Radiation Enhanced Diffusion of Nd in UO₂

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Abstract

Single crystal UO₂ thin films with Nd as tracer elements in the film mid-plane have been grown on yttria-stabilized zirconia (YSZ) substrates. The films were irradiated with 1.8 MeV Kr⁺ ions in the temperature range from 400 °C to 1113 °C, where an evident enhanced diffusion was found in UO₂. The temperature dependent measurements have shown an activation energy of 0.56 ± 0.04 eV below 800 °C, and 1.9 ± 0.3 eV above 900 °C. The rate-dependent measurements have shown a linear dependence on the radiation flux, which indicates radiation enhanced diffusion (RED) is in the sink limited kinetics regime. Comparison of the RED results between UO₂ and CeO₂ has shown significant differences, which indicates that CeO₂ used as UO₂ surrogate may be questioned in terms of cation diffusion.

Keywords: Radiation enhanced diffusion, single crystal UO₂, CeO₂

1. Introduction

Radiation Enhanced Diffusion (RED) was originally considered in the early 1940s [1]. The first experimental demonstration was performed by Blewitt and Coltman in 1952 [2], and the first rate theory model was solved by Lomer [3]. Many experiments have been carried out in metals and alloys. Some consistency with the theoretical predictions have been found: recombination-limited kinetics in the low temperature range with a square root dependence on the radiation rate and a transition to sink limited kinetics in the high temperature range with a linear dependence on the radiation rate have all been demonstrated in metals [4, 5, 6, 7, 8].

However, it has been found that RED in oxide ceramic system is different from that in metals. After the technology of making good quality thin films became available, single crystal films with tracer layers in the film mid-plane could be fabricated. The first trial of RED in single crystal MgO thin films was performed by Van Sambeek *et al.* [9]. They found sink limited kinetics in the low temperature range and recombination-limited kinetics in the high temperature range on the anion sublattice, which were the opposite of the traditional theoretical prediction for metals. Thus, a modified model was developed to explain the results. A similar set of experiments was performed in CeO₂ with La as the tracer element on the cation sublattice by Pappas *et al.* [10]. In the low temperature range, 400 – 600 °C, the data were explained based on the recombination-limited kinetics, however, rate-dependent (or flux-dependent) experiments in this temperature

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range has not been performed to confirm their conclusion. La exhibits a large thermal diffusivity so that the radiation enhanced diffusivity quickly merges with the thermal diffusion at 800 °C.

CeO₂ has been widely considered to be a UO₂ surrogate because the crystal structure is identical with similar lattice constants. However, the diffusion properties are different as demonstrated here. For example, no measurable diffusion coefficient has been reported below 1200 °C on uranium self-diffusion in UO₂ [11, 12, 13, 14, 15, 16], whereas apparent diffusion has been found on the cation sublattice in CeO₂ [10]. Thus, it is necessary to perform a set of experiments to investigate the diffusion properties of the two materials under similar conditions. Another objective of this work is to add more experimental data for RED in ceramic materials.

The experimental procedures are presented in the next section. This will include the film growth, characterization and irradiation conditions. The determination of the diffusion coefficients, results of the temperature and rate-dependent measurements will be presented in Section 3. Finally, discussion and conclusion will be given in Section 4 and Section 5 respectively.

2. Experimental

2.1. Film Growth and Characterization

843 Å thick single crystal UO₂ thin films were grown simultaneously on 4 YSZ substrates with a reactive-gas magnetron sputtering system. These 4 samples were 46A, 46B, 46C and 46D, and each one was cut into 4 to 9 pieces for various temperature and irradiation treatment, as listed in Table 2. In the mid-plane of the film, a thin layer of (U, Nd)O₂ was added during the film growth, where the Nd/U ratio is ~11.5%. The base pressure was $\sim 2 \times 10^{-8}$ Torr at room temperature (RT). Films were grown at 700 °C with research grade Ar as the sputtering gas and O₂ as the reactive gas. The partial pressure of Ar was $\sim 6 \times 10^{-4}$ Torr, and the partial pressure of O₂ was $\sim 2 \times 10^{-7}$ Torr. A depleted uranium metal target and a neodymium target were used as the sputtering targets. More details of the film growth can be found in the related publication [17].

Specular $2\theta - \omega$ scans from XRD measurements have shown single crystal feature of the UO₂ film, as indicated in Fig. 1. Film peaks are the three low intensity reflections which are indexed as (0 0 2), (0 0 4) and (0 0 6) plane. The strong reflections on the right hand side of each film peak are from the YSZ substrate reflection. Films show a preferential [0 0 1] growth direction, and the lattice strain in this direction is $\varepsilon \sim 3.5 \times 10^{-3}$. Both the as-grown and high temperature irradiated samples have shown single crystal feature of the films, and the lattice strain is slightly smaller after at-temperature irradiation, which is $\varepsilon \sim 2.8 \times 10^{-3}$.

In Fig. 2, the lattice mismatch is shown in the interface between the UO₂ film and the YSZ substrate. Because the lattice parameter of the UO₂ (5.464 Å) is larger than that of the YSZ (5.125 Å), there is a mismatch between the film and the substrate which is shown as an misfit dislocation in the interface.

