Multiscale simulation of xenon diffusion and grain boundary segregation in UO_2

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Abstract

In light water reactor fuel, gaseous fission products segregate to grain boundaries, resulting in the nucleation and growth of large intergranular fission gas bubbles. The segregation rate is controlled by diffusion of fission gas atoms through the grains and interaction with the boundaries. Based on the mechanisms established from earlier density functional theory (DFT) and empirical potential calculations, diffusion models for xenon (Xe), uranium (U) vacancies and U interstitials in UO_2 have been derived for both intrinsic (no irradiation) and irradiation conditions. Segregation of Xe to grain boundaries is described by combining the bulk diffusion model with a model for the interaction between Xe atoms and three different grain boundaries in UO_2 ($\Sigma 5$ tilt, $\Sigma 5$ twist and a high angle random boundary), as derived from atomistic calculations. The present model does not attempt to capture nucleation or growth of fission gas bubbles at the grain boundaries. The point defect and Xe diffusion and segregation models are implemented in the MARMOT phase field code, which is used to calculate effective Xe and U diffusivities as well as to simulate Xe redistribution for a few simple microstructures.

1. Introduction

In UO_2 nuclear fuel, the retention and release of fission gas atoms such as xenon (Xe) are important for nuclear fuel performance. For example, the formation of fission gas bubbles induces fuel swelling, which contributes to mechanical interaction with the clad thereby increasing the probability of clad breach. Fission gas bubbles also decrease the thermal conductivity of the fuel. Alternatively, fission gas can be released from the fuel to the plenum. This increases the pressure on the clad walls and decreases the gap thermal conductivity. In order to predict the fuel performance as function of burn-up, the redistribution of fission gas atoms must be understood [1]. Most fission gases have low solubility in the fuel matrix, which is especially pronounced for large fission gas atoms such as Xe. As a result there is a significant driving force for segregation of gas atoms to extended defects, e.g. grain boundaries and dislocations, and subsequently for nucleation of gas bubbles at these sinks. After segregating to grain boundaries, fission gases may be released to the fuel plenum, either by fast diffusion of individual gas atoms along grain boundaries or by interlinked gas bubbles forming percolation networks.

Several empirical or semi-empirical models have been developed for fission gas release in nuclear fuels, e.g. Refs. [2–7]. One of the most commonly used models in fuel performance codes was published by Massih and

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Forsberg [4, 5, 7]. This model is similar to the early Booth model [2] in that it applies an equivalent sphere to separate bulk UO_2 from grain boundaries represented by the circumference. Compared to the Booth model, it also captures trapping at grain boundaries, fission gas resolution and describes release from the boundary by applying time-dependent boundary conditions to the circumference. In this and most other release models the bulk fission gas diffusion rates are taken from the analysis of Turnbull *et al.* [8], which captures both intrinsic and radiation-enhanced diffusion. This model divides the diffusivity into three regimes. At high temperature ($T > 1650$ K) intrinsic diffusion dominates and the diffusivity for stoichiometric UO_2 was taken from Davies and Long [9]. In the intermediate temperature range ($1381 < T < 1650$ K), radiation-enhanced diffusion is the main contribution to fission gas transport [8, 10]. The rate depends on the concentration of radiation-induced vacancies, which is proportional to the square root of the fission rate. The intrinsic and radiation-enhanced diffusivities are compared to our modeling predictions in Sec. 2.5. Below 1381 K, Xe diffusion is athermal and again assumed to be proportional to the fission rate [8, 10, 11]. The total fission gas diffusivity is obtained as the sum of the three separate contributions. The model derived by Turnbull *et al.* [8] describes diffusion of through bulk UO_2 and does not account for trapping and resolution by small intragranular bubbles [3, 12]. We call this the unperturbed fission gas diffusivity. The effective diffusivity used in fuel performance fission gas release models can be obtained from the unperturbed diffusivity by scaling with the trapping and resolution rates according to the rate theory treatment of this process ($D' = Db'/(b' + g)$, where D' is the effective diffusivity, D is the unperturbed diffusivity calculated in this work, b' the trapping rate and g the resolution rate of Xe in small intragranular fission gas bubbles) [3, 12]. In order to provide more detailed insight into the role of microstructure, several authors have applied phase field models to simulate evolution of fission gases and related properties in nuclear fuels [13–18]. Others approach the same problem using rate theory models [6, 19–23].

