Bubble formation and Kr distribution in Kr-irradiated UO₂

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ABSTRACT

In situ and *ex situ* transmission electron microscopy observation of small Kr bubbles in both single-crystal and polycrystalline UO₂ were conducted to understand the inert gas bubble behavior in oxide nuclear fuel. The bubble size and volume swelling are shown as weak functions of ion dose but strongly depend on the temperature. The Kr bubble formation at room temperature was observed for the first time. The depth profiles of implanted Kr determined by atom probe tomography are in good agreement with the calculated profiles by SRIM, but the measured concentration of Kr is about 1/4 of the calculated concentration. This difference is mainly due to low solubility of Kr in UO₂ matrix and high release of Kr from sample surface under irradiation.

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1. Introduction

Uranium dioxide (UO_2), a fluorite-structured ceramic, is the main fuel used in commercial light water reactors. Its physical, chemical and thermodynamic properties have been studied extensively for over half a century by both experimental and theoretical methods. Inert fission gases such as Kr and Xe significantly impact the performance of UO_2 both during reactor operation and in interim storage or in a disposal repository [1]. These gases have a large yield of approximately 25% and have a low solubility in UO_2 . A fraction of fission gases precipitate into small bubbles during reactor operation, while the rest finds its way outside of the fuel pellet through complex mechanisms involving both the lattice and microstructural levels [1]. The precipitation of fission gases leads to swelling of the fuel, which promotes clad outward creep, leading to stresses that can shorten the cladding lifetime [1]. Upon escaping to the fuel pin plenum, fission gases increase the gas pressure inside the cladding and may lead to cladding rupture, which can limit the fuel utilization. A similar risk exists for the containers of nuclear waste in storage conditions. On the other hand, the precipitation of fission gases in the fuel matrix in the form of bubbles of low thermal conductivity will decrease the overall thermal conductivity of the fuel in the same manner as the porosity left from fuel fabrication [1]. The impact of bubbles on thermal transport is thus a key performance and safety issue for UO_2 fuel. For these reasons, the behavior of fission gases has been the subject of extensive experimental and theoretical research [2,3].

Despite the importance of the behavior of fission gas in fuels, a comprehensive atomic level understanding of the evolution of fission gas bubbles in fuels and their interaction with the microstructure is still lacking. Such a fundamental understanding will enable the design of high

burn-up fuels by making possible the prediction of the thermal and mechanical behavior of these fuels under reactor conditions. In this regard, characterizing fission gases in the fuel is important. For example, Transmission Electron Microscopy (TEM) studies of both neutron and ion irradiated UO_2 have been widely conducted to understand the development and evolution of gas bubbles and their size distribution in UO_2 [4-14]. However, *in situ* TEM observations of dynamic bubble evolution in UO_2 is still lacking [13]. In addition, there is a lack of literature focusing on Kr and Xe distribution and stoichiometry change in UO_2 under ion irradiation [14]. It is well known that the stoichiometry change of UO_2 could have a strong impact on its thermal conductivity. First-principles calculations could help elucidate the origin of the observed deficiencies of experiments.

In this work, both *in situ* and *ex situ* TEM characterization of bubbles have been conducted in UO_2 irradiated with Kr ions at room temperature, 600 °C and 800 °C to track the bubble formation as a function of dose and temperature. The depth distribution of Kr and stoichiometry of the irradiated UO_2 were determined by Atom Probe Tomography (APT) and Electron Energy Loss Spectroscopy (EELS), respectively. The difference between the Kr distribution measured by APT and the Kr distribution computed using SRIM was explained by the theoretically calculated Kr solubility and chemical equilibrium in UO_2 .

