairly low migration energy of He required to hop through a uranium or oxygen vacancy, which is nearly 0.79 eV and 0.41 eV, respectively [24]. This vacancy-assisted diffusion of He is expected to increase the He concentration into grain boundaries and lead to formation He bubbles on the account of the here found clustering tendency. If the He concentration is consistently increased in spent nuclear fuel containing minor actinides, the He-clustering would be an important behavior in UO_2 matrix. We note that the concentration of He atoms is quite high in the 96-atom supercell used in the current study. However, using a larger one is computationally too demanding and we expect that the use of a 96-atom supercell give the same trend for the clustering behavior of He atoms compared to those using a lager supercell. We also have not considered spin-orbit coupling effect in the present study. The short-ranged van der Waals interaction between He atoms is estimated to be very small. However, the spin-orbit effects of uranium atoms should be treated in the energetic calculations of He bubbles by using a larger supercell in near future.

4. Conclusion

We have performed first-principles atomistic modeling to investigate the collective action of He atoms in the UO_2. We found that He atoms tend to form a cluster around the center of the relative large space of OIS in the UO_2 matrix. In addition, point defects were found to be created by the He-induced strain energy. Both the clustering and formation of U and O defects will affect the mechanical properties of UO_2 in a local area. An *ab initio* quantization of the degradation of mechanical properties is a topic of further investigation.

Acknowledgements

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 also was supported by the Korea Research Foundation Grant funded by the Korean Government (MOEHRD)(KRF-2007-35-D00283).

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