Effects of microstructural constraints on the transport of fission products in uranium dioxide at low burnups

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1. Abstract

Diffusion of fission gases in UO_2 is studied at low burnups, before bubble growth and coalescence along grain boundaries (GBs) become dominant, using a 3-D finite element model that incorporates actual UO_2 microstructures. Grain boundary diffusivities are assigned based on crystallography with lattice and GB diffusion coupled with temperature to account for temperature gradients. Heterogeneity of GB properties and connectivity can induce regions where concentration is locally higher than without GB diffusion. These regions are produced by “bottlenecks” in the GB network because of lack of connectivity among high diffusivity GBs due to crystallographic constraints, and they can lead to localized swelling. Effective diffusivities were calculated assuming a uniform distribution of high diffusivity among GBs. Results indicate an increase over the bulk diffusivity with a clear grain size effect and that connectivity and properties of different GBs become important factors on the variability of fission product concentration at the microscale.

2. Introduction

In oxide nuclear fuels, the transport and the release of insoluble fission gases and other fission products are important to the design and operation of water reactors, and the technical and scientific problems related to measuring and modeling this behavior have received a lot of attention over the years, e.g., see [1-7] and references therein. In particular, microstructural features such as grain size distribution and GBs are known to affect the transport behavior, especially at low burnup [8-10]. Early modeling works, which were mostly based on Booth’s model [11], generally assumed a single representative spherical grain where fission gases are generated and diffuse to its GBs, from which they are assumed to be released. This works fairly well when intergranular bubbles dominate the behavior at the GBs, as concluded in [12]. Recent models [1, 13-15] have been used to conduct simulations from the atomistic to the macro scale, with polycrystalline models considered at the microscale level. However, these simulations were conducted using numerically generated microstructural networks, and the effect of crystallographic constraints, which are known to affect the behavior of mass transport through GB networks [16] do not seem to be fully considered. In this regard, it is known that GB diffusion can affect the transport behavior in many materials, including metals and oxide ceramics [17, 18]. In addition, GB properties are known to be affected by GB character [19]. The work in [20] took this variation into account to study the percolation behavior associated to GB diffusion, and the results showed that effects of GB diffusion become significant when the contrast in GB diffusivities, i.e., the ratio of GB diffusivity to bulk diffusivity, is above 10^4 , in agreement with analytical solutions [21]. The percolation study reported in [20] was based on a large, simulated 2-D network to describe a general behavior. When the scale is limited, it is known that the percolation behavior can be strongly affected by local geometry and dimensionality. The complex microstructure of polycrystalline materials in 3-D can change the outcome of such models, especially on a local scale. In addition, the distribution and connectivity of different GBs and the percolation behavior can be affected by certain crystallographic constraints as suggested in [16, 22], which adds another source of variability to the simulated networks.

In the study of fission gas transport in UO_2 , GB diffusion is generally ignored due to the trapping effect. However, the work in [12] has suggested that GB diffusion can contribute to the release of fission gases at the early stage of fuel life, before intergranular bubble formation, since the release mechanism is consistent with sequential lattice and GB diffusion [12]. In addition,

experimental work [23, 24] has shown that bubble morphology varies in different GBs, suggesting that there is variability in fission gas transport to and along GBs, likely due to heterogeneous boundary properties in UO_2 as affected by crystallography. The work presented here studies these effects using a 3-D microstructurally explicit model. It tackles the problem of fission gas transport at very low burnups and the distribution of the fission gas under the effect of grains and GBs is studied. The model, which is built using actual microstructural information from UO_2 as characterized by scanning electron microscopy (SEM) and electron backscattering diffraction (EBSD), can be used to study the effects of microstructure heterogeneity and crystallographic constraints of the GB network on transport behavior of fission gas at low burnups and fission gas release from post-irradiation annealing treatments in fuel samples that have experienced trace irradiations [12].

The development of the model begins with serial sectioning and 3-D reconstruction of a UO_2 microstructure. The models need to contain microstructural features, such as grain bulks and GBs, in order to capture fission gas transport from grain bulks to boundaries. In these models, solid-state diffusion will serve as the main mechanism for fission gas transport at low burnup, and the interplay between bulk and GB diffusion is studied. The heterogeneous properties for GBs are assigned based on the individual GB character, as determined by their crystallography measured using EBSD. The effect of temperature is also considered due to the large temperature gradient that is usually present in oxide fuels used in water reactors [7]. The material properties can vary significantly depending on the temperature; therefore, material properties used in the models are temperature dependent.