In-plane (1 1 1) ϕ scans shown in Fig. 3 further demonstrate the one domain, single crystal feature of the films. The four-fold symmetry of the ϕ scan is the expected result of single crystal UO₂. A highly textured polycrystalline film may show similar specular $2\theta - \omega$ spectrum as the true single crystal film. However, the former would not exhibit sharp peaks but instead would either be featureless or be broad weak peaks in an in-plane ϕ scan. Fig. 3 also shows that the high-temperature, heavy ion bombardment does not affect the single crystal structure.

The results of the rocking curve $\Delta\omega$ scans are shown in Fig. 4. $\Delta\omega$ rocking curve scans are used to measure the crystal mosaic. For the as-grown sample, the rocking curve is characterized

Figure 1: Normalized $2\theta - \omega$ scan of the typical as-grown samples and the samples irradiated at elevated temperature. Each scan is normalized to the area from the (0 0 2) film reflection. Samples are irradiated by 1.8 MeV Kr^+ ions and the radiation fluence Φ is 1.0×10^{16} ions/ cm^2 . An intensity scale graduated in power of ten has been plotted and each curve has been shifted vertically for clarity.

Figure 2: TEM image of the interface between the UO_2 film and the YSZ substrate. The lattice mismatch between the film and the substrate is shown as a misfit dislocation around the interface. The interface is indicated by the yellow dashed line and the misfit dislocation is represented by the symbol τ [18].

Figure 3: Normalized X-ray diffraction ϕ scans of the (1 1 1) in-plane reflection from the as-grown sample and the samples irradiated at elevated temperatures. Each scan is normalized to the peak intensity of the first reflection. The irradiated sample was bombarded to a fluence of 1.0×10^{16} ions/cm² with 1.8 MeV Kr⁺ ions. A linear intensity scale has been plotted and each curve has been shifted vertically for clarity.

by both a broad mosaic component and a narrow mosaic component [19]. The narrow component indicates that a portion of the UO₂ film is commensurate or in registry with the YSZ substrate while the broad component is associated with film volume not in registry. Since the area of the narrow component is relatively large it indicates good crystallinity of the film. After irradiated at elevated temperatures, a systematic transition is observed. As the irradiation temperature increases, the narrow component decreases and the broad component increases, which is attributed to the dislocation generation associated with radiation damage.

To be considered single crystal a thin film must satisfy the following conditions: preferred or highly textured out-of-plane growth which can be inferred by $2\theta - \omega$ scan; in-plane ϕ scans characterizing a single growth domain; and narrow rocking curve signifying a commensurate crystal lattice without large-angle tilt boundaries [19]. Since the UO₂ film we have grown satisfy all the three conditions, we conclude the UO₂ film used here are all single crystal.

It is very important that the UO₂ film studied here is single crystal rather than a polycrystalline or a highly textured polycrystalline films because it allows us to attribute the measured Nd diffusivities to a cation diffusion process that is not influenced by large-angle grain boundaries.

In addition, X-ray reflectivity (XRR) analysis was performed to calibrate the film thickness [17, 19], which is $843 \pm 21 \text{ \AA}$. The deviation of the thickness is taken from the four samples we have grown simultaneously, which also indicate that the film is uniform across the growth plane. One example of X-ray reflectivity is shown in Fig. 5.

Secondary ion mass spectroscopy (SIMS) was performed using a Physical Electronics PHI Trift III to determine the depth profile of the as-grown and irradiated samples. This instrument has excellent mass-resolution and can run in a time-of-flight (TOF) mode. 2 keV O₂⁺ beam was

Figure 4: Normalized X-ray diffraction rocking curve scans across the (0 0 2) reflection of the as-grown and at-temperature irradiated single crystal UO_2 film. Each scan is normalized to the peak intensity. The irradiated samples were bombarded to a fluence of 1.0×10^{16} ions/cm². A linear intensity scale has been plotted and each curve has been shifted vertically for clarity.

Figure 5: A typical XRR measurement of the samples used in this analysis. This measurement is used to calculate the film thickness, which allows the SIMS depth scale to be set. The data were normalized by setting the plateau to one (total external reflection). Log scale plotted.

used for sputtering erosion, rastered over a $400 \times 400 \mu\text{m}$ crater. While 22 keV Au^+ analytical beam was used for data collection with a raster size of $50 \times 50 \mu\text{m}$ in the middle of the O_2^+ beam crater. These two beams were cycled to produce depth profiles; a typical example is shown in Fig. 6. There are 7 isotopes for Nd and they were summed to produce the Nd peak. Since the diffusivity of Nd in UO_2 is found to be very low, the asymmetry of the Nd peak toward the free surface (0 depth) is not due to the diffusion of Nd atoms. It is likely due to Nd atoms in the chamber after the Nd deposition. However, the peak asymmetry is very small on a linear scale. Another feature in Fig. 6 is the signal of Nd on the substrate side. This is possibly because of the difference between the film and the substrate for the ion yield.