The success of phase field, rate theory and other meso-scale models to capture the evolution of fission gases relies on accurate representation of the underlying atomistic mechanisms and parametrization of the driving forces and kinetics of these mechanisms. Even though effective diffusivities under specific conditions may be derived from integrated fission gas annealing experiments, it is very difficult to obtain information about the underlying atomistic mechanisms. For this reason, many atomistic studies of fission gas properties in UO_2 have been performed [24–41]. Here, we rely on mechanisms and data determined from density functional theory (DFT) and pair potential calculations [24–26, 42, 43] to derive models for Xe, uranium (U), uranium vacancy (V_U) and uranium interstitial (U_I) diffusion as well as for segregation to grain boundaries in UO_2 . The models describing these mechanisms apply concepts from both classical reaction rate theory and from phase field theory. The MARMOT phase field code [44–46] is used to estimate effective Xe and U diffusivities under both intrinsic and different irradiation conditions as well as to simulate the fission gas evolution for a few simple microstructures. The aim of this study is not to present a complete fission gas release model. Rather, we focus on the mechanistic aspects of a few specific steps of the release process with the ultimate goal of determining the fundamental mechanisms needed to develop a more comprehensive model. Finally, in this study we calculate the unperturbed bulk Xe diffusivity. However, the effect of trapping and resolution can be included by scaling the bulk diffusivity with the trapping resolution rates (see above) [3, 12].

2. Xe, U vacancy and U interstitial reaction diffusion models

The redistribution of Xe, U vacancies and U interstitials is at the highest level described by the diffusion equation (Fick’s second law):

$$\frac{\partial y_X}{\partial t} = \nabla \cdot (D_X \nabla y_X), \quad (1)$$

where X denotes either Xe, U vacancies or U interstitials, y_X is the corresponding concentration (fractional) and D_X the effective diffusivity, which could be a function of, e.g., the species concentration, irradiation conditions, microstructure and temperature. In order to accurately express the diffusivities as function of these parameters, we develop models that capture the mechanistic aspects of diffusion. These models are then solved to extract the effective diffusivity, D_X , which can be used in simulations of fission gas segregation and release. We address this problem by applying defect reaction rate theory [47] tailored to the properties

of UO_2 . This includes diffusion of the mobile Xe-U vacancy cluster, U vacancies and divacancies and U interstitials as well as formation and annihilation of these defects by damage processes, reactions among defects and reactions with sinks in the fuel. However, the diffusivity calculated in this study does not include trapping and resolution of fission gas (Xe) atoms in small intragranular bubbles. As explained in Sec. 1 this follows the original treatment by Turnbull *et al.* [8]. The effective diffusivity that includes trapping and resolution can be obtained following to the rate theory treatment of this process [3, 12]. In Sec. 2.1 the diffusion equations are derived and in Sec. 2.2 the reaction rate equations, which when combined give the reaction-diffusion model for Xe transport in UO_2 .