2. Experimental and Computational Studies

2.1 Experimental

Depleted UO_2 single crystal was fabricated in Chalk River Laboratories by heating fused hyperstoichiometric UO_2 to 1900 K in hydrogen. A stoichiometric O:U ratio close to 2 was determined by neutron diffraction measurements [15]. The polycrystalline UO_2 pellet was

prepared at Los Alamos National Laboratory. Depleted UO_2 powders were ball-milled for 15 minutes, sieved and uniaxially pressed into a 6.22 mm diameter pellet with a single action die at roughly 80 MPa. Densification was performed in a tungsten metal furnace under an argon atmosphere for 4 hours at 1650 °C. Subsequently, the atmosphere was switched to argon containing 6% hydrogen during cooling in order to obtain stoichiometric UO_2 . The produced pellets had a relative density of 95% and an average grain size of about 5 μm . Both single crystal and polycrystalline thin-foil specimens for TEM observation were prepared by slicing, mechanical grinding to ~100 μm thickness, dimpling down to ~20 μm thickness, and ion milling with Ar ions at 4.0 keV to perforation. Final polishing was done with a 3 keV Ar ion beam.

In situ irradiation with ion beams was carried out using a Tandem implanter, coupled with a 300 kV Hitachi 9000 NAR TEM, at the Intermediate Voltage Electron Microscope (IVEM)-Tandem facility at Argonne National Laboratory. The 30° incidence of the ion beam from the microscope optical axis, along with the integrated cameras, permits continuous observation and data recording during irradiation. Since the specimen was normally tilted about 15° facing the ion beam during irradiation, the actual angle between the ion beam and normal direction of specimen surface was about 15°. 150 keV single-charged and 1 MeV double-charged Kr ions were selected to produce the desired irradiation damage levels and depths. The samples were irradiated with 150 keV Kr at 25 °C and 600 °C and with 1 MeV Kr at 800 °C. The foil thickness, t , of plain view samples was determined using a thickness fringe method [16], and was used to calculate the volume density of bubbles and bubble swelling. The TEM observed zones of bubbles are typical within an average thickness of 12 nm. Bright field images were taken at under-focus and over-focus conditions to confirm the presence of bubbles in the sample.

Typically, small bubbles are seen as white and black dots at under and over-focus conditions, respectively. Bubble swelling, S_b , was calculated according to Equation 1, where d_i is the measured bubble diameter, s is the area for estimating the bubble number, and t is the average foil thickness.

$$S_b = \frac{\frac{1}{6}\pi \sum_i d_i^3}{st} \times 100\% \quad (1)$$

The measurements of bubble size and density were conducted manually. Each reported value was the average of 5 measured areas for the number density measurements and of over 300 measured features for the size measurements. Statistical errors were calculated from the measurements, which are with 20% of their size, density and swelling. However, some sources of uncertainties could not be well quantified, such as “biased” mind of the persons performing the measurements, translation of the 2-D measurement results to their 3-D counterparts due to slight thickness change during irradiation.

Post-irradiation microstructure of Kr bubbles was also investigated via a Tecnai TF30-FEG STwin TEM at the Center for Advanced Energy Studies (CAES), Idaho Falls, Idaho. A cross section sample perpendicular to 1 MeV Kr-irradiated TEM disc was prepared in a focused ion beam (FIB) system (Quanta 3D FEG, FEI). The sample was thinned to a final thickness of roughly 100 nm using 30 keV Ga ions and the final cleaning was conducted using 2 keV Ga ions. EELS was employed to study the composition and microchemistry of the irradiated UO₂. The EELS spectrum images were taken in energy filtered STEM mode with a 24.5 mrad convergence angle, 52 mrad collection angle and 0.8 eV energy resolution.

APT is a technique capable of providing highly spatially and chemically resolved information of materials. It was employed to reveal the Kr distribution in as-irradiated UO_2 samples. Polycrystalline UO_2 samples irradiated with Kr ions of 1 MeV at 800 °C and 150 keV at 600 °C, both to an ion fluence of 5×10^{15} ions/cm² were investigated using APT. Samples were prepared with a FIB using conventional atom probe lift out techniques, mounted onto an array of silicon microposts and annularly sharpened in the FIB [17]. The atom probe used in this investigation was a CAMECA LEAP 4000X HR with an ultraviolet (UV)-laser for assistance in evaporation. The atom probe operation conditions were: 50 pJ laser energy, 100 kHz pulse repetition, 1% detection rate, and 50 K specimen temperature. For the 1 MeV sample, 50 million ions were collected and for the 150 keV sample, 5 million ions were collected. The data collected from the atom probe was reconstructed using CAMECA's Interactive Visualization and Analysis Software (IVAS) package, version 3.6.4. To determine the depth dependent Kr concentration, a 1-dimensional concentration profile was taken from the reconstruction, making the top of the tip equal the surface (distance at surface = 0).

