Calculation of the Effect of Temperature and Xenon Gas on the Defect Formation in Irradiated UO_2 Using Molecular Dynamics Simulation

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1. Introduction

Nowadays, Uranium Dioxide (UO_2) is widely used as a main fuel material for Light Water Reactors (LWR). Along with nuclear fission, fission products are accumulated in the UO_2 matrix.

The amount of fission product elements varies with the irradiation conditions, but the cumulative fission yield data suggest that Cesium (Cs), Iodine(I), Xenon (Xe), Molybdenum (Mo), Strontium (Sr) and Niobium (Nb) are the main fission product elements.[1] Among them, Xe is the richest gas element that is associated with the fuel swelling and degradation by forming bubbles inside the UO_2 microstructure.[2] While the swelling behavior and Xe bubble nucleation have been studied,[3-7] computational studies on the defect formation and radiation resistance behavior of UO2 focused on the pure UO_2 system.[5][6]

The Threshold Displacement Energy (TDE, E_d) is an essential quantity for assessing the radiation resistance of a given material. Basically, E_d is a minimum kinetic energy given for an atom in the lattice to escape its original position and form a stable point defect.[8-10] Therefore, it is well known that the number of stable point defects formed is proportional to the initial kinetic energy given to Primary Knock-on Atom (PKA) and inversely proportional to the E_d, as described by Norgett et al.[8]

Several methods were applied to investigate the E_d. Bauer and Sosin [7] experimentally measured the E_d of metals by shooting electrons directly into metals. However, this TEM method was unsuccessful due to the uncontrollable factors such as sample inhomogeneity, lattice imperfections and sensitivities, resulting in a large deviation of the detected values. For UO_2, Soullard [9] reported the approximated Ed value of Uranium PKA of about 40eV by the TEM method. However, the methodology of investigating microscopic energy values faced a new era with the development of computer and computational material science. Computational methods such as Molecular Dynamics (MD) or Density Functional Theory (DFT) emerged, and several researchers have already studied about irradiation simulation with UO_2 system. [5][6] However, those studies focused on pure UO_2 microstructure regardless of impurities.

In this work, a repetitive PKA simulation is applied to the fluorite UO_2 microstructure to investigate the influence of Xe atoms inserted in the UO_2 supercell by using MD simulation. The E_d of UO_2 system with different conditions (Temperature or existence of Xenon) is calculated, while the formation and annihilation of point defects under different conditions are investigated.

2. Methods

MD simulations were performed via Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) developed by Sandia National Laboratory. Details and methodologies are described in this section.

2.1 Interatomic Potential

In this simulation, an EAM interatomic potential function made by Cooper et al. [10] was used as a base function because it successfully describes the interaction between ceramic oxides including UO_2 and fission gases (Xe, Kr), validated by trapping energy calculation. Together with the Cooper potential, Ziegler-Biersack-Littmark (ZBL) functional was used to as a spline due to its suitability on collision-related interactions at a short range. The ZBL spline range of each interaction (U-U, U-O, O-O) was reported in Dacus et al. [6]

2.2 Pre-Simulation Detail

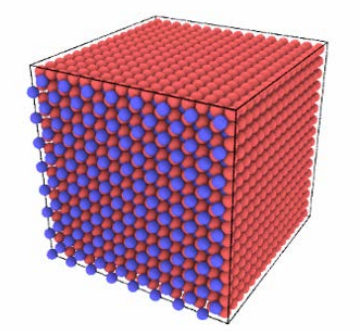

Fig. 1. Initially built $8 \times 8 \times 8$ pure UO_2 supercell. Red – Oxygen / Blue – Uranium

The Unit cell of initial fluorite UO_2 structure contains 4 Uranium atoms and 8 Oxygen atoms with a lattice constant of 5.468 Å. Before equilibration (a.k.a. relaxation), the unit cell is replicated in 3 dimensions to construct the sufficient size of the simulation system to prevent a spurious interaction between neighboring supercells.

