Journal of Nuclear Materials 485 (2017) 47–55

Contents lists available at ScienceDirect

Journal of Nuclear Materials

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

Fission gas in thoria

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HIGHLIGHTS

- We have considered Xe and Kr in point defects and defect clusters (neutral and charged) using Density Functional Theory (DFT) with a dispersion correction.
- The most favourable charge state for a point defect (vacancy or interstitial) is that with full ionic charge and we have found that in all cases gas atoms occupy the fully charged vacancy sites.
- The number of fission gas atoms accommodated in ThO_2 is linearly proportional to the number of neutral tri vacancies (NTVs) present in the system.
- In ThO_{2-x} the most favourable solution equilibrium site is the NTV1 while in ThO_2 it is the di-vacancy (DV).

ARTICLE INFO

Article history:
Received 20 October 2016
Accepted 6 December 2016
Available online 20 December 2016

Keywords:
Thoria
DFT
Defects
Xenon
Krypton
Nuclear fuel

ABSTRACT

The fission gases Xe and Kr, formed during normal reactor operation, are known to degrade fuel performance, particularly at high burn-up. Using first-principles density functional theory together with a dispersion correction (DFT + D), in ThO_2 we calculate the energetics of neutral and charged point defects, the di-vacancy (DV), different neutral tri-vacancies (NTV), the charged tetravacancy (CTV) defect cluster geometries and their interaction with Xe and Kr. The most favourable incorporation point defect site for Xe or Kr in defective ThO_2 is the fully charged thorium vacancy. The lowest energy NTV in larger supercells of ThO_2 is NTV3, however, a single Xe atom is most stable when accommodated within a NTV1. The di-vacancy (DV) is a significantly less favoured incorporation site than the NTV1 but the CTV offers about the same incorporation energy. Incorporation of a second gas atom in a NTV is a high energy process and more unfavourable than accommodation within an existing Th vacancy. The bi-NTV (BNTV) cluster geometry studied will accommodate one or two gas atoms with low incorporation energies but the addition of a third gas atom incurs a high energy penalty. The tri-NTV cluster (TNTV) forms a larger space which accommodates three gas atoms but again there is a penalty to accommodate a fourth gas atom. By considering the energy to form the defect sites, solution energies were generated showing that in ThO_{2-x} the most favourable solution equilibrium site is the NTV1 while in ThO_2 it is the DV.

1. Introduction

There is considerable interest in finding an alternative to urania fuel (UO_2), which remains the main fissile component in nuclear reactors. Materials that can replace UO_2 should have low cost, high abundance, high proliferation resistance and be able to facilitate high burn-up [1]. Thoria (ThO_2) has been identified as a possible alternative, partly because spent ThO_2 fuels give rise to considerably smaller inventories of minor actinides, especially Pu. Further, ThO_2 is a highly stable oxide, and exhibits higher thermal conductivity, higher melting temperature, higher corrosion resistance and lower thermal expansion compared to UO_2 [2].

The fission product inert gases Xe and Kr, are estimated to be 15% of the total fission yield [3] but are insoluble in the fuel matrix. At high fuel temperatures, gas atoms migrate and are accommodated at point defect sites in the fuel matrix. Over time some of these aggregate into bubbles. Formation of bubbles is important as it leads to swelling and degrades mechanical properties of the

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http://dx.doi.org/10.1016/j.jnucmat.2016.12.011
0022-3115/

material. Some gas atoms make their way to the fuel clad gap, which leads to an increase in the temperature in the fuel matrix due to a decrease in thermal conductivity across the fuel clad gap. This also increases the internal rod pressure. In order to understand fuel performance, it is necessary to understand the interaction of gas atoms with point defects.

Considerable work has already been carried out on gas atoms in UO_2. It is, for example, energetically unfavourable for the large Xe or Kr gas atoms to occupy interstitial sites in UO_2 (and ThO_2) [3–6]. Thus, the formation of defect clusters can be favoured. The smallest, charge neutral group of vacancies in UO_2 or ThO_2 consists of one uranium and two oxygen vacancies (the neutral tri-vacancy NTV) [7], which offers a greater volume than an interstitial or a single point defect to accommodate a large gas atom. Simulations predict that the incorporation of noble gas atoms in a UO_2 NTV is favourable because of the strain relief introduced by this defect [5,6,8]. Using high energy resolution X-ray absorption spectroscopy, Bes et al. [9] have reported experimental evidence for the presence of Xe incorporated in a UO_2 NTV. Using molecular dynamics simulations, Murphy et al. [5] reported that the most favourable trap site for a Xe atom is a NTV in UO_2 and this defect has little or no effect on the free energy of incorporation up to 1050 K. In order to accommodate gas clusters or bubbles in the fuel matrix, a number of NTVs are thought necessary to create larger space.