The Stopping and Range of Ions in Matter (SRIM) computer code [18] was used to simulate the profiles of Kr concentration in UO_2 as a function of depth. The threshold displacement energies for oxygen and uranium are 20 and 40 eV, respectively, which were determined by Soullard in his electron irradiation experiments in UO_2 [19]. The incidence angle of Kr was 15° in the calculation. The simulation, as shown in Fig. 1, implies that the Kr concentration reaches a peak value of ~1.15 at.% at a depth of 40 nm for 150 keV Kr and of ~0.23 at.% at a depth of 225 nm for 1 MeV Kr.

2.2. Density Functional Theory Calculations

We apply spin-polarized density-functional theory (DFT) + U approach (where U is a Hubbard-like term describing the on-site Coulomb interactions) with the PBE (Perdew-Burke-Ernzerhof) exchange-correlation functional [20] to calculate the Kr solubility in UO_2 . The Kohn-Sham equations were solved using the projector-augmented-wave (PAW) method [21,22], as implemented in VASP (Vienna Ab-initio Simulation Package) [23,24]. Standard library PAW-PBE pseudopotentials for ‘U’, ‘O’, and ‘Kr’ were used with a plane-wave cutoff energy of 500 eV. Periodic boundary conditions (PBC) were used in all calculations. The materials were fully relaxed until the minimized energy levels were reached. Gaussian smearing was used with a smearing parameter of 0.05 eV. The Brillouin-zone integrations were performed using the Monkhorst-Pack grids, and employed $(2 \times 2 \times 2)$ for all calculations with/without defects. Aligned with the LDA+ U formalism proposed by Dudarev *et al.* [25], a value of 3.96 eV for effective U was used for uranium for all studied compounds. This value of effective U corresponds to $U = 4.50$ eV and $J = 0.54$ eV, which were determined in UO_2 by Yamazaki and Kotani [26] based on the analysis of x-ray photoemission spectra. Supercells containing defects were generated by constructing a $2 \times 2 \times 2$ conventional 12-atom unit cell. All atoms and cell parameters of each structure were fully relaxed until the Hellmann-Feynman forces on each ion were negligible (< 0.001 eV/Å). All calculations are performed with spin polarization to reproduce each structure with the antiferromagnetic ground state. To avoid local energy minima for finding low-energy 5f orbital occupations in UO_2 , the procedure of U-ramping method is used [27]. Our tests are also consistent with the observation in Refs. 27 and 28 in which for low-symmetry calculations in UO_2 with oxygen distortions, the spread in energy of the different orbital occupations is significantly reduced and thus the ground state is easily found.

3. Results and discussion

3.1 Bubble formation

Figures 2 and 3 show TEM images of Kr bubbles in both single crystal and polycrystalline UO_2 irradiated with 150 keV at 25 °C and 600 °C, and 1 MeV Kr at 800 °C. The bubble size, density and bubble swelling were measured and summarized in Fig. 4. All the bubbles were assumed to have a spherical shape. The bubble size, number density and volume swelling are weakly dependent on the Kr ion dose at 600 °C in polycrystalline UO_2 . From a dose level of 1×10^{15} to 5×10^{15} ions/cm², the average bubble size, number density and volume swelling increase by 8.7%, 29% and 66%, respectively. The bubble size and density in UO_2 irradiated with 150 keV Kr at 600 °C is comparable to those observed by Evans [6] under similar irradiation conditions. The bubble size and density in polycrystalline UO_2 implanted with 200 keV Kr up to 5×10^{15} ions/cm² at 600 °C are 1.5 nm and over 10^{24} m⁻³, respectively [6]. The Kr bubble size and densities are also close to those in UO_2 irradiated by Xe and Cs up to 10^{16} ions/cm² and post-irradiation annealed at 600 °C [4]. At this temperature the bubbles were 1.8 ± 0.3 nm in size, with a density of $(4 \pm 2) \times 10^{23}$ m⁻³ for Xe and 1.7 nm in size with a density of $(1 \pm 0.5) \times 10^{24}$ m⁻³ for Cs [12]. The bubble size and volume swelling are strongly dependent on the irradiation temperature regardless of Kr ion energy. At room temperature, the average bubble size in polycrystalline UO_2 with 150 keV Kr is 1.1 nm, the size increases to 1.8 nm at 600 °C and then to 2.1 nm at 800 °C; the bubbles occupy 0.35% of the volume at room temperature, 1.22% of the volume at 600 °C, and then 1.94% of the volume at 800 °C. The temperature effect on bubble growth under irradiation is in good agreement with the results of in-pile irradiation by Une et al. [8-10]. The bubble size with an equivalent burnup of $\sim 7.5 \times 10^{26}$ fissions/m³ at 600 °C