2.1. Diffusion equations

DFT and empirical potential calculations have shown that Xe atoms occupy U vacancy trap sites, which may also include oxygen vacancies depending on the $\text{UO}_{2\pm x}$ (non-)stoichiometry [25, 26, 29, 30]. In this study we assume nearly stoichiometric UO_2 , for which the preferred trap site is a U vacancy coordinated with one oxygen (O) vacancy (Xe_{UO}) [25, 26, 29, 30]. The charge state of this cluster (the number of bound holes) is also important and for stoichiometric UO_2 it is fully charged (no bound holes, Xe''_{UO} in modified Kröger-Vink notation) [26]. O defects or ions will not be explicitly treated in this study, because their dynamics [48–50] are many orders of magnitude faster than for Xe atoms and U ions, which implies that O defect concentrations are close to equilibrium conditions at temperatures of interest for this study ($T > 1000$ K), assuming rather low damage rates relevant for reactor operating conditions. The same conclusion applies to electronic defects. At low temperature these simplifications may not hold. Any contribution from diffusion of Xe interstitials that form due to radiation damage [24] is not included in the present model (assumed to be small). Again, this assumption should hold at high temperature but may be violated at low temperatures, which will be investigated in future work.

The Xe_{UO} cluster is not mobile due to the high migration barrier associated with cation exchange mechanisms, but diffusion rather occurs by binding another U vacancy to the trap site, which in stoichiometric UO_2 creates a cluster denoted Xe_{U_2O} (Xe occupying a trap site consisting of two U vacancies and one O vacancy, which is fully charged, Xe''''_{U_2O} in Kröger-Vink notation). DFT and empirical potential calculations of the migration and binding properties have established that for Xe the mobility is given by the cluster migration properties. The Xe atom can easily move between the two vacancies of the mobile cluster, because it has a low migration barrier compared to migration of U ions, which explains why the rate limiting step for Xe_{U_2O} cluster diffusion is migration of one of the U vacancies to a next nearest site. This is equivalent to the cluster diffusing via an exchange mechanism involving two U atoms. For additional details, see Refs. [25, 26].

Based on this mechanism, the Xe diffusion rate is expressed as ($y_{Xe}^{TOT} = y_{Xe_{UO}} + y_{Xe_{U_2O}}$):

$$\left(\frac{\partial y_{Xe}^{TOT}}{\partial t} \right)_D = \left(\frac{\partial y_{Xe_{U_2O}}}{\partial t} \right)_D = \nabla \cdot (M_{Xe_{U_2O}} y_{Xe_{U_2O}} \nabla (\mu_{Xe_{U_2O}} - (2\mu_U + \mu_O))), \quad (2)$$

where $M_{Xe_{U_2O}}$ is the mobility of the Xe_{U_2O} cluster, $y_{Xe_{U_2O}}$ is the cluster concentration, $\mu_{Xe_{U_2O}} - (2\mu_U + \mu_O)$ is the diffusion potential for the above mechanism and $-\frac{M_{Xe_{U_2O}} y_{Xe_{U_2O}}}{V_m} \nabla (\mu_{Xe_{U_2O}} - (2\mu_U + \mu_O))$ is the flux ($J_{Xe_{U_2O}}$). The gradient of the diffusion potential is the driving force for diffusion. V_m is the molar volume, which is here assumed to be a constant. The mobility (M) is related to the diffusivity (D) by $M = \frac{D}{k_B T}$, where k_B is the Boltzmann constant. The chemical potential gradients, representing the gradient of the diffusion potential, are used in order to be consistent with phase field models. Eq. 2 corresponds to the Cahn-Hilliard equation in phase field theory. Under certain conditions, primarily $y_{Xe} \ll 1$, the right hand side of Eq. 2 can be simplified to the regular diffusion equation (Fick's second law)

$$\left(\frac{\partial y_{Xe}^{TOT}}{\partial t} \right)_D = D_{Xe} \nabla^2 y_{Xe}. \quad (3)$$

In Eq. 3, D_{Xe} is a function of the cluster diffusivity, $D_{Xe_{U_2O}}$, and the concentration of this cluster, $y_{Xe_{U_2O}}$. By calculating the cluster concentrations $y_{Xe_{UO}}$ and $y_{Xe_{U_2O}}$, the effective diffusivity, D_{Xe} , can be obtained

from $D_{Xe_{U_2O}}$. The concentration $y_{Xe_{U_2O}}$ is usually expressed as an Arrhenius relation involving the vacancy formation energy plus the binding energy of the vacancy to the Xe trap site, see Ref. [26] for derivation of the corresponding analytical diffusion model. Xe atoms in trap sites without a bound U vacancy (Xe_{UO}) are immobile and thus do not contribute to diffusion and do not appear in Eq. 2. Also, the oxygen chemical potential, μ_O , disappears when the gradient is applied since it is assumed to fulfill equilibrium conditions ($\nabla\mu_O = 0$) at the temperatures of interest to this study. The D subscript indicates that the time derivative only refers to the contribution from diffusion. Additional contributions will be defined below.