In consideration of Xe atom insertion, the linear Schottky trio near the center of the supercell is deleted 1) to make the space for Xe atoms 2) and to ensure the charge neutrality of the system. To study the effect of Xe atoms, 3, 2, and 1 Xe atoms are implanted in the Schottky trivacancy site. Allocation of Xenon insertion referred to

previous research. Matzke et al. [11] introduced that the diffusion of Xe atoms normally occurs in Schottky trivacancy in the UO_2 system. Geng et al. [12] investigated that Xe insertion in (111) direction is the most stable form for Xe implant in UO_2 trivacancy.

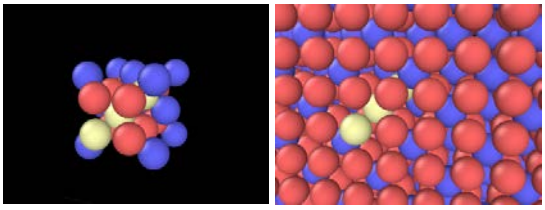

Fig. 2. Initial 8×8×8 3-Xe-inserted UO_2 Supercell
Xenon expressed by Yellow Atoms
Supercell is sliced to show the central part (left)

The initialized supercell is placed under Nose-Hoover style isothermal-isobaric ensemble (NPT ensemble) and equilibrated at a target temperature for 50 picoseconds(ps), with a single timestep of 2 femtoseconds(fs). The target equilibration temperature for pure UO_2 supercell is 300K, 600K and 1200K, and only 1200K for Xe-inserted UO_2 supercell.

2.3 Selection of PKA Direction Vectors

Chen et al. [13] suggested that some of the crystallographic directions reveal local minima of E_d and identifies the directions to defect channeling directions. Due to the dependency between the PKA direction and defect formation behavior, the PKA direction must be taken into account.

PKA directions that target the actual radiation events in the UO2 fuel grid must have an even distribution on a unit sphere. However, a perfectly even distribution of the direction vectors is practically impossible due to the limited computing power.

Alternatively, Robinson et al. [8] suggested Thompson's Problem solution vectors with large N can successfully represent the uniform directional distribution. In this study, N=40 solution vectors for the pseudo-uniform PKA direction selection were adopted.

For each direction, 20 times of repeats are tried by varying the random seed of the velocity generation algorithm in LAMMPS.

2.4 PKA Simulation

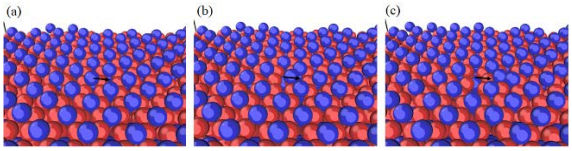

Fig. 3. PKA Simulation Slice Snapshot at
(a) The Beginning (b) Right After the Beginning (c) The Secondary Collision

After the system is equilibrated at the target temperature, PKA energy is given to the Uranium PKA in the form of velocity vector that is a multiple of norm and unit direction vector chosen in 2.3. For the collisional condition, the system is set in the microcanonical (NVE) ensemble. A single timestep is 1fs, which is small enough to avoid atomic overlap.

The formation of a point defect is assessed using a Voronoi Tessellation algorithm (a.k.a. Wigner-Seitz Analysis) in the LAMMPS system. Point defects that are still alive after 5000 timestep (5ps) are considered "stable Frenkel pair".

Hence, with regard to the individual temperature, PKA Uranium and PKA Energy, 800 repetitive simulations (40 directions and 20 repetitions per direction) are carried out and the formation of the stable Frenkel pair is checked.

3. Results and Discussion

3.1 Stoichiometric UO_2 supercell

As discussed in 2.4, the existence of a Frenkel pair is assessed at 5ps after the PKA event. As a result, Stable Frenkel Pair Formation Probability (P_{form}) is calculated using the result from 800 repetitive calculations.