is about 1 nm and that with a burnup of $\sim 6 \times 10^{26}$ fissions/m³ at about 800 °C is approximately 2 nm. Evans [7] did not observe nanoscale bubbles in Kr-irradiated polycrystalline UO₂ at irradiation temperatures below 400 °C and associated this threshold to the temperature of U vacancy migration. However, our observation may indicate that U vacancy is mobile at room temperature or that Kr bubbles directly nucleate at the vacancy clusters produced in cascades and such a process does not require Kr and uranium vacancies to be diffusive. In single crystal UO₂, the bubble size and volume swelling at 800 °C in single crystal UO₂ are factors of 1.4 and 2.3 higher than those at 600 °C, respectively. The bubble size, number density and bubble swelling at the dose of 5×10^{15} ions/cm² in polycrystalline and single crystal UO₂ are very close under the same irradiation condition (150 keV Kr and 600 °C). There is no preferential bubble aggregation at grain boundaries in polycrystalline UO₂ samples (Figs. 2 and 3).

In an extremely thin foil, or at positions very close to surfaces, the surface sink could become dominant and absorb the point defects [29]. This makes it difficult for defect accumulating at the edge areas of the foil. Our previous work shows the surfaces act as strong sinks for the defects, resulting in the formation of a near-surface interstitial dislocation loop denuded zone (around 20-30 nm depth for 1 MeV Kr-irradiated UO₂ single crystal) [16]. However, a similar denuded zone was not observed for Kr bubbles. At irradiation temperatures ranging from room temperature to 800°C, Kr bubbles were present in the edge region. Surfaces can absorb more interstitials than vacancies because of the higher mobility of interstitials, resulting in an unbalance in concentrations of interstitials and vacancies, especially at positions close to the surface [30]. The unbalanced vacancies may trap the implanted Kr ions and finally form Kr bubbles at the edge

areas. On the other hand, the bubble formation can accommodate implanted Kr, relieving stress arising from the inserted atoms.

Preferential accumulation of gas bubbles at grain boundaries (GBs) has frequently been observed in UO_2 fuel [30]. In simulations of polycrystalline materials, the gas atom formation energy is decreased within the GB and triple junction regions, leading to segregation and heterogeneous nucleation at these features [31]. However, preferential bubble segregation at GBs was not observed in the current work based on limited observations of GBs (Figs. 2 and 3). Generally, the preferential nucleation and growth of Kr bubbles at GB can result in reduced Kr concentration at the bulk near GBs. Theoretical modeling shows that lower vacancy mobility and/or higher vacancy generation rates are in favor of the formation of intragranular gas bubbles [32]. In the present work, the vacancy generation rate should be very high during Kr implantation and these vacancies trapped Kr atoms quickly to form bubbles. It is expected that the vacancy mobility in UO_2 is relatively low at temperatures up to 800 °C and post-irradiation annealing at higher temperatures could promote the bubble aggregation at GBs. However, preferential accumulation of gas bubbles at GBs shall also depend on the misorientation angle of the grain boundary. For a low angle GB with a few degrees of misfit, this effect may not even be observed after annealing.