While a significant body of experimental and theoretical data have been reported on the defect chemistry and incorporation of Xe in UO_2, fewer studies have been reported for ThO_2. Using density functional theory (DFT), Lu et al. [10] calculated defect formation energies in ThO_2 and concluded that the most favourable disorder process is oxygen Frenkel [consisting of an unoccupied oxygen lattice site (ie. a vacancy) and an interstitial O^{2-} ion]. The reaction energy order (O Frenkel < Schottky < Th Frenkel) found in their study is in agreement with other DFT and empirical studies [10–13]. Yun et al. [14] performed DFT total energy calculations to establish defect energies and Xe diffusion in UO_2 and ThO_2. They suggested that formation and migration energies of vacancy defects for ThO_2 were much higher than for UO_2 because of the restricted oxidation state of Th and stronger bonds between thorium and oxygen ions. Incorporation of fission products incuding Xe has been considered in ThO_2 and CeO_2 using DFT within the local density approximation, where all vacancy and interstitial defects were treated as neutral [4]. In ionic materials, however, defects should also be considered with appropriate full ionic charge.

In this study, we have used DFT simulations to carry out a detailed survey of the relative energetics for the formation of intrinsic defects with appropriate charges and the incorporation of Xe and Kr atoms in defect structures of ThO_2. DFT calculations, in addition to giving structural information, predict electronic structure and electronic properties of the defects containing noble gas atoms.

2. Computational methods

The calculations were carried out using the spin-polarized mode of DFT as implemented in the VASP package [15,16]. The exchange-correlation term was modelled using the generalized gradient approximation (GGA) parameterized by Perdew, Burke, and Ernzerhof (PBE) [17]. The standard projected augmented wave (PAW) potentials [18] were employed and a plane-wave basis set with a cut off value of 500 eV was used in all calculations. The valence electronic configurations treated for Th, Xe, Kr and O were $6s^2\ 6p^6\ 6d^2\ 7s^2$, $4s^2\ 4p^6$, $5s^2\ 5p^6$ and $2s^2\ 2p^4$ respectively. In order to describe the behaviour of the localized Th *f* states we included the orbital-dependent, Coulomb potential (Hubbard *U*) and the exchange parameter *J* within the DFT + U calculations, as formulated by Liechtenstein et al. [19]. We applied the values of U = 4.5 eV and J = 0.5 eV to the localized *f* states of Th. Charged defects interact with their next periodic images in all three directions. To compensate, we applied the Madelung correction [20] as described by Leslie and Gillan [21] using the experimental dielectric constant of 18.9 reported by Axe et al. [22].

For bulk Th metal, we used an 8 × 8 × 8 Monkhorst-Pack [23] *k*-point mesh, which yielded 35 k points in the irreducible part of the Brillouin-zone and for bulk ThO_2, a 4 × 4 × 4 Monkhorst-Pack *k*-point mesh, which yielded 10 k points. A 2 × 2 × 2 supercell containing 96 atoms was used for the defect calculations. For defect clusters consisting of multiple NTV units, we used a 3 × 3 × 3 supercell containing 324 atoms. Structural optimizations were performed using a conjugate gradient algorithm [24] and the forces on the atoms were obtained from the Hellman-Feymann theorem including Pulay corrections. In all optimized structures, forces on the atoms were smaller than 0.001 eV/Å and the stress tensor was less than 0.002 GPa.

The inclusion of van der Waals (vdW) interactions is particularly important for the incorporation of highly polarizable noble gas atoms into ThO_2. In this work, dispersion has been included by using the pair-wise force field as implemented by Grimme et al. [25] in the VASP package.

3. Results and discussion

3.1. Calculations on bulk Th and ThO_2

Single point calculations were performed on bulk Th and ThO_2 structures to obtain the equilibrium lattice constants and bulk modulus, thereby enabling an assessment (through comparison with experimental values) of the quality of the pseudopotentials and basis set used for Th and O. The unit cell volume was varied within ±5% of the equilibrium volume and a cohesive curve was plotted by fitting values of the calculated energy to the Murnaghan equation of state [26] (see Fig. 1). The calculated equilibrium lattice constants and bulk modulus, derived from the Murnaghan fit, are in excellent agreement with the experimental values and with the results of other plane wave calculations (see Table 1).

ThO_2 is a typical insulator. The band gap energy calculated here for ThO_2 is 4.72 eV, which underestimates the experimental band gap value of 5.75 eV [31] but is consistent with other DFT calculations [11,14]. The underestimation of the band gap is due to the use of the exchange-correlation approximation [34].

3.2. Intrinsic point defects and clusters

A series of isolated point defect (vacancy and interstitial) energies were calculated and combined to determine the formation energies for Frenkel and Schottky disorder. Calculated formation energies for all point defects and clusters together with the methodology used in this study are reported in the electronic supplementary information (ESI). Our calculations suggest that the most favourable charge state for a point defect (vacancy or interstitial) is that with the full ionic charge. The oxygen interstitial defect (O^{2-}) exhibits a negative formation energy, meaning that O^{2-} can be easily incorporated with the release of 0.65 eV (this is because O^{2-} is not a stable isolated species) [35]. Lu et al. reported that the Th interstitial with +4 charge has the lowest and negative formation energy [10]. The study by Murphy et al. shows that Th vacancy with −4 charge is the most favourable point defect [11]. Defect formation energies calculated using different methodologies, particularly in the case of charged defects, are difficult to compare. However, Schottky and Frenkel energies (i.e. complete disorder processes) calculated by combining corresponding point