Diffusion of U via vacancy mechanisms has also been investigated by DFT calculations [25, 43]. For the high vacancy concentrations that may occur under irradiation, these calculations emphasize the importance of vacancy clustering (U divacancies, V_{U_2}) due to attractive vacancy binding energies and the much higher mobility of clusters compared to single vacancies. Both single vacancies and divacancies are fully charged in nearly stoichiometric UO_2 , i.e. in Kröger-Vink notation the defects are V_U'''' and V_{U_2}'''''' . The diffusion of vacancies and divacancy clusters is described by:

$$\left(\frac{\partial y_{V_U}}{\partial t}\right)_D = \nabla \cdot (M_{V_U} y_{V_U} \nabla (\mu_{V_U} - \mu_U)) \quad (4)$$

and

$$\left(\frac{\partial y_{V_{U_2}}}{\partial t}\right)_D = \nabla \cdot (M_{V_{U_2}} y_{V_{U_2}} \nabla (\mu_{V_{U_2}} - 2\mu_U)), \quad (5)$$

where M_{V_U} and $M_{V_{U_2}}$ are the vacancy mobilities and $(\mu_{V_U} - \mu_U)$ and $(\mu_{V_{U_2}} - 2\mu_U)$ the corresponding diffusion potentials giving rise to the fluxes $-\frac{M_{V_U} y_{V_U}}{V_m} \nabla (\mu_{V_U} - \mu_U)$ and $-\frac{M_{V_{U_2}} y_{V_{U_2}}}{V_m} \nabla (\mu_{V_{U_2}} - 2\mu_U)$. These vacancy fluxes give rise to a flux of U ions in the opposite direction. The time evolution of the total vacancy concentration ($y_V^{TOT} = y_{V_U} + 2y_{V_{U_2}}$) is expressed as the sum of these two contributions. The interpretation of these parameters and the relation to the diffusion equation follow the discussion for Eq. 2. The subscript D has the same meaning as in Eq. 2.

Finally, diffusion of U interstitials is described by:

$$\left(\frac{\partial y_{U_I}}{\partial t}\right)_D = \nabla \cdot (M_{U_I} y_{U_I} \nabla (\mu_{U_I} - \mu_{V_I})), \quad (6)$$

where M_{U_I} is the mobility of interstitials and $(\mu_{U_I} - \mu_{V_I})$ is the diffusion potential for interstitials (V_I denotes empty interstitial sites), which results in a flux equal to $-\frac{M_{U_I} y_{U_I}}{V_m} \nabla (\mu_{U_I} - \mu_{V_I})$. Again, the subscript D represents the diffusion contribution to the time derivative and the parameters and relation to the diffusion equation is the same as for Eq. 2.

2.2. Reaction rate equations

Eqs. 2, 4, 5 and 6 contain five independent concentration variables; $y_{Xe_{UO}}$ (concentration of Xe in vacancy trap sites), $y_{Xe_{U_2O}}$ (concentration of Xe trap sites with a bound U vacancy), y_{V_U} (concentration of U vacancies), $y_{V_{U_2}}$ (concentration of U divacancies) and y_{U_I} (concentration of U interstitials). The concentration of U ions on the cation sublattice (denoted U_U) and vacancies on the interstitial sublattice (denoted V_I) are dependent variables given by site conservation. In addition to the diffusion equations above, these five variables are coupled by cluster formation and recombination reactions. Under equilibrium conditions, vacancies and interstitials are created and annihilated at sources and sinks, such as dislocations, grain boundaries and voids or gas bubbles. However, under irradiation, cascade events are the major source of vacancies and interstitials. All of these reactions may be captured by reaction rate equations, which, unlike the diffusion equations, do not involve any gradients.