Figure 5 shows the lattice images of Kr bubbles in polycrystalline UO_2 . The bright spots in the low-magnification underfocus images (Fig. 5a) correspond to Kr bubbles and the higher magnification image (Fig. 5b) shows the interaction of Kr bubbles with UO_2 lattice. The lattice images show no significant difference in the bubble areas and UO_2 matrix, implying that there should be no solid Kr precipitates in the bubbles. Solid precipitates in bubbles were found in

spent UO₂ fuel pellets, MgO and metals [9,10,33,34]. A common feature for the presence of solid Kr precipitates is the Moiré fringes caused by the lattice mismatch between solid Kr precipitates and matrices revealed by high resolution transmission electron microscopy (HRTEM) image. However, similar Moiré fringes were not found in the Kr bubbles in this work, confirming the lack of solid precipitates, which is the same with Kr bubbles in CeO₂ [35].

3.2 Kr distribution

Figure 6 shows the APT-measured Kr distribution in the polycrystalline UO₂ samples irradiated at 150 keV at 600 °C (a) and 1 MeV at 800 °C (b) and, both to a dose of 5×10^{15} ions/cm². Figure 7 shows the distribution of Kr within UO₂ for 150 keV at 600 °C (a) and 1 MeV at 800 °C (b) where the Kr ions are exaggerated in size relative to the other species to highlight its distribution. Additionally, a cluster size distribution algorithm was carried out for Kr indicating that the distribution is random. Both measured profiles of the Kr distribution in Figures 6 and 7 show a good agreement with those calculated by SRIM. However, the measured concentration of Kr is about 1/4 of the calculated profile. Since Kr is in the gas phase within the bubble, when the bubble surface is perforated during ion evaporation in atom probe, the Kr gas inside the bubble can be lost to the vacuum within the analysis chamber or detected as background noise in the mass spectrum [36]. A portion of the Kr detected by atom probe may be attributed to the trapping of implanted Kr in UO₂ by the large number of irradiation defects, limiting complete diffusion of the Kr gas to the bubbles [37]. This can explain why the measured Kr profile is similar, but at a lower concentration than expected from the SRIM calculations. A

detailed discussion of the relationship between Kr solubility and irradiation defects is included in the following section.

To reveal the stoichiometry of irradiated UO_2 , EELS measurement as a function of depth on the cross section of 1 MeV Kr irradiated samples was conducted. Figure 8(a) is the EELS spectra as a function of the depth to the surface showing the M_4 and M_5 edges of U. To isolate the white line intensity contributions from the background, the second derivative numerical filtering technique was used [38]. Afterwards, the U-M edge intensities were determined by integrating the intensity of the respective peaks above the zero-value linear function. Colella et al. [39] have established the proportionality between U-M edge intensities and the $5f$ occupancy of U. Following Colella et al, we prepared a branching ratio, $M_5/(M_5+M_4)$, and a profile as a function of the distance to the surface (Fig. 8(b)). In the whole distance range, the branching ratio of M-edge is between 0.691 and 0.715, which mostly overlaps the range of 0.695-0.720 for U^{4+} measured by Colella et al. This implies that stoichiometry is unaffected in Kr-irradiated UO_2 single crystal during irradiation.

In order to shed some light on why the measured concentration of Kr by APT is smaller than that of SRIM calculated, we investigated the solubility of Kr atom in UO_2 matrix with DFT calculations. Similar to previous DFT calculations for Xe in UO_2 by Yu et al. [40], it is convenient to envisage that a Kr atom may be trapped in a specific site of UO_2 with two steps: defect formation and Kr incorporation corresponding to insertion of an extrinsic defect into an intrinsic defect site. Similar to [40], six possible Kr trapping sites are studied: octahedral interstitial site (O_{IS}), oxygen vacancy (V_{O}), uranium vacancy (V_{U}), oxygen Frenkel pairs (O_{FP}),

uranium Frenkel pairs (U_{FP}) and Schottky defects (Sch). The corresponding solution energy E^S is the summation of the formation energy E^F and incorporation energy E^I [28,41]