3. Modeling Approach

The modeling work starts with 3-D microstructure reconstruction using serial sectioning EBSD data of UO_2 samples collected at Los Alamos National Laboratory [25]. The data collected were first processed using Dream3DTM for data segmentation according to local crystallographic orientation, and this was followed by interpolation, surface reconstruction and tetrahedral meshing using AVIZOTM. The final product of the procedure is a 3-D mesh that contains grains and their boundaries. The meshed geometries are then imported to COMSOL MultiphysicsTM finite element code to create a 3-D microstructurally explicit model, containing the characterized geometry of grains and GBs from the samples, to be used as a tool to study the effect of microstructure on the transport of fission gases, with techniques similar to those presented in [25, 26].

3.1. Meshing and model formulation

The meshed geometries from the 3-D reconstructions for three different 3-D regions within bulk UO_2 samples are shown in Figure 1. The grain bulks are meshed with 3-D tetrahedral elements and the grain boundaries are meshed with 2-D triangular elements. The mesh is refined closed to the boundaries to better capture the effect of GB diffusion. Figure 1 shows that both models 1 and 3 have a combination of large columnar grains and small grains while model 2 has a relatively uniform grain size distribution. This differentiation can be easily overlooked in 2-D models depending on the observed planes. The size of the models ranges between $14000 \mu\text{m}^3$ to $22000 \mu\text{m}^3$, each with about 200 grains or more. Note that according to [26], at least 50 grains are needed in a 3-D finite element model of a polycrystal to calculate the average diffusivity due to the combined effects of grain bulk and GB diffusion. The objective of this work, though, is to look for local variability due to GB connectivity, so a larger number of grains is used to allow for

a larger sampling of the GB network as well as to examine potential effects due to local variations of grain size. While long range diffusion of fission gases is unlikely due to both intra- and inter-granular trapping, the size of the model is adequate for studying short range diffusion as affected by local microstructures, which is expected to be important at early stages of fuel life and during annealing of trace-irradiated fuels. Furthermore, the results should be applicable, at least qualitatively, to other fission products that might experience transport due to solid-state diffusion in UO_2 , e.g., Cs and I [27, 28].

Figure 1: Meshed models for the three samples: (a) model 1, (b) model 2, and (c) model 3.

The minimum mesh density needed to achieve convergence was estimated from similar work found in the literature for 2-D and 3-D cases [26, 29]. The work from [29], suggests that roughly 20 rectangular elements per grain are needed for convergence, which can be roughly extrapolated to about 90 hexahedral elements per grain in 3-D. Furthermore, a published study comparing the performance of tetrahedral and hexahedral meshes suggests that a first order tetrahedral mesh with 6 times the number of elements as a hexahedral mesh should have similar numerical errors in the main variable [30]. This points to about 600 elements per grain, but to insure that both concentration and concentration gradients can be obtained as accurately as possible, a tetrahedral mesh with at least 10 times that number of elements per grain was used. This is a much denser mesh than what was used in [26, 29]. Nonetheless, the convergence of the resulting meshes was verified by comparing results obtained from model 1 with 3 different mesh densities.

To set up the numerical simulations, finite elements in the grain bulk are formulated in COMSOLTM using Equation (1) where C stands for fission gas concentration, t stands for time and D_{bulk} stands for fission gas diffusivity in the grain bulk. For the GBs, the model uses the same approach that was used in [25, 26] in order to reduce the computational cost, which incorporates the GB thickness in the element formulation. Equation (2), which is derived from Equation (1) by calculating the average concentration across the boundary thickness (δ), is used to formulate the 2-D boundary elements. The term, j_{bulk} , is the mass flux perpendicular to the GBs and can be expressed in terms of D_{bulk} multiplied by the concentration gradient at the boundary. Equations (1) and (2) are coupled by enforcing continuity in concentration and mass flux at the interface between 3-D and 2-D elements. The details of the derivation can be found in [25]. A similar approach can be taken to model diffusion in triple junctions, which is also known to be a fast diffusion path [31]; however, the work presented here will focus on the effect of GBs. Other effects, such as irradiation enhanced diffusion and fission gas trapping and resolution [5] as well as fission gas segregation [32, 33], all of which are important and require modifications to the equations, typically through an effective diffusivity coefficient [5, 32], are excluded from the present model so that effects of the GB connectivity on local concentration distribution of fission products can be explored as a standalone phenomenon. Coupling of crystallographic constraints in GB connectivity with the effects mentioned above will be the subject of future work.

$$\frac{\partial C}{\partial t} + \nabla \cdot (-D_{bulk} \nabla C) = 0 \quad (1)$$

$$\frac{\partial C}{\partial t} \delta + \nabla \cdot (-\delta D_{GB} \nabla C) = D_{bulk} \left(\frac{\partial C}{\partial z} \Big|_{z=\delta} - \frac{\partial C}{\partial z} \Big|_{z=0} \right) = j_{bulk} \quad (2)$$