The critical step of the SIMS analysis is to convert the time scale to depth, the latter needed to determine the diffusivity. For the as-grown samples, the thickness was determined by XRR, which is $843 \pm 21 \text{ \AA}$, as shown in Fig. 5. . However, for the irradiated samples, total thickness of the film is not conserved because of ion surface sputtering during heavy ion irradiation. Thus, the distance from the center of the Nd peak to the film-substrate interface was assumed to be constant because the radiation has little effect on this distance. The film-substrate interface is set by the time when the UO signal drops to half of the nearly constant value in the film, which is indicated in in Fig. 6. Therefore, the sputtering rate of the depth profiling is determined by dividing the thickness from XRR analysis by the time from the Nd peak center to the film-substrate interface.

Figure 6: SIMS depth profile of the Nd tracer atoms in the as-grown sample. All Nd isotopes are summed to produce the Nd peak and the estimated peak concentration is $\sim 11.5\%$. The arrow indicates the location of the film-substrate interface.

Although the absolute concentration of Nd cannot be determined from SIMS, we have found the ratio of Nd/U from the Rutherford backscattering spectrometry (RBS) is consistent with the power ratio during film growth. Therefore, to calibrate the absolute concentration of the SIMS results, a series of standard specimens with uniform distribution of Nd were grown by fixing the power of the sputtering guns and RBS was performed to confirm the absolute Nd concentration. The RBS results are shown in Fig. 7 and the fitting parameters are listed in Table 1.

The power ratio during the film growth is compared with the fitting parameters, which are roughly in agreement. We have not determined the source of the large deviation of the U peaks for sample 53 in Fig. 7, but we are confident of the power ratio from our previous film growth experience. The result of this calibration is shown in Fig. 8.

A miscibility gap exists in the U-Nd-O system when the Nd/(U+Nd) ratio is greater than 3% and the O/M (M stands for metal) is less than two [20]. The Nd/(U+Nd) ratio we used here roughly ranges from 2% to 12%, right in the range of the miscibility gap. However, the strongest XRD peaks in the $2\theta - \omega$ specular scan have shown different characteristics from that in [20], where two distinct phases were determined from the Rietveld refinement. Although we have not performed a Rietveld analysis, the XRD peaks of our representative samples seem not to show a two-phase feature, as illustrated in Fig. 9. And the O/M ratio is unknown in our case, which may not be less than 2 because the temperature during film growth is low (UO_{2-x} exists at higher temperatures [21]). Furthermore, the fabrication processes of these two studies, magnetron sputtering growth of thin film vs. sintering of bulk samples, are different. Therefore, we conclude that the Nd in the thin film we studied here is probably in a solid solution within the UO_2 matrix.

The XRD results have shown high quality single crystal feature of the UO_2 film, and the SIMS results have shown a well defined UO_2 -(U,Nd) O_2 - UO_2 sandwich structure which is ideal for the RED study, and the RBS results roughly confirmed the concentration of Nd in the film. However, the exact stoichiometry of the film, which is a critical parameter to study diffusion in UO_2 , cannot be determined by the current techniques. One of the reasons is that the surface of thin film is affected by environmental oxidation, which will certainly create none-uniform stoichiometric distribution and affect the overall stoichiometry of the film [17]. The other reason is that the current film depth-profiling techniques, e.g., AES or XPS, will make un-avoidable preferential sputtering of the lighter elements, which may change the initial stoichiometry. Other effects, such as the introduction of the Nd layer and the interaction between the film and the substrate, make the determination of the exact stoichiometry of the film even more difficult. Therefore, the absolute value of x in the $\text{UO}_{2\pm x}$ film is unknown, which must has a complex distribution over the thickness of the film. Annealing the samples in gas mixtures at certain temperatures might give us an overall idea about the stoichiometry [22, 23, 24], however, the annealing process was not performed after the film growth.

Table 1: Fitting parameters for the RBS results with uniformly distributed Nd in UO_2 film.

Sample	Layer	Thickness ($\times 10^{15}$ Atoms/cm 2)	Atomic Concentration			Nd/U (%)	Power Ratio (%)
			U	Nd	O		
52	1	300	0.243	0.027	0.730	11.2	17.2
	2	470	0.220	0.030	0.750		
53	1	100	0.400	0.025	0.575	8.6	8.6
	2	530	0.300	0.030	0.670		
54	1	200	0.335	0.010	0.655	3.0	4.3
	2	420	0.320	0.010	0.670

Figure 7: RBS results for three uniformly distributed Nd in UO_2 film with different concentrations. The oxygen peaks are around 770 keV which is shown as a small edge just above the substrate background. The Nd peaks have some overlap with the U peaks, which is indicated by the double peaks. Fitting parameters are listed in Table 1.

Figure 8: Calibration of the SIMS results to Nd concentration showing expected linear dependence of Nd concentration (Nd/U) which is taken from the power ratio during the film growth, with the Nd/UO ratio in the SIMS results.