$$E^S = E^F + E^I, \quad (2)$$

in which E^F and E^I are defined in [40]. The values of solution energy E^S at 0 K from DFT calculations under O-rich condition for these six Kr trapping sites are shown in Fig. 9(a). Our study indicates that the solution energies are positive in all cases, corresponding to 7.89, 9.91, 13.21, 12.38, 1.65 and 5.40 eV for O_{IS} , O_{FP} , U_{FP} , V_O , V_U and Sch as the Kr trapped site, respectively. It clearly shows that Kr is unstable in the UO_2 system. Interestingly, in contrast to the neutral trivacancies, i.e. a Schottky trio, as the most energetically favorable trap site for Xe in UO_2 observed experimentally [2] and predicted by DFT calculations [40], it is most likely that the Kr atom prefers to be trapped by the uranium vacancy site V_U . The solution energies for O_{IS} and Sch as the Kr trapped site from our DFT + U calculations compare well with previous DFT + U calculations in Ref. [28] as 8.06 and 5.08 eV, respectively. However there is a large variation of solution energies for O_{IS} , V_O , V_U and Sch as the Kr trapped site between our DFT + U calculations and the recent DFT calculations in Ref. [42] as 6.83, 8.38, 6.01 and 2.98 eV, respectively, though positive solution energies were predicted. It is not clear whether the authors in Ref. [42] attempted to account for metastable orbital occupations in their calculations.

The energy to form a defect at a given temperature and pressure is the Gibbs energy. However, in theoretical calculations of DFT, the energies such as defect formation, incorporation and solution are typically calculated at $T=0$ K. Contacting with external reservoirs such as oxygen gas, the solution energy E^S related to oxygen defect such as V_O and V_U depends on the chemical potential of the O_2 molecule μ_{O_2} as a function of temperature T and partial pressure P using standard thermodynamic expressions. The chemical potential of O (μ_O) is defined as:

$$\mu_{O_2} = \frac{1}{2} \mu_{O_2} = \frac{1}{2} [E_{O_2} + \mu_{O_2}(T, P^0) + k_B T \ln(\frac{P_{O_2}}{P^0})] \quad (3)$$

Where E_{O_2} is the total energy of O_2 molecule from the standard DFT calculation. The reference states of $\mu_{O_2}(T, P^0)$ at different temperatures can be obtained from experimental specific heat [43] data at $P^0 = 0.1$ atm. Thus the solution energy E^S related to oxygen defect at different temperatures and pressures can be obtained from 0 K *ab initio* values and integration of the chemical potential of the O_2 molecule. Given the solution energy $E^S_{(T, P_{O_2})}$, the solubility of Kr per lattice site in UO_2 as a function of temperature T and oxygen partial pressures P_{O_2} may be defined as $c = e^{\frac{E^S}{k_B T}}$. Fig. 9(b) shows the solubility of Kr at oxygen partial pressures $P_{O_2} = 0.21$ atm (correspond to 1 atm) from 0 K to 3500 K. Our study strongly indicates that Kr is basically insoluble in UO_2 matrix regardless of defect site in the whole temperature range.

In the case of irradiated UO_2 , the partitioning of Kr between the UO_2 matrix and bubbles can be fixed by equating the chemical equilibrium Kr in the matrix and bubbles. Chemical potential equality gives

$$\mu_{Kr}^b = \mu_{Kr}^m, \quad (4)$$

where μ_{Kr}^b is the chemical potential of Kr in the bubble and μ_{Kr}^m is the chemical potential of Kr in the matrix. Equation (4) can be rewritten in the form

$$\mu_{Kr}^0(T) + k_B T \ln p = E^S + k_B T \ln c, \quad (5)$$

where $\mu_{Kr}^0(T)$ is the reference chemical potential at temperature T , p is the Kr gas pressure in the bubble, E^S is the solution energy and c is the molar concentration of Kr in the oxide. The equilibrium distribution of Kr between bubbles and the matrix is constrained by the conservation of the total number of Kr atoms introduced to the system through ion irradiation, that is

$$\frac{n_b V_b p}{k_B T} + c N_A = \frac{p' V_b n_b}{k_B T}, \quad (6)$$

where n_b is the number of bubbles formed per unit volume of the sample, V_b is the average bubble size, p is the pressure inside the bubbles and p' is the pressure inside the bubble assuming that all the implanted Kr ions have relocated into the bubbles. Substituting c in Equation (6) using (5) yields

$$p = \frac{1}{1 + \frac{k_B T}{n_b V_b} \exp\left(-\frac{E^S - \mu_{Kr}^0(T)}{k_B T}\right)} p'. \quad (7)$$