In addition to studying local variability on concentration distributions, the simulations were also used to derive effective diffusivities by a methodology similar to that proposed by [26], with one variation: instead of imposing a concentration gradient $\Delta C / \Delta z$ and calculating the resulting flux j across the model along the direction of the imposed gradient, a flux was imposed and the resulting gradient was obtained, and the effective diffusivity, given in Equation (3) due to the combined effects of GB and bulk diffusion is obtained as the absolute value of the ratio of the imposed flux to the resulting concentration gradient. This approach calculates the overall diffusivity of the representative volume element studied as affected by GB diffusion and can provide an indication of the significance of the effect of microstructural features and crystallography, and represents the diffusivity that a homogeneous material should have in order to produce the same flux as the representative volume element used here for the same imposed concentration gradient. This effective value is what is actually measured during integral experiments such as fission gas release during heat treatments after irradiation. The results from [26] suggest that the number of grains used in this work should be enough to get representative values of the effective diffusivity.

$$D_{eff} = - \frac{j}{\Delta C / \Delta z} \quad (3)$$

3.2. Property assignment and data selection

Information on misorientation angles and coincident site lattice (CSL) for GBs is available from the EBSD data. The location of each boundary in the individual 2-D EBSD map obtained from serial sectioning is matched with the 3-D models so that the boundary properties in the 3-D model can be assigned based on actual characterization data. Unfortunately, despite the fact that the heterogeneity in GB properties has been studied for a long time, the data for UO_2 system is scarce, and available work has been mostly done for special grain boundaries only [6, 19, 33]. Due to the lack of information for GB diffusivity of fission gases as a function of crystallography in oxide and UO_2 systems, the GB diffusivity data from an experiment in the Au/Ag system [18], shown in Figure 2, is used as a reference to assign a two level GB diffusivity scheme to the models, which is commonly used in studies of this nature [20, 26] and it is usually enough to identify potential effects due to GB connectivity. Grain boundaries with misorientation angles between 30 to 55 degrees are assigned with a high diffusivity value (D_{GB_high}), and GBs with misorientation angle outside this range along with low CSL ($\Sigma 3$ -11) GBs are assigned with a low diffusivity value (D_{GB_low}).

Both experimental and computationally obtained xenon diffusivities in bulk UO_2 have a very large discrepancy, a spread that can be 5 orders of magnitude or larger, depending on the temperature [13, 34, 35]. Some authors [5, 12, 35] argue that the spread is actually closer to 2 orders of magnitude, so there is room for interpretation. The value for D_{bulk} in this work follows the data by Davies and Long [36] as it is commonly used as the intrinsic diffusivity by many researchers [12, 34]. For the GB diffusivity, the difference in temperature dependency is ignored here given the uncertainty in the applied data and the limited temperature range used in the model. The value for D_{GB_high} is taken to be $10^5 D_{bulk}$, a contrast just high enough to see appreciable effect of GB diffusion according to the literature [20, 21]. Although the available data on UO_2 grain boundary diffusivities is scarce and the spread is large, the chosen value for the contrast has been observed in some oxide systems [17, 37]. There are also works that showed the D_{GB} can be 5 orders of magnitude higher than the D_{bulk} value applied in UO_2 system [12, 38]. It has been reported both through experiments [39] and modeling [2, 3] that uranium diffusion along GBs in UO_2 is indeed about 5 orders of magnitude faster than bulk diffusion. Furthermore, it is also well recognized that diffusion of fission gases like Xe in UO_2 occurs through vacancy assisted migration [2, 3] and the same activation energy for U and Xe diffusion along GBs in UO_2 has been reported from atomistic calculations [2, 3], suggesting that they indeed follow the same mechanisms. Hence, given the facts described above, the contrast between bulk and boundary diffusion assumed for this work was considered reasonable as is supported by both experimental and modeling results.

The relationship between GB diffusivity and GB character, however, is not well established. The study by Williams, 2015 shows that O diffusivity in UO_2 is indeed larger along special GBs, but only by a factor of at most 40 times. This is not enough to show a significant effect on overall diffusion in polycrystalline UO_2 , since a much higher contrast, $D_{GB} > 10^4 D_{bulk}$ is needed for this [20, 21], which is consistent with experimental observations of no significant differences between O diffusion in monocrystalline and polycrystalline UO_2 [39]. Therefore, the value for D_{GB_low} , is taken to be 2 orders of magnitude lower than D_{GB_high} , a value within the range of the spread that is typically found in the study of fission gas diffusivity in UO_2 [5, 34]. This is also consistent with the fact that in several oxides the GB diffusivity has been reported to

be at least two orders of magnitude larger than pipe diffusion, i.e., along dislocations [17], and that lower angle GBs can be sometimes modeled as arrays of dislocations [40]. Upon assigning the GB properties to the models, the area fraction of high diffusivity GBs is calculated and listed in

Table 1, along with other statistics of the models. The data show that the fractions of high diffusivity GBs are over 65% for all three models, a much higher value than the percolation threshold in a cubic lattice network [41]. However, the volumes studied might not be large enough to lead to full percolation behavior along the GB network.