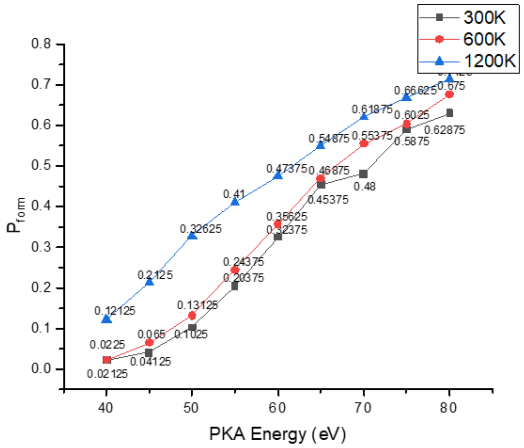

Fig. 4. PKA Energy - P_{form} graph of Uranium PKA in stoichiometric UO_2 supercell

According to the linear interpolation based on Fig. 5, Ed of Uranium PKA at 300K, 600K and 1200K pure UO_2 supercell is approximated in Table 1.

Table 1: TDE of Uranium and Oxygen in UO_2, Reference and this work

Source	Evaluation Method	System Temperature (K)	E_d (eV)
Dacus et al. [9]	MD, PKA Simulation	1500	60~65
Meis et al. [8]	DFT, Sudden Approximation Calculation	Very Low T	50
Soullard et al. [13]	TEM (Electron Beam Experiment)	300	40~50
This work	MD, PKA Simulation	300	**65~70 (69)**
		600	**65~70 (67)**
		1200	**60~65 (62)**

From the calculation operated in this study, it appears that P_{form} has a strong positive correlation with temperature. There are previous studies which mentioned temperature as a parameter for stable Frenkel pair formation. E. Chen. [13] stated that an increase in temperature leads to a weakening of the lattice bond with a high probability of defect formation in alpha and gamma uranium systems. In contrast, Beeler et al. [14] explained about the temperature-induced negative correlation with P_{form} of the bcc iron system due to the acceleration of diffusion and recombination of point defects.

From the references above, the temperature effect seems that a stable defect formation mechanism contains 2-steps of 'PKA penetrating lattice and forming Frenkel pairs' and 'Delaying of Frenkel pair recombination'.

3.2 Xe-inserted UO_2 supercell

In the pure UO_2 system, the selection of PKA Uranium is not important because the surrounding lattice geometry of each uranium atom is identical. However, the Uranium atoms in the Xe-inserted UO_2 supercell do not have the identical relative geometry. Therefore, P_{form} curve and E_d of each PKA are individually different.

Table 2: Calculated Uranium PKA E_d of triplet-Xe inserted UO_2 system (1200K)

Distance in Å	dist(Xe1)	dist(Xe2)	dist(Xe3)	E_d(eV)
PKA 1	**4.947**	**3.913**	**4.895**	**25.8**
PKA 2	**2.683**	**4.400**	**7.079**	**12.1**
PKA 3	**4.144**	**6.787**	**9.778**	**36.4**
PKA 4	**6.879**	**8.685**	**11.116**	**51.7**
PKA in Pure UO_2	∞	∞	∞	**62.0**
PKA 5	10.237	12.232	14.838	54.5
PKA 6	4.915	4.060	5.263	26.0
PKA 7	8.492	6.642	6.154	31.1
PKA 8	10.241	8.880	8.342	50.5
PKA 9	6.680	4.096	2.778	12.1
PKA 10	13.209	11.321	9.670	52.9
PKA 11	18.554	16.715	14.939	58.3
PKA 12	10.452	7.843	5.713	44.0
PKA 13	32.461	29.651	26.652	59.9
PKA 14	37.295	37.973	39.296	60.5

14 PKAs were selected. The fact that there were 2,047 U atoms in this system made it difficult and time-consuming to calculate the average E_d of Uranium in the UO_2 system. Thus, this study applied a linear interpolation scheme in MATLAB™ to interpolate the E_d of every U atom in the system.