Figure 9: The (2 0 0) reflection of the $2\theta - \omega$ scans of representative samples. The peak Nd/U ratio for sample 32 and 46B4 are $\sim 2.3\%$ and $\sim 11.5\%$ respectively. Nd in sample 52 is $\sim 17.2\%$ with uniform distribution. Each curve has been normalized to the area. A linear intensity scale has been plotted and each curve has been shifted vertically for clarity.

2.2. Irradiation Conditions

Each deposition was cut into 4~9 pieces to provide a series of measurements on identical specimens from the same deposition. Specimens were irradiated with 1.8 MeV Kr^+ ions using a High Voltage Engineering Van de Graaff accelerator at the University of Illinois. Both temperature dependent and rate-dependent experiments were performed.

For temperature dependent experiments, the current of the Kr^+ ions was fixed to a flux ϕ of 3.47×10^{12} ions/cm²/s. The temperature range from 500 °C to 1113 °C was investigated. Three stages were used for these irradiations and are described in detail in [25]. Briefly, for $T \leq 600$ °C, an open face hot stage with copper plate was used and the temperature was measured with type K thermal couple. For 600 °C $< T \leq 850$ °C, an open face hot stage with molybdenum plate was used and the temperature of the sample surface was measured with type K thermal couple. For $T > 850$ °C, a tubular stage with a length to diameter ratio of ≈ 5 was used to prevent loss by black body radiation and the temperature was measured with type R thermal couple. To ensure the beam stability, a Faraday cup was inserted into the beam path and the current was verified at ~ 10 minutes intervals during irradiation.

Half of all irradiated specimens were blocked to obtain the un-irradiated diffusivity associated with the thermal diffusion coefficient under the same thermal history. However, the thermal diffusion coefficient of Nd in UO_2 was found to be too small to be measured in the temperature range from 500 °C to 1113 °C under the current experimental conditions, which is discussed in Section 4. It must be mentioned that the temperature were measured in the blocked region and the effect of beam heating was not taken into account in the current study. The beam heating had been estimated to be less than 10 °C under similar experimental conditions [9], and this amount of beam heating was comparable to the uncertainties of the measured temperature during our

experiment.

The rate-dependent measurements were performed at 610 °C. Both the current of the Kr^+ beam and the irradiation time were varied so that the fluence Φ was kept constant. No Kr was found in the UO_2 film during the SIMS depth profiling because the range of Kr^+ was more than 6000 Å estimated by SRIM [26], which is much larger than the film thickness, and Kr is difficult to be ionized in SIMS.

3. Results

The Nd peaks, normalized to total area, irradiated at various temperatures but the same fluence Φ of 1.0×10^{16} ions/cm² are shown in Fig. 10. Each peak has been fitted with a Gaussian function from which we obtain the standard deviation σ , given in Table 2.

Figure 10: Nd depth profiles for single crystal UO_2 films irradiated at a fluence of 1.0×10^{16} ions/cm² at the temperatures indicated. The solid lines are best-fits of a Gaussian function. The standard deviations obtained from these best-fits are listed in Table 1. The peak concentration of the as-grown sample is estimated to be $\sim 11.5\%$. A linear intensity scale has been plotted and each peak has been normalized by the peak area.

The diffusion coefficient is given by,

$$2Dt = \sigma_{irr}^2 - \sigma_{unir}^2 \quad (1)$$

where D is the diffusion coefficient, t is the irradiation time, σ is the standard deviation from the Gaussian fitting of the Nd peak, the subscript *irr* represents the irradiated width and *unir* represents the un-irradiated width at temperature. This equation assumes 1-D diffusion geometry.

The radiation enhanced diffusion coefficient D_{rad} is given by,

$$D_{rad} = D_{total} - D_B \quad (2)$$

where D_{total} is the total diffusion coefficient and D_B represents the effective diffusion coefficient because of ballistic mixing. These two coefficients are given by,

$$D_{\text{total}} = \frac{\sigma_{\text{irr},T}^2 - \sigma_{\text{unir},RT}^2}{2t} \quad (3)$$

$$D_B = \frac{\sigma_{\text{irr},RT}^2 - \sigma_{\text{unir},RT}^2}{2t} \quad (4)$$

If the irradiation time are the same, the radiation enhanced diffusion coefficient is in the form of

$$D_{\text{rad}} = \frac{\sigma_{\text{irr},T}^2 - \sigma_{\text{irr},RT}^2}{2t} \quad (5)$$

And the thermal diffusion coefficient is given by

$$D_{\text{th}} = \frac{\sigma_{\text{unir},T}^2 - \sigma_{\text{unir},RT}^2}{2t} \quad (6)$$

It has been found that below 800 °C, the thermal diffusion coefficient D_{th} can be neglected for Nd diffusion in UO_2 [27]. In the current measurement, we find D_{th} very small up to 1113 °C, as indicated in Table 2.

Eq. (5) is used to calculate the radiation enhanced diffusion coefficients at elevated temperatures and various fluxes in the current study, and the results are listed in Table 2. Note that at temperatures above 900 °C, several depth profiles were performed at different locations of the same specimen which gave different diffusion coefficients. This phenomenon has been observed by others [9, 25] and we believe this is due to non-uniform temperature in the irradiated region of the specimen associated with the tubular stage.