Figure 2: A two level GB diffusivity scheme is assigned to the models based on GB diffusivity measurements in the Au/Ag system. Plot created with data from [18]. High angle GBs are assigned with a high diffusivity while low angle GBs and CSL grain boundaries are assigned with a low diffusivity.

Table 1: Statistical data for the three reconstructed models.

Model	1 (200 grains)	2 (248 grains)	3 (196 grains)
Average grain size (μm)	4.28	3.55	4.36
High diffusivity grain boundary fraction (area)	0.755	0.716	0.676
Dimensions (μm)	29 x 25 x 31	27 x 26 x 20	30 x 25 x 25
Number of elements (million)	1.49	2.09	1.36

Note from Table 1 that the minimum number of elements per grain is about 6900 for model 3, in agreement with the discussion in section 3.1. Furthermore, note that the number of elements per grain increases as grain size decreases, i.e., about 7450 elements per grain in model 1 and ~ 8400 elements per grain in model 2. This allows representing the geometry better and also leads to better numerical performance of the mesh for smaller grains. The material properties needed for the simulations are all temperature dependent, especially the diffusivities,

which have an Arrhenius dependence on temperature, implying that the diffusivities can span a few orders of magnitude given the high temperature gradient that can be found in cylindrical fuel pellets. The effect of temperature is studied by applying a temperature gradient parallel to the concentration gradient. For the cases when a temperature gradient is present, the heat transport is modeled following classical heat conduction theory, as shown in Equation (4). The thermophysical properties for the model, i.e., density (ρ), heat capacity (C_p) and thermal conductivity (k), follow the recommendations from Fink [42]. Table 2 lists all the variables applied to the models.

$$\rho C_p \frac{\partial T}{\partial t} + \nabla \cdot (k \nabla T) = 0 \quad (4)$$

Table 2: Material Properties of UO₂.

Property	Value	Unit	Source
ρ	$10.963 \times (9.9672 \times 10^{-1} + 1.179 \times 10^{-5}T - 2.429 \times 10^{-9}T^2 + 1.219 \times 10^{-12}T^3)^{-3}$	Mg.m ⁻³	[42]
C_p	$52.1743 + 87.951t - 84.2411t^2 + 31.542t^3 - 2.6334t^4 - 0.71391t^2$ $t = T/1000$	J.kg ⁻¹ .K ⁻¹	[42]
k	$\frac{100}{7.5408 + 17.692t + 3.6142t^2} + \frac{6400}{t^{5/2}} \exp\left(\frac{-16.35}{t}\right)$	W.m ⁻¹ .K ⁻¹	[42]
D_{bulk} (Xenon)	$7.6 \times 10^{-6} \exp\left[\frac{-293 \text{ kJ/mol}}{RT}\right]$	cm ² .s ⁻¹	[36]
δ	1	nm	[37]

The simulations are conducted by applying a fixed concentration and temperature gradient along z direction with a zero flux condition on the side boundaries, as shown in Figure 3. The applied boundary conditions were chosen to develop a macroscopic 1-D driving force to observe any deviation from the 1-D behavior. In particular, any lateral variation in concentration and mass flux would indicate the effect of microstructure heterogeneity. The concentration is normalized to values between 0 and 1. Steady state solutions are obtained for all equations using the stationary solver in COMSOL MultiphysicsTM.

Figure 3: Boundary conditions for the simulations. T: temperature, C: fission gas concentration.

The purpose of this work is to find the effect of GB diffusion and the heterogeneous boundary properties on the distribution of fission gas under concentration and temperature gradients. The simulations conducted can be summarized in three cases: uniform GB property, heterogeneous GB properties and the temperature effect. The first case, denoted as Case I, is conducted with all boundaries assigned with the high diffusivity value to serve as baseline result to be compared to the other simulations. The temperature for the baseline model is set to be 1585 K, a value that is comparable to the centerline temperature of a UO_2 fuel pellet in light water reactors [7]. Case II introduces high and low diffusivity boundaries assigned in two different ways: one assigns values based on EBSD data and the other assigns at random. The results are compared with Case I to observe the effect of heterogeneous GB properties and their connectivity. The third case includes the effect of temperature by assigning a gradient of about 10^4 K/cm, the highest observed temperature gradient suggested in [7], to the model in Case II with EBSD based GB properties. Then, a sensitivity analysis is conducted to study the effect of uncertainties in the fission gas/product diffusivities. Finally, effective values of diffusivities for each of the models are calculated using a methodology similar to that reported in [26], which can provide some insight into GB effects on experiments where integral measurements are made, e.g., the study of fission product release using post-irradiation annealing.