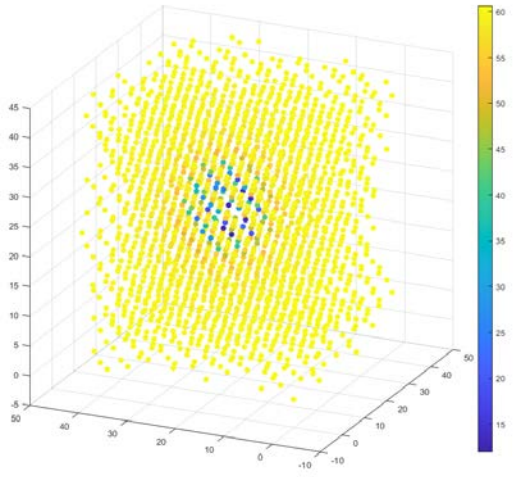

Fig. 5. 3D Scatter Plot of Uranium Ed in triplet-Xe inserted UO2 system

The identical procedure was operated to calculate the duplet-Xe inserted and single-Xe inserted UO_2 system. As shown in Fig. 5, Ed of Uranium atoms are reduced in the Xe-inserted UO2 systems. This tendency increased with an increasing number of Xe atoms in Schottky trivacancy. In order to analyze this tendency, temporal number of Frenkel pairs in two systems with identical temperature (1200K) and PKA energy (50eV) is plotted in Fig. 6.

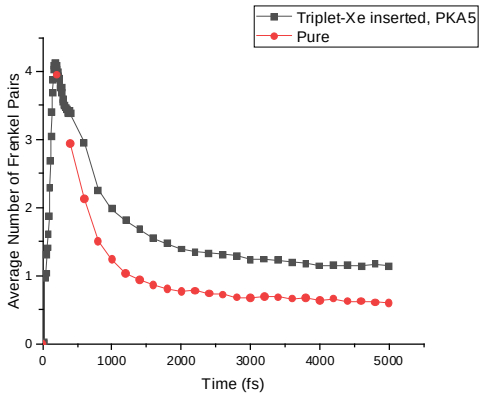

Fig. 6. Time - Average Number of Frenkel Pair Graph for Pure & Triplet-Xe inserted cell (PKA 5)

The comparison in Fig 3.14 show that the presence of Xe in the UO_2 has only a minor influence on the initial stage of defect formation. However, Xe atoms seem to interfere with the recombination of the Frenkel pairs after 1 ps. The mechanism of the recombination disturbance is currently unclear. However, regarding the Frenkel pair recombination process as a stochastic and thermal micro process, it is natural to assume that the energetic pathway from the Frenkel pair to the recombined perfect lattice state is disturbed. In other words, the level of the

Minimum Energy Path (MEP) may have changed due to the presence of the Xe atoms.

4. Conclusions

E_d is one of the most important key parameters for understanding the radiation resistance and point defect formation of an irradiated material. The formation of point defects and E_d of the pure and Xe-inserted UO_2 system was investigated by PKA simulation calculations using LAMMPS. From the analysis of the result of temporal defect formation, the point defect formation was divided into two processes: 1) Initial displacement of PKA making Frenkel pairs and 2) Frenkel Pair recombination by movement of the atoms. The temperature rise strongly activates both processes, and depends on the material and temperature range, dominating process can be different. If the effect of 1) dominates, the P_{form} increases and E_d decreases as shown in this study and E. Chen [7]. It is simulated that the presence of Xe atoms retard Frenkel pair by increasing the energy barrier of the Frenkel pair recombination path.

ACKNOWLEDGMENTS

This study was supported by the National Research Foundation of Korea (NRF-2018M2A8A1083889).

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