Table 2: Irradiation conditions, measured standard deviations and the corresponding diffusion coefficients of Nd in UO_2 .

Sample†	T (°C)	Φ ions/cm ²	ϕ ions/(cm ² s)	σ Å	D_{rad} cm ² /s
46A	RT	0	0	30.8 ± 0.3	—
46B	RT	0	0	31.4 ± 0.4	—
46C	RT	0	0	30.5 ± 0.3	—
46D	RT	0	0	34.9 ± 0.5	—
46B4	915 ^a	0	0	30.8 ± 0.2	—
46B4	915 ^a	0	0	34.4 ± 0.5	—
46C1	1012 ^a	0	0	32.4 ± 0.4	—
46C1	1012 ^a	0	0	31.9 ± 0.5	—
46C2	1113 ^a	0	0	31.7 ± 0.5	—
46C2	1113 ^a	0	0	32.1 ± 0.5	—
46B1B	RT ^b	1.0×10^{16}	3.47×10^{12}	36.4 ± 0.3	6.4×10^{-18}
46A7	610	1.0×10^{16}	3.47×10^{12}	38.8 ± 0.3	3.1×10^{-18}
46B3B	710	1.0×10^{16}	3.47×10^{12}	40.9 ± 0.3	5.9×10^{-18}
46B3A	806	1.0×10^{16}	3.47×10^{12}	44.4 ± 0.4	1.1×10^{-17}

(cont.)

Table 2(cont.)

Sample [†]	T (°C)	Φ ions/cm ²	ϕ ions/(cm ² s)	σ Å	D_{rad} cm ² /s
46B4	915	1.0×10^{16}	3.47×10^{12}	44.7 ± 0.3	1.2×10^{-17}
46B4	915	1.0×10^{16}	3.47×10^{12}	44.9 ± 0.2	1.2×10^{-17}
46B4	915	1.0×10^{16}	3.47×10^{12}	53.3 ± 0.5	2.6×10^{-17}
46C1	1012	1.0×10^{16}	3.47×10^{12}	61.2 ± 0.4	4.2×10^{-17}
46C1	1012	1.0×10^{16}	3.47×10^{12}	79.9 ± 0.9	8.8×10^{-17}
46C1	1012	1.0×10^{16}	3.47×10^{12}	89.8 ± 1.2	1.2×10^{-16}
46C1	1012	1.0×10^{16}	3.47×10^{12}	74.8 ± 0.4	7.4×10^{-17}
46C1	1012	1.0×10^{16}	3.47×10^{12}	90.9 ± 1.1	1.2×10^{-16}
46C1	1012	1.0×10^{16}	3.47×10^{12}	72.4 ± 0.4	6.8×10^{-17}
46C2	1113	1.0×10^{16}	3.47×10^{12}	155 ± 9.5	3.9×10^{-16}
46C2	1113	1.0×10^{16}	3.47×10^{12}	153 ± 9.9	3.8×10^{-16}
46C2	1113	1.0×10^{16}	3.47×10^{12}	145 ± 8.9	3.4×10^{-16}
46C2	1113	1.0×10^{16}	3.47×10^{12}	111 ± 1.4	1.9×10^{-16}
46A8	610	1.0×10^{16}	2.08×10^{13}	38.7 ± 0.3	1.8×10^{-17}
46A9	610	1.0×10^{16}	1.39×10^{13}	40.3 ± 0.3	2.0×10^{-17}
46A6	610	1.0×10^{16}	6.94×10^{12}	39.2 ± 0.4	7.2×10^{-18}
46B1A	600	1.0×10^{16}	2.08×10^{12}	50.9 ± 0.3	1.3×10^{-17}

[†] Sample 46A6 – 46A9 were the pieces cut from 46A for irradiation with various fluxes, similarly, 46B1 – 46B4, 46C1 – 46C2 were the pieces cut from 46B and 46C respectively. 46B1A is one of the pieces cut from 46B1, and the same nomenclature can be applied to 46B1B, 46B3A, and 46B3B.

a The unirradiated region of sample 46B4, 46C1 and 46C2. The annealing time is 48 minutes, which is the same as the irradiated region.

b The diffusion coefficient at room temperature under heavy ion bombardment is not D_{rad} , but represents ballistic mixing D_B .

The temperature dependent results are shown in an Arrhenius plot in Fig. 11. Solid lines fit of $D = D_0 \exp(-E_a/kT)$ to the experimental results. This analysis clearly shows two temperature regions. In the low temperature region (≤ 800 °C), an activation energy of $E_{a1}=0.56$ eV is obtained. In the high temperature region (≥ 900 °C), an activation energy of $E_{a2}=1.9$ eV is obtained. A similar transition from the low temperature region to the high temperature region with an increase of the activation energy has also been found in MgO on the anion sublattice [9]. The dashed line in Fig. 11 represents the ballistic mixing which is an interfacial mixing across boundaries. When an energetic ion slows down in a solid, target atoms can be permanently displaced from their lattice sites and relocated several lattice sites away, resulting in interface mixing at the boundary separating two different materials [28]. Ballistic mixing is characterized as a temperature independent process with an effective diffusion coefficient D_B . In the current study, we take the average standard deviation of 46A, 46B and 46C as $\sigma_{unir,RT}$, and 46B1B as $\sigma_{irr,RT}$ from Table 2. Plugging these values in Eq. (4) with irradiation time of 48 minutes and it gives $D_B = 6.4 \times 10^{-18}$ cm²/s for ballistic mixing. The fitting constants for the temperature dependent results are listed in Table 3.