4. Results and Discussion

4.1 Case I: Uniform Grain Boundary Properties

4.1.1 Concentration and Concentration Gradient

Case I assumes uniform, high diffusivity boundaries throughout the model, and the temperature is taken as a constant to build a baseline to study potential effects of microstructure and GB diffusion heterogeneity. The resulting concentration profile on the surface of the microstructure for Model 1 is shown in Figure 4. A non-uniform lateral distribution is present, despite the fact that boundary conditions impose a macroscopic 1-D concentration gradient along the z direction, as pointed out above. This implies that, although the properties are uniform throughout the model, the concentration distribution is strongly affected by the boundaries. In

this case, all of them act as fast diffusion paths; therefore, the rate of fission product transport is higher in the regions with more boundaries, i.e., small grain regions, and is lower in regions with less boundaries, i.e., large grain regions. Regions with faster transport would have a smaller concentration gradient as compared with regions with slower transport when exposed to the same driving force. Along the applied concentration gradient, when a cluster of small grains meets a large grain, as circled in Figure 4, a sharp change in concentration occurs to compensate for the different GB densities in the two regions.

Figure 4: Concentration profile in the 3-D microstructure of Model 1 with a sharp lateral concentration variation circled.

The sharp change in concentration observed in Figure 4 is examined in more detail by plotting its gradient in a vertical, cross-sectional cut plane, which can reveal more information on the effects of local microstructure on the concentration. A 2-D concentration gradient profile along a x-z plane is plotted in Figure 5a, along with the profiles in x-z planes of Model 2 and 3, as shown in Figure 5b and 5c, respectively. Each of these concentration gradient profiles reveals information of diffusive mass flux as affected by local microstructure, which is reflected, in this case, by the grain size and GB distributions. Regions with larger grains have slower transport paths and thus have higher concentration gradients. In Model 2, which has a more uniform grain size distribution, the difference in lateral concentration gradient is much smaller than in Models 1 and 3. In particular, the large grain at the lower left corner of Figure 5a creates a region with an absence of GBs. This results in a large local concentration gradient so the continuity of the mass flux can be maintained, given the difference between the high GB and the low bulk diffusivities. The surrounding small grain regions, which contain many more boundaries, allow the fission gas to travel laterally to regions with more small grains and higher GB density, despite the fact that the imposed concentration gradient is vertical. Figure 6 compares the vertical concentration distribution of the three models with the changes in slopes indicating the variation in concentration gradient. It shows that each model has several slope changes as affected by the local microstructure. The difference in concentration distribution suggests that the local behavior is sensitive to the neighboring geometry and GB distribution, and that overall statistical information alone is not enough to capture this effect. While the long-range diffusion of fission gas is not experimentally observed at medium to large burn-ups due to trapping, these results suggest that the local microstructure can still affect the distribution of fission gases and other fission products for regimes in which transport via solid-state diffusion is dominant.

Figure 5: Magnitude of concentration gradient in a vertical cut plane in (a) Model 1, (b) Model 2 and (c) Model 3.

Figure 6: Concentration profiles along the red lines in (a), (b), and (c) to compare the variation in the three models.

One of the implications of the results presented in Figures 4 through 6 is that for a high contrast of GB to bulk diffusivity, along with a heterogeneous grain size distribution, can lead to situations where the concentration and the concentration gradient need to increase locally, as compared to what they would be without GB diffusion, in order to keep continuity of the mass flux at sites where there is a jump in diffusivity, e.g., at locations where there is a large number of GBs with high diffusivity (regions with small grains) next to a large grain, with a correspondingly low diffusivity. In 3-D, these regions can be surrounded by volumes with lower concentration (see circle in Figure 4). This, in turn, can lead to these areas of large local concentration to develop more swelling due to fission product accumulation [3, 7] as compared to the surrounding areas. Furthermore, these regions might also lead to the formation of bubbles earlier than the surrounding areas, as the bubbles might precipitate as the solubility limit for the fission gas or other product is reached at these locations earlier than in its surroundings.

The location chosen for the concentration gradient plots shown in Figure 5 and the concentration line profiles in Figure 6 for model 1 include a location where one grain has a rounded corner with a high concentration gradient. This provides a good location to test mesh convergence, as discussed next.

4.1.2 Mesh Convergence

Three different tetrahedral meshes were used to discretize model 1, which led to about 380k elements for mesh #1, 1,200k elements for mesh #2 and 1,500k elements for mesh #3. The latter is the mesh density that was used to obtain all results. Boundary conditions similar to those described in Figure 3 are used, as well as all the same properties of model 1. Contour plots of concentration gradient were obtained, as well as line profiles for concentration that went through the tip of the grain with the corner. Results are shown in Figures 7 and 8 for a subsection on the upper right of Figure 5a.