In our model the formation of Xe_{U_2O} clusters occurs according to the following reaction:

The corresponding reaction rate is expressed as (Reaction 7):

$$\left(\frac{\partial y_{Xe_{U_2O}}}{\partial t}\right)_{R_1} = y_{Xe_{U_2O}} y_{V_U} \frac{M_{V_U}}{S^2} \cdot Z (\mu_{Xe_{U_2O}} - (\mu_{Xe_{UO}} + \mu_{V_U})), \quad (8)$$

where S is the atomic jump distance for the defects, Z is the number of sites from which reaction between Xe_{UO} and V_U is inevitable (related to the reaction radius) and the difference in chemical potential represents the driving force for the reaction. Note that if the driving force is negative, the rate changes sign and thus the net direction of the reaction. The subscript R_1 denotes that the time derivative refers to the reaction rate associated with Reaction 7 only and not the total time derivative. Eq. 8 corresponds to a typical rate theory equation using the equilibrium concentration of defects to express the driving force and the diffusivity for the rate constant [47]. We use the form in Eq. 8 in order to be consistent with phase field models. This convention applies to all reaction rate equations below. The mobility of Xe in the vacancy trap site ($M_{Xe_{UO}}$) is zero and it is thus not included in Eq. 8. In the general case, the mobility factor in this equation is the sum of the mobility of the individual defects, $\frac{M_{Xe_{UO}}}{S^2} + \frac{M_{V_U}}{S^2}$, which simplifies to $\approx \frac{M_{V_U}}{S^2}$ for this special case. The driving force in Eq. 8, as well as the forces in the other reaction rate theory equations below, are formulated such that thermodynamic equilibrium is attained at steady state, $\frac{\partial y_X}{\partial t} = 0$.

U interstitials may annihilate with Xe_{U_2O} clusters to form a single Xe atom in a trap site without a bound vacancy ($Xe_{U_2O} + U_I \rightleftharpoons Xe_{UO} + V_I + U_U$), the rate of which is given by:

$$\left(\frac{\partial y_{Xe_{U_2O}}}{\partial t}\right)_{R_2} = -y_{Xe_{U_2O}} y_{U_I} \left(\frac{M_{Xe_{U_2O}}}{S^2} + \frac{M_{U_I}}{S^2}\right) \cdot Z (\mu_{Xe_{U_2O}} + \mu_{U_I} - (\mu_{Xe_{UO}} + \mu_{V_I} + \mu_{U_U})). \quad (9)$$

The total Xe_{U_2O} reaction rate is obtained as the sum of Eqs. 8 and 9.

The formation of U vacancy clusters (V_{U_2}),

$$V_U + V_U \rightleftharpoons V_{U_2}, \quad (10)$$

occurs with the following rate

$$\left(\frac{\partial y_{V_{U_2}}}{\partial t}\right)_{R_1} = y_{V_U} y_{V_U} \frac{2M_{V_U}}{S^2} Z (\mu_{V_{U_2}} - 2\mu_{V_U}). \quad (11)$$

The vacancy clusters may be annihilated by U interstitials ($V_{U_2} + U_I \rightleftharpoons V_U + V_I + U_U$) and at sinks according to the following rate:

$$\begin{aligned} \left(\frac{\partial y_{V_{U_2}}}{\partial t}\right)_{R_2} &= -y_{V_{U_2}} y_{U_I} \left(\frac{M_{V_{U_2}}}{S^2} + \frac{M_{U_I}}{S^2}\right) \cdot \\ &Z (\mu_{V_{U_2}} + \mu_{U_I} - (\mu_{V_U} + \mu_{U_U} + \mu_{V_I})) - \\ &M_{V_{a2}} y_{V_{U_2}} k_{V_{U_2}}^2 (\mu_{V_{U_2}} - 2\mu_{U_U}). \end{aligned} \quad (12)$$