The rate-dependent (or flux-dependent) results are shown in Fig. 12. For the rate dependence, we are interested in the slope of the fitted curve which reveals the defect annealing kinetics during irradiation. The fitting result has shown a slope of 1.2 ± 0.3 , which indicates a regime

Figure 11: Measured radiation enhanced diffusion coefficients of Nd in UO_2 during 1.8 MeV Kr^+ irradiation. The solid circles are the experimental data. The solid lines indicate best fits to the data. The dashed line represents the ballistic mixing D_B measured at room temperature.

Table 3: Fitting constants for at-temperature irradiated diffusion of Nd in UO_2 .

Type	T(°C)	$D_0(\text{cm}^2/\text{s})$	$E_a(\text{eV})$
D_{rad}	900–1113	$2(\pm 6) \times 10^{-9}$	1.9 ± 0.3
D_{rad}	600–800	$4.5(\pm 1.8) \times 10^{-15}$	0.56 ± 0.04
D_B	RT	$6.4(\pm 0.5) \times 10^{-18}$	-

of sink-limited kinetics [6]. Similar results has also been found on the anion sublattice in MgO [9]. However, this result is just the opposite of the traditional RED theory which predicts a recombination-limited kinetics in the low temperature range [6]. The data point of the lowest flux (80min) has shown an unexpected high diffusion coefficient. The possible reasons for this data point are, when the flux is very low, defects have greater opportunity to make long range migration which results in a higher diffusion coefficient. It may also be an indication of transient behavior. We therefore do not include this data point in the analysis.

Since there are some other incomplete but relevant results of RED [27], it would be very interesting to compare the current results with those. Thus it is necessary to clearly describe those samples in the first place. Sample 32 is a single crystal thin film UO_2 with a Nd layer in the film mid-plane grown on YSZ substrate. The thickness of the film is 666 Å and the standard deviation of the Nd layer is $\sigma \sim 24$ Å. Sample 36 is the same as sample 32 with a thickness of 780 Å and $\sigma \sim 26$ Å for the Nd layer.

In Fig. 13 the RED results of sample 46 and 32 are compared. By applying the calibration in Fig. 8, the Nd concentration in sample 32 is determined to be $\sim 2.3\%$, which is lower than that in sample 46 ($\sim 11.5\%$). The radiation enhanced diffusion coefficient was measured in

Figure 12: Dependence of radiation enhanced diffusion coefficient on ion flux ϕ during 1.8 MeV Kr⁺ irradiation at 610 °C. The irradiation time is identified at each flux.

the temperature range between 400 °C and 800 °C for sample 32 and an activation energy of $E_a = 0.42 \pm 0.05$ eV is obtained. The radiation enhanced diffusion coefficient of sample 32 is higher than that of sample 46 but the diffusion coefficient for ballistic mixing D_B is lower, which may be because of the different Nd concentrations of the two samples. This concentration effect will be discussed in Section 4.

The thermal diffusion coefficient of Nd in UO₂ has been measured as well, as shown in Fig. 14. A very small but observable thermal diffusion coefficient of Nd in UO₂ is found at 800 °C. We performed relatively long-time annealing (~50 hours) on sample 36 where the standard deviation σ of the Nd layer is similar to that of sample 32. Higher temperature annealing was precluded due to the temperature limit of the current furnace and the sublimation of the substrate at higher temperatures for long annealing times. The radiation enhanced diffusion coefficient is about 3 orders of magnitude higher than the thermal diffusion coefficient below ~ 800 °C, which demonstrates that the diffusion of Nd in UO₂ is greatly enhanced under irradiation conditions.

Since CeO₂ is often used as a UO₂ surrogate, it is useful to compare the experimental RED and thermal diffusion results of the two materials. Experimental data of CeO₂ is available in [10] and we plot them together with that of UO₂ in Fig. 14. It must be noted that La was used in CeO₂ as a tracer element while Nd is used here. As illustrated in Fig. 14, the thermal diffusion coefficient of La in CeO₂ is nearly 5 orders of magnitude greater than that of Nd in UO₂ at 800 °C. The radiation enhanced diffusion coefficient is approximately 30 times higher in CeO₂ than that in UO₂ and this difference depends on temperature. And the activation energy in CeO₂ is 0.19 eV while in UO₂ it is 0.42 eV (sample 32) or 0.56 eV (sample 46) in the low temperature range.