Figure 7. Contour plots of concentration gradient for 3 different meshes. (a) Mesh #3; (b) Mesh #2 and (c) Mesh #1. The scale to the right applies to all plots.

Figure 8. Concentration profiles along a line crossing the rounded corner of a grain with a high concentration gradient in model 1 for all 3 meshes used in the convergence analysis.

Results indicate that all three meshes used in the analysis lead to essentially the same distribution for the concentration gradient and for the concentration profile across the tip of the grain with the rounded corner. Given that the mesh with the highest density was used, results can be considered converged.

The results from Case I involve the interaction of the geometrical heterogeneity of the microstructure, as determined by the grain sizes and shapes of each model, and the contrast in diffusivity between the boundaries and the bulk. These results are in agreement with what one would expect from these local microstructure effects. However, the situation can be much more complex if heterogeneous GB properties and temperature effects are considered. The former of these two conditions will be considered next.

4.2 Case II: Two-level Grain Boundary Diffusivity

In Case II, the effects of heterogeneous GB properties are included by using the two-level diffusivity scheme described in previous sections, so that now low angle and CSL grain boundaries have the chosen low diffusivity value, two orders of magnitude large than that of grain bulks, whereas high angle boundaries have high diffusivities. The distribution of the low diffusivity grain boundaries for Model 2 is shown in Figure 9a. With everything else kept the same, the concentration distribution of fission gas in Case II is plotted in Figure 9b, in comparison with the result from Case I plotted in Figure 9c. It is seen that the presence of low

diffusivity grain boundaries increases the level of non-uniformity in the fission gas distribution. The results can be better illustrated by plotting cross sections of the concentration profile for Model 2, as shown in Figure 10a, and compare it with the results for Case I shown in Figure 10b. It is clearly seen that the lateral concentration gradient is much higher in Case II. The presence of low diffusivity boundaries breaks the network of high diffusivity GB and lead to a more heterogeneous fission gas/product distribution. It adds another factor to the study of fission gas/product transport, in addition to the microstructure geometry.

Figure 9: Results for Model 2. (a) Distribution of low diffusivity GBs (dimensions in μm). (b) Normalized concentration profile for the simulation with two-level GB properties. (c) Normalized concentration profile for the simulation with uniform high diffusivity boundaries (Case I).

Figure 10: Cross sectional concentration profiles in the x-y plane, which is perpendicular to the applied concentration gradient, for Model 2 from (a) Case II with a two-level GB diffusivity (b) Case I with a uniform GB diffusivity.

To explain the formation of the high concentration regions, the local grain structure and the GB properties around them are examined. Figures 11a and b show two concentration contour plots in x-y plane cross sections, perpendicular to the direction of the applied concentration gradient ($-z$), in models 2 and 3, respectively. Each of these plots contains at least one grain with high concentration of the diffusing species and the local 3-D microstructure around these grains is also displayed.

Figure 11: Concentration contour plots in the x-y plane, perpendicular to the applied concentration gradient, showing grains with high concentration of fission gas/products and their surrounding high diffusivity GBs for (a) Model 2 (b) Model 3. The circles indicate the discontinuity in high diffusivity boundaries.

The high diffusivity GBs are highlighted in the 3-D microstructure for each case shown in Figure 11. In both cases, the grains with high concentration are surrounded by high diffusivity boundaries that become disconnected from other high diffusivity boundaries beneath the grain, i.e., along the direction of the applied concentration gradient. The presence of low diffusivity boundaries in some regions forces the fission gas to take other routes. If a high diffusivity path does not connect all the way to a sink, a region with high concentration, as compared to its surroundings, can form. This discontinuity in the fast diffusion paths causes the accumulation of fission gases in regions that would not have been predicted without the actual microstructure and crystallographic information. The difference in concentration between these locations and their surroundings is about 10%, and one could assume, to a first approximation, that this is also the difference in swelling strain between them. Now, assuming a level of 0.6% swelling strain due to fission gas in the lattice [3], the difference in volumetric strain between adjacent regions due to concentration differences would be about 6×10^{-4} , which is a significant level of strain for a brittle material. For pure elastic strains, this could lead to significant tensile stresses locally. However, creep and plasticity at high temperature are likely to relieve some of these stresses, and any residual stresses might lead to variability that could contribute to scatter on cracking, creep and plasticity when superimposed to other stress sources, e.g., thermal stresses due to steep temperature gradients. Numerical simulations with a full coupling between diffusion, swelling and stress-strain behavior would be needed to quantify this effect, which is beyond the scope of this work.