Now the situation depends on the solution energy of Kr in UO_{2+x} , E^S . The solution energy depends on the available defects on which Kr atoms reside. Such defects are also controlled by the off-stoichiometric state of the oxide. The abundance of such defects is determined based on their free energy of formation which is a strong function of the oxide's off-stoichiometric state, i.e. a function of temperature and oxygen partial pressure. The solution energy calculated by DFT for the most favored trap site, i.e., U vacancy is shown to equal 1.65 eV for introducing a Kr atom into a U vacancy, thus the stability of Kr in UO_2 can be sensed. The temperature and oxygen pressure-corrected free energy of formation for the U vacancy was calculated by Hassan et al. [44] based on the results by Crocombette et al., [45] and was found to be around 2 eV, which is close to exact stoichiometry. Given such parameters, the concentration of Kr in the

matrix can be estimated. In this case, the concentration will be very low and the proportion of Kr atoms in the matrix tends to a vanishingly small value as the oxide equilibrates. Therefore, the coefficient of p' in Equation (5) tends to the identity. The pressure inside the bubble is given as a consequence of the chemical equilibrium as shown. The stress introduced by the existence of the bubble at such value of pressure can be equilibrated by modifying the defect concentrations around the bubble [46,47].

Both DFT calculations and chemical equilibrium analysis revealed that the equilibrium thermodynamic solubility of Kr atom in UO_2 matrix is essentially zero and majority of Kr atoms should precipitate into a high density homogeneous population of very small bubbles. However, in the presence of radiation, radiation induced re-solution occurs and lead to a much faster reentry of the gas or release of the gas from traps [48]. The effective diffusivity of a gas atom, $D_{\text{eff}} = Db/(b+g)$, where D is the diffusivity in the presence of both traps and irradiation, b and g are the gas atom re-solution and capture probability, respectively [48,49]. This expression indicates that there is always a certain amount of gas in dynamic solution [50,51]. Fission induced re-solution of inert gases from bubbles has been well-documented and re-solution of inert gas by ion implantation was first shown by Evans [52]. The large Xe bubbles in UO_2 were resolved by 200 keV Kr at a dose of 2×10^{15} ions/cm² and ambient temperatures [52]. In addition, the solubility is affected by the defects in UO_2 such as dislocations and grain boundaries. These defects will results in a much higher solubility limit in their vicinity [53]. In the present work, the TEM foil is pretty thin and the Kr release from bubbles and other defects to sample surface under irradiation could be considerably high, especially at elevated temperatures. Assuming all the implanted gas exists in the bubbles and according to the average bubble size and density, the

estimated Kr density in bubbles of polycrystalline UO_2 at a dose of 5×10^{15} ions/cm² are 15.3, 3.9, and 2.6 g/cm³ at 25, 600 and 800°C, respectively. However, the density of solid Kr is only 2.8 g/cm³ [54]. Such high Kr density in UO_2 is impossible and a large fraction of implanted Kr must escape from the sample surface and/or exist in dynamic solution in the matrix and reside in tiny defects below TEM detect limit. However, no Kr ion clusters have been detected by the current APT analysis and more work is needed in the future. Given that much higher Kr density in the sample irradiated at room temperature, there should be less Kr released from the sample surface and more Kr trapped in the matrix.