The mixing parameter ξ has been measured for both UO₂ and CeO₂ [27], as shown in Fig. 15. The mixing parameter is a proportionality between the total mean square displacement (Dt) in-

Figure 13: Arrhenius plot of sample 46 and 32, which are similar samples under the same irradiation conditions. The two samples have significantly different Nd concentrations: the peak concentration of Nd in sample 46 is $\sim 11.5\%$ and in sample 32 $\sim 2.3\%$.

duced by cascade damage and the total nuclear differential energy deposition (ΦF_d) [10],

$$\xi = \frac{Dt}{\Phi F_d} \quad (7)$$

where Dt is obtained from Eq. (1), Φ is the ion fluence, and F_d is the nuclear differential energy deposition. For a thin UO_2 film irradiated with 1.8 MeV Kr^+ , $F_d \approx 130 \text{ eV}/\text{\AA}/\text{ion}$, which is calculated from the SRIM simulation [26].

If only direct recoil and cascade mixing (ballistic type mixing) are present, transport calculations predict a mixing parameter of approximately $1.0\sim 2.0 \text{ \AA}^5/\text{eV}$ which is roughly independent of the material [25]. The analysis of UO_2 yields $\xi = 1.7 \pm 0.1 \text{ \AA}^5/\text{eV}$, which indicates that ballistic mixing is the dominant mechanism of ion mixing and thermal spikes are not significant. The mixing parameter of CeO_2 is $\xi = 3.6 \pm 0.5 \text{ \AA}^5/\text{eV}$ [10], which is about twice as large as that in UO_2 .

4. Discussion

Atom transport can be enhanced by irradiation by two different processes. First, at low temperatures, where defects are not mobile under thermal equilibrium, transport of mass is mainly through ballistic mixing which includes recoil mixing and cascade mixing. The ballistic mixing is temperature independent and usually described as diffusionlike process, with a diffusion coefficient D_B [8, 9, 10, 28]. The dashed line in Fig. 11 represents the measured ballistic mixing D_B of Nd in UO_2 .

Figure 14: Thermal diffusion coefficient and radiation enhanced diffusion coefficient of Nd in UO_2 (black and red points) compared with the corresponding coefficients of La in CeO_2 (blue points) [10].

Figure 15: Product Dt (the total mean square displacement in one-dimensional diffusion) versus fluence Φ for heavy ion bombardment at room temperature in UO_2 and CeO_2 . The solid and dashed lines are linear fits which are forced through the origin (zero displacement at zero dose) [10].

Second, irradiation produces a supersaturation of point defects over the thermal equilibrium. At elevated temperatures where defects are mobile, atoms can make long-range transport which is described by the radiation enhanced diffusion coefficient D_{rad} [8].

From the Arrhenius plot for the temperature dependent results, as shown in Fig. 11, we observe two temperature regions for RED. In the low temperature region, an activation energy of 0.56 eV is obtained. This measured E_a below 800 °C contradicts the RED study on UO_2 where a temperature independent diffusion was found below 1000 °C [29]. One of the possible reasons lied in the accuracy of the diffusion coefficient measurement: in the Arrhenius plot, it was possible that an additional activation energy between 700 °C and 1000 °C existed, but was not resolved in [29]. In the current study, a low activation energy below 800 °C is clearly identified. The phenomenon of low activation energy in the low temperature range has been found before, both in CeO_2 and MgO [9, 10]. As temperature increases above 900 °C, the diffusion coefficient increases sharply. Although the data points at a given temperature are widely spread, the data clearly show a large increase of the activation energy in the high temperature range, $E_a = 1.9$ eV. Similar phenomenon has been found in MgO around 1100 °C [9], and in UO_2 around 1000 °C [29].

As mentioned before, the current RED results of Nd in UO_2 (sample 46) is compared with a similar set of experiment (sample 32) where the Nd concentration is lower, as shown in Fig. 13. To interpret the data it is important to investigate the effects of adding Nd in UO_2 first, of which the most important one the electroneutrality. The electroneutrality in Nd doped UO_2 is maintained by one of the three possible defect equilibria: 1) create oxygen vacancies; 2) create holes; 3) U(+4) shift to higher valence state of U(+5).

Previous studies of the electrical conductivity in yttria doped urania have shown that only condition 2 was realized. There was no evidence that significant amount of oxygen vacancies were created [24]. Recently XRD and X-ray absorption spectroscopy (XAS) measurements have confirmed the presence of U(+5) in Am doped urania [30]. Since both Y and Am are trivalent, which is the same as Nd, we may expect holes are created or U(+4) shift to U(+5) in the Nd doped UO_2 in our study. The stoichiometry of the two samples (46 and 32) are likely the same because the temperature and oxygen partial pressure during the film growth are similar. The major difference of these two samples are the Nd concentration, roughly $\sim 11.5\%$ in sample 46 and $\sim 2.3\%$ in sample 32 for the Nd peaks. Thus, the creation of holes or the shift of uranium to higher valence state may affect the diffusion properties. However, the details of the effect on the transport mechanisms are unknown. On the other hand, as shown in Fig. 13, the effect of the Nd concentration seems to be small because the two activation energies, 0.56 ± 0.04 eV for sample 46 and 0.42 ± 0.05 eV for sample 32, are essentially the same with respect to additional errors not resolved in the current measurement. And the diffusion coefficients of ballistic mixing D_B of the two samples are close although the Nd concentration varied a lot. Therefore, more experimental results are necessary to investigate a systematic trend as the Nd concentration varies.