The developed models can also be used to illustrate the importance of assigning boundary properties based on characterization data. It has been discussed that GB connectivity is affected by crystallographic constraints and that the resulting GB network is different from a random network as suggested in [16, 22]. The models with heterogeneous grain boundary properties, which are assigned based on the GB crystallographic character, can be considered as a correlated network. A different simulation can be conducted by assigning boundary properties at random to represent a random network. Using Model 2 as an example, the random GB network can be created by assigning the same area fraction of high diffusivity boundaries using a random number generator. The simulation is conducted using the same boundary conditions, and the resulting concentration profiles under the effect of correlated and random GBs are plotted in Figure 12 along with the distribution of the assigned low diffusivity GBs.

The difference between the two cases is significant as the random network results in a much more uniform concentration profile. It also appears that the low diffusivity GBs are distributed more evenly in the random case. In principle, this agrees with literature reports [16] that suggest that two CSL grain boundaries connected at a triple junction (TJ) require a third CSL grain boundary, with the implication that the correlated grain boundary model has a better connected network of low diffusivity grain boundaries, which should lead to a higher lateral variation in concentration. Note that the fraction of CSL GBs is fairly small in the models studied here, and a bigger network along with more analysis will be needed before a general conclusion can be

drawn. However, the evidence presented here clearly indicates that a network with randomly distributed boundaries with high diffusivity will in general have better connectivity and thus a more even fission gas/product distribution as compared with a network that follows crystallographic constraints.

Figure 12: Concentration profiles in a y-z plane for model 2 using (a) correlated grain boundaries (b) random grain boundaries. The 3-D network of low diffusivity GBs is shown for each case.

4.3 Case III: Effect of Temperature Gradient

The effect of an applied temperature gradient is examined in Model 1. By assigning the top boundary with 1600K and the bottom boundary with 1570K, a uniform temperature gradient, is applied in the same direction as the concentration gradient. The temperature gradient is comparable to the upper bound gradient a UO_2 pellet sees in the reactor [7], and the temperature is set to be close to the fixed temperature applied in the previous two cases. The ratio of D_{GB_high} to D_{bulk} is kept the same at 10^5 . Results are compared with the previous simulations conducted without a temperature gradient. The temperature gradient introduces a higher diffusivity in the hot region and a lower diffusivity in the cold region. The vertical concentration profiles along two lines at different locations, as shown in Figure 13a, are plotted and shown in Figure 13b. In both concentration profiles, the temperature effect introduces a higher and flatter concentration profile in the hot region as a result from the higher diffusivity followed by a sharper drop in the

cold region. The behavior is expected given that the fission gas/product travels faster in the hot region and then slows down in the cold region. The change in diffusivity increases the discontinuity in the concentration gradient and thus can introduce more non-uniformity in fission gas/product distribution.

Figure 13: (a) Two vertical lines indicating the locations along which the concentration profiles are plotted. Line 1 on the left and line 2 on the right. (b) Vertical concentration profiles along lines 1 and 2 comparing the results with the temperature gradient with the base simulation in the Model 1 microstructure.

4.4 Sensitivity Analysis.

It is known that the experimentally measured diffusivity of fission gas, e.g., xenon, in UO_2 has a large spread between different experiments, and as a consequence, the diffusivity along GB tends to be poorly defined [12]. A sensitivity analysis is conducted to study the effect

of this uncertainty by running simulations using different D_{GB_high} to D_{bulk} ratios. Model 3 with the two-level GB properties is given diffusivity contrasts of 10 , 10^3 , 10^5 and 10^7 . The resulting concentration profiles are plotted and compared in Figure 14. The results agree with reports from [20, 21] and show that the effect of GB diffusion is only significant when the ratio D_{GB_high}/D_{bulk} is 5 orders of magnitude or higher.

Figure 14: Concentration profiles along a line for simulations conducted using four different diffusivity contrasts.

The results presented in the three case studies have shown that the distribution of fission gases/products can be a function of local grain size, GB distributions, temperature and variation in GB properties. In addition to the geometry of the microstructures, it is suggested that both temperature and heterogeneous grain boundary properties contribute to produce local regions with high concentrations, which can lead to early swelling induced stresses and perhaps early nucleation and collapse of bubbles as burn-up of fresh fuel takes place. Note that this study is based on the assumption that grain boundaries have higher diffusivity for noble fission gases and the effect of fission gas resolution and trapping are not considered. However, this work developed a framework to study fission product diffusion at the early stage of fuel life and also for study of fission product release in trace-irradiated material through annealing studies. One aspect of the modeling approach taken here that can be helpful to interpret gas release from annealing experiments is that the models can be used to calculate effective diffusivity and to understand the effect of microstructure in this parameter. This will be discussed next.