In Eq. 12 $k_{V_{U_2}}^2$ is the strength of fixed vacancy sinks. The driving force for the sink term ($\mu_{V_{U_2}} - 2\mu_{U_U}$) changes sign to give production if the defect concentration is below the equilibrium value and it is zero at equilibrium. As for the Xe_{U_2O} clusters, the total V_{U_2} reaction rate is obtained as the sum of Eqs. 11 and 12.

The formation rate of vacancies (K_{V_U}) and interstitials ($K_{U_I} = K_{V_U}$) is determined by the irradiation conditions. The possibility of forming more complex clusters of vacancies and interstitials directly from the damage event is presently not accounted for (it would change the $K_{U_I} = K_{V_U}$ assumption). Vacancies and interstitials may be annihilated by mutual recombination or by reactions with fixed sinks such as voids,

fission gas bubbles, grain boundaries and dislocations. The interstitial and vacancy sink strengths are labeled $k_{U_I}^2$ and $k_{V_U}^2$, respectively. This gives the following reaction rate equations:

$$\begin{aligned} \left(\frac{\partial y_{V_U}}{\partial t} \right)_{R_1} &= K_{V_U} - M_{V_U} y_{V_U} k_{V_U}^2 (\mu_{V_U} - \mu_{U_U}) - \\ &\quad \left(\frac{M_{V_U}}{S^2} + \frac{M_{U_I}}{S^2} \right) Z y_{V_U} y_{U_I} \cdot \\ &\quad (\mu_{V_U} + \mu_{U_I} - (\mu_{U_U} + \mu_{V_I})) \end{aligned} \quad (13)$$

and

$$\begin{aligned} \left(\frac{\partial y_{U_I}}{\partial t} \right)_{R_1} &= K_{U_I} - M_{U_I} y_{U_I} k_{U_I}^2 (\mu_{U_I} - \mu_{V_I}) - \\ &\quad \left(\frac{M_{V_U}}{S^2} + \frac{M_{U_I}}{S^2} \right) y_{V_U} y_{U_I} Z (\mu_{V_U} + \mu_{U_I} - (\mu_{U_U} + \mu_{V_I})). \end{aligned} \quad (14)$$

The total V_U reaction rate is obtained as the sum of Eq. 13, the negative of Eq. 11, Eq. 8 and Eq. 9 as well as the interstitial term in Eq. 12. Similarly, the total interstitial reaction rate is given by the sum of Eqs. 6, 9 and the interstitial term in Eq. 12.

For simplicity, the above model is limited to Xe clusters involving one bound U vacancy. Tentative results indicate that contributions from larger clusters are important for explaining all aspects of the behavior observed in experiments. However, this will be investigated in a future study. As explained in Sec. 1, we are modeling the unperturbed Xe diffusivity, i.e. trapping and resolution of Xe atoms is not included in our model, which explains why there are no sink terms for any of the Xe species. The effect of fission gas trapping and resolution can be accounted for a posteriori, following the standard rate theory treatment [3, 12].

2.3. Model parameters

Most of the parameters in Eqs. 2, 4, 5, 6, 8, 9, 11, 12, 13 and 14 have been calculated using DFT and empirical potentials in Ref. [26]. The defect diffusivities are listed in Table 1, expressed as $D = D_0 e^{-E_m/k_B T}$. In order to obtain the chemical potentials and the differences in chemical potentials defining the driving forces, we express the total free energy of the $(U_U, V_U, V_{U_2}, Xe_{UO}, Xe_{U_2O})(V_I, U_I)O_2$ system, where the parentheses separate different sublattices and the symbols indicate the defect types that are contained on each sublattice. Xe atoms are assumed to exclusively occupy vacancy trap sites, i.e. the concentration of interstitial Xe atoms is negligible. By applying a quinary regular solution model for the cation sublattice and an ideal solution model for the interstitial sublattice as well as the gradient energy terms used in phase field models to describe dissolution kinetics, the following free energy density functional is obtained:

$$\begin{aligned} \frac{G_m^{Total}(y_s, T)}{N_A} &= \sum_s y_s {}^oG_s^{UO_2} + \\ &\quad \sum_s k_B T (y_s \ln(y_s)) + \sum_{s_1, s_2, s_1 \neq s_2} {}^0L_{s_1, s_2} y_{s_1} y_{s_2} + \\ &\quad \sum_s \frac{\epsilon_s}{2} (\nabla y_s)^2. \end{aligned} \quad (15)$$

Here, s covers all species on the cation and interstitial sublattices ($U_U, Xe_{UO}, Xe_{U_2O}, V_U, V_{U_2}, U_I$ and V_{U_I}), y_s are the site fractions and ϵ_s the gradient energy coefficient of species s . ${}^0L_{s_1, s_2}$ are the regular solution parameters for interaction between species s_1 and s_2 on the cation sublattice (s_1 and s_2 are $U_U, Xe_{UO}, Xe_{U_2O}, V_U$ and V_{U_2}). N_A is Avogadro's number converting the left hand side of the equation to energy per atom rather than mole (this convention will be applied throughout this work). Site conservation implies that:

$$y_{U_U} + y_{Xe_{UO}} + 2y_{Xe_{U_2O}} + y_{V_U} + 2y_{V_{U_2}} = 1 \quad (16)$$

and

$$y_{U_I} + y_{V_I} = 1. \quad (17)$$

The ${}^oG_s^{UO_2} = {}^oH_s^{UO_2} - T {}^oS_s^{UO_2}$ terms were defined according to the defect formation (V_U and U_I) or solution (Xe_{UO}) energies and entropies combined with cluster binding energies and entropies (V_{U_2} and Xe_{U_2O}), as calculated from DFT and empirical potentials (see Table 1). These parameters are all functions of the $UO_{2\pm x}$ non-stoichiometry [26]. The data in Table 1 assumes nearly stoichiometric UO_2 , but can easily be extended to other non-stoichiometries based on data presented in, e.g., Ref. [26]. The Xe reference state is defined as the gas phase at 298 K and 0.1 MPa. The ${}^oG_U^{UO_2}$ reference is set to 0 eV. The ${}^oG_s^{UO_2}$ parameters are constants and thus only relevant for the reaction rate equations ($\nabla {}^oG_s^{UO_2} = 0$ in the diffusion equations). The regular solution parameters ${}^0L_{s_1, s_2}$ were calculated from the DFT binding energies (E_B) and the number of available binding sites (Z_B):

$${}^0L_{s_1, s_2} = \frac{Z_B}{2} E_B. \quad (18)$$

Only the most stable site for each defect was considered. The temperature dependence of the regular solution parameters (${}^0L_{s_1, s_2} = {}^0L_{s_1, s_2}^0 + {}^0L_{s_1, s_2}^1 T$) was set to zero (${}^0L_{s_1, s_2}^1 = 0$ eV). The ${}^0L_{s_1, s_2}$ values are summarized in Table 1. The values reflect the strong binding between Xe atoms and vacancies as well as that between Xe atoms themselves, which capture the tendency to nucleate fission gas bubbles. However, the present model is not optimized to capture the properties of bubbles. This topic is left as future work. We did not attempt to calculate the gradient energy coefficients (ϵ_s) from either DFT or empirical potentials. Careful determination of these parameters is also left as future work. The chemical potential differences in the diffusion and reaction rate equations are calculated from the free energy density in Eq. 15 according to:

$$\begin{aligned} \mu_A - \mu_B &= \frac{\delta}{\delta y_A} \left(\int_{\Omega} G_