4. Conclusions

In this work, we investigated the bubble formation and Kr distribution in Kr-irradiated UO_2 . Specifically, the microstructure of Kr bubbles in UO_2 as a function of dose and temperature was characterized by *in situ* and *ex situ* TEM. Our results indicate that the bubble formation under room temperature irradiation indicates that U vacancies may be mobile at the temperature below room temperature or imply that Kr bubbles may directly nucleate at the vacancy clusters produced in cascades at room temperature and such a process does not require Kr and U vacancies to be diffusive. Preferential bubble aggregation at grain boundaries were not observed mainly due to low mobility of vacancy and high vacancy generation rates under the given irradiation conditions. No solid Kr precipitates in bubbles were revealed by the lattice images.

The Kr distribution in as-irradiated UO_2 was studied by APT. The depth profiles of Kr measured by APT are in good agreement with those calculated by SRIM, but the measured

concentration of Kr is about 1/4 of calculated one. DFT calculations and thermodynamic analysis as well as chemical equilibrium analysis revealed that the low solubility of Kr atom in UO_2 matrix is the major reason for the lower measured concentration of implanted Kr determined by APT compared with calculated one by SRIM. The irradiation-induced resolution and irradiation-enhanced Kr diffusion result in high release of Kr from thin sample surface as well as dynamic solution of Kr around the defects in the matrix. In addition, the stoichiometry of UO_2 is relatively stable during irradiation under vacuum at temperatures below 800 °C as determined by EELS. The study of the bubble formation and Kr distribution in UO_2 in this work could further enrich the fundamental understanding of nucleation and evolution of inert gas bubbles in nuclear fuels at atomic level.

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Figure captions

Fig. 1 Depth profile of Kr gas concentration obtained from SRIM simulation of UO₂ subjected to 150 keV and 1 MeV Kr ion irradiation with a total dose of 5×10^{15} ions/cm².

Fig. 2 Sequential *in situ* TEM images showing the nucleation and growth of bubbles in polycrystalline UO₂ irradiated with 150 keV Kr at 600 °C at various dose levels. (a and f) No dose, (b and g) 1×10^{15} ions/cm², (c and h) 2×10^{15} ions/cm², (d and i) 3×10^{15} ions/cm², and (e and j) 5×10^{15} ions/cm². Figures (a-e) are underfocus images and Figures (f-j) are overfocus images.

Fig. 3 TEM images showing bubbles in UO_2 irradiated with 150 keV Kr at 25 °C (a) and 600 °C (c) and with 1 MeV Kr at 800°C (b and d) all up to a final dose of 5×10^{15} ions/cm². (a) and (b) are polycrystalline UO_2 ; (c) and (d) are single crystal UO_2 .

Fig. 4 Dose dependence of (a) bubble size, (b) bubble density and (c) swelling in single crystal (SC) and polycrystalline (PC) UO_2 irradiated with 150 keV Kr at 25 °C and 600 °C, and 1 MeV Kr at 800 °C.

Fig. 5 Lattice images of Kr bubbles in polycrystalline UO_2 irradiated with 150 keV Kr at 600 °C up to 5×10^{15} ions/cm² when the electron beam is parallel to the [011] zone axis: (a) Low-magnification underfocus image; (b) high-resolution image. (Some bubbles in (b) are marked by arrows.)

Fig. 6 Kr depth-profile measured by atom probe tomography in polycrystalline UO_2 samples irradiated at (a) 150 keV at 600 °C and (b) 1 MeV at 800 °C, both to a fluence of 5×10^{15} ions/cm².

Fig. 7 Atom probe tomography reconstruction of Kr-irradiated UO_2 representing the distribution of Kr (gold dots) for (a) 150 keV at 600°C and (b) 1 MeV at 800°C

Fig. 8(a) EELS spectra as a function of the depth to the surface showing the M_4 and M_5 edges of U in 1 MeV Kr-irradiated UO_2 up to a dose of 5×10^{15} ions/cm². (b) Branching ratio, $M_5/(M_5+M_4)$, profile as a function of the distance to the surface.

Fig. 9(a) Kr solution energy at 0 K under oxygen-rich condition from DFT calculations in UO_2 . (b) Kr solubility in UO_2 as a function of temperature contacting with 1 atm air or oxygen with 0.21 atm partial pressure.

Figures
Figure 1

Figure 2

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