4.5 Effective Diffusivity

As described in section 3.1, the effective diffusivity can be calculated by running the same simulations. In this case, a mass flux is applied as the boundary condition, while applying the same general procedure described in [26]. For all three models, a fixed flux of $4.0 \times 10^{-15} \text{ mol.m}^{-2}.\text{s}^{-1}$, which is a value comparable to bulk diffusional flux, is used, and the calculated values are shown in Table 3. The model 2 microstructure has the highest effective diffusivity, which is expected due to its small grain size and uniformly distributed GBs. Model 1 and Model 3 microstructures have similar grains size, but Model 3 has a higher effective diffusivity. It is most likely the result of several very large grains that block the diffusion paths in Model 1. These effective diffusivity values are calculated for the three base simulations, which assume a uniform distribution of high diffusivity GBs.

Table 3: Calculated D_{eff} from the Case I Simulations using Equation (3)

Model	Average Concentration	$D_{eff} (\text{m}^2.\text{s}^{-1})$	D_{eff} / D_{bulk}
1	0.925	1.69E-18	10.1
2	0.968	3.03E-18	18.1
3	0.953	2.57E-18	15.3

These numerical estimates can be compared with the approximations reported in [26], where effective diffusivity for a system with high contrast can be estimated using Equation (5):

$$D_{eff_2} = D_{bulk} + q\beta \frac{\delta}{d} D_{GB} \quad (5)$$

Where q and β are numerical factors that depend on microstructure, equal to 0.63264 and 3.1685 for a 3-D Voronoi microstructure [26], δ is the GB thickness and d is the grain size. Using Equation (5) results in values of D_{eff_2}/D_{bulk} of 47.8, 57.5 and 47.0 for models 1, 2 and 3, respectively. Although these estimates are on the same order of magnitude than the numerical solutions, lower values should be expected in the latter, given the presence of large grains that serve as effective “bottlenecks” for diffusion given the applied concentration gradient. This is not taken into account in Equation (5), since it is deduced from numerical simulations in artificial microstructures with uniform grain size.

The baseline models have shown the effect of microstructure and GB diffusion on the distribution of FGs. Several regions with different grain size distributions are identified, and it is shown that they can affect the fission gas/product concentration distribution and the local effective diffusivity. It was also shown that the presence of large grains can reduce the effective diffusivity by up to 44% (comparing Models 1 and 2), due to effects of the variation in microstructures of the studied models, suggesting that fission product transport can be modified

locally by changing the grain size distribution. In the future, the models will be modified to include other parameters such as TJ diffusion, lower temperature gradients, more heterogeneous GB properties and mass generation to make the model more realistic in terms of simulating the actual fuel behavior in a reactor.

5. Conclusions

The release of fission gases, in particular, and other fission products, in general, is an important factor in the design and performance of oxide nuclear fuels, but the actual mechanisms are still being investigated. It is known that the microstructure of UO_2 plays an important role in fission gas release, and work has shown that grain boundary diffusion can contribute to the release mechanism before bubble interlinkage [12]. Despite the importance of the microstructure, most of the modeling work has been conducted without actual microstructural or crystallographic information. The work presented here utilized reconstructed 3-D microstructures for UO_2 , aiming to simulate the fission gas behavior before the formation of interconnected bubbles. The models couple the bulk and GB diffusion along with the effect of temperature, in order to take into account the high temperature gradient in a fuel element and the temperature dependent material properties. The models also look at the effect of heterogeneous GB properties by assigning a two-level diffusivity to different GBs based on their crystallography, as characterized based on EBSD data. Finally, effective diffusivity values for the value of material represented in the models are calculated.

- The simulation results showed that when the grain boundaries act as the fast diffusional paths the distribution of fission gas/product is a strong function of grain size and GB distributions and connectivity. A transition from a small to a large grain region can result in the local accumulation of fission gases/products due to the difference in grain boundary coverage and a lack of connectivity.
- When the two-level diffusivity scheme was applied to GBs, the connectivity of the high diffusivity boundaries added another factor to the distribution of fission gases, and again, the high concentration regions were identified to be where the high diffusivity GBs became disconnected.
- Conducting the same simulation using randomly distributed boundaries resulted in a more uniform fission gas distribution, which was expected given that the distribution of low diffusivity grain boundaries were more evenly distributed and not bounded by the crystallographic constraints. This difference stressed the importance of knowing the actual crystallographic information of GBs and their connectivity in the studied microstructure.
- The addition of a temperature gradient induced a sharper concentration drop from the hot region to cold region due to the temperature dependent diffusivity in the bulk and along the boundaries, and the concentration is more evenly distributed inside the hot region.

- Finally, the values of effective diffusivity calculated from the models indicate that the presence of high diffusivity GBs increases the overall diffusion coefficient under the conditions used in the model and that the results are indeed sensitive to grain size and potentially to grain size distribution. The presented model provides a tool to understand better the release of fission gas at low burnup and the potential early development of localized swelling where high concentrations can appear due to low connectivity of high diffusivity boundaries.

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