For the thermal diffusion of Nd in UO_2 , as shown in Fig. 14, the diffusion coefficient is very low. No obvious thermal diffusion has been measured from the unirradiated region of the specimens in RED experiment up to 1113°C due to the short annealing time. The only observed thermal diffusivity was at 800°C for 50 hours, which is shown as the open square. At higher temperatures and for longer annealing time, excessive substrate sublimation prevent us from measuring the thermal diffusion coefficient of Nd. However, from the current result, we have the knowledge that Nd diffusion in UO_2 is considerably low.

Since CeO_2 has been considered as a UO_2 surrogate because of many similarities, such as crystal structure and lattice parameters, we may expect similar diffusion properties in these two materials as well. However, the low diffusivity of Nd in UO_2 is quite beyond our expectation because La has shown obvious thermal diffusion in CeO_2 even at 600°C , as indicated by the open triangle in Fig. 14. Although comparing Nd and La does not quite substantiate the conclusion that the diffusion properties of UO_2 and CeO_2 are very different, the valence state and the ionic radius do indicate some similarities of Nd and La. Therefore, the current observed experimental results may indicate that some major differences between UO_2 and CeO_2 in terms of diffusion, as summarized below:

- (i) No obvious thermal diffusion is found in UO_2 below 1113°C , but apparent diffusion coefficient is measured at 600°C in CeO_2 on the cation sublattice.
- (ii) Radiation enhanced diffusion coefficient in UO_2 is much larger than the vacancy self-diffusion (VSD) even at $\sim 1113^\circ\text{C}$. However, the RED in CeO_2 quickly merged with the VSD at 800°C .
- (iii) From the RED study on UO_2 , an activation energy of 0.56 eV is obtained in the low temperature range, which is obviously larger than the value of 0.19 eV in CeO_2 .
- (iv) The radiation enhanced diffusion coefficient D_{rad} in UO_2 is about 30 times lower than that in CeO_2 .
- (v) The mixing parameter of UO_2 ($\xi = 1.7 \text{ \AA}^5/\text{eV}$) is about twice as low as that in CeO_2 ($\xi = 3.6 \text{ \AA}^5/\text{eV}$).

Based on the differences above, we may conclude that CeO_2 and UO_2 have very different diffusion properties although CeO_2 is used as a UO_2 surrogate, and we believe these differences

are not because of the external conditions, such as impurity levels and deviation from stoichiometry. One of the possible reasons lies in the valence state of UO_2 and CeO_2 . Uranium atom can be in the valence states of +3, +4, +5 and +6, cerium is only found in +3 and +4 valence state. The introduction of trivalent impurities in stoichiometric UO_2 could cause uranium atoms shift to higher valence state instead of creating oxygen vacancies or holes; this cannot occur in CeO_2 since Ce does not have a +5 valence state. Therefore, the intrinsic properties of diffusing species such as valence are very important to diffusion besides the mass, the atomic size, lattice parameter and crystal structure.

For the results of the rate dependence (Fig. 12), a slope of 1.2 ± 0.3 is found, which indicates that RED is in the regime of sink-limited kinetics. Similar result has been found in MgO , where a sink-limited kinetics is found in the low temperature region [9].

5. Conclusion

Radiation enhanced diffusion of Nd in single crystal UO_2 thin film has been studied, which gives an activation energy of $E_{a1} = 0.56$ eV in the low temperature region (≤ 800 °C) and $E_{a2} = 1.9$ eV in the high temperature region (≥ 900 °C), and an effective diffusion coefficient of $D_B = 6.4 \times 10^{-18}$ cm²/s for ballistic mixing. The flux-dependent results at 610 °C have shown a linear dependence, which indicates a sink limited kinetics in the low temperature range. The current RED results have been compared with another set of experimental results where the Nd concentration in the sample is much lower. However, no big difference has been found which possibly indicates the impurity concentration effect on RED in UO_2 is small. On the other hand, comparison with the RED results in CeO_2 has shown big differences between the two materials. The radiation enhanced diffusion coefficient D_{rad} in UO_2 is much larger than the thermal diffusion coefficient in the whole temperature range (up to 1113 °C), which clearly shows an evident enhanced diffusion under radiation, while D_{rad} in CeO_2 quickly merges with the thermal diffusion at 800 °C. The activation energy of RED in the low temperature range for UO_2 is 0.56 eV, whereas a much lower value of 0.19 eV is observed in CeO_2 . The mixing parameter of UO_2 is $\xi = 1.7 \text{ \AA}^5/\text{eV}$, which is about half of that in CeO_2 ($\xi = 3.6 \text{ \AA}^5/\text{eV}$). All these results have shown that the diffusion properties of UO_2 and CeO_2 are different: atomic movement on the cation sublattice in UO_2 is much slower than in CeO_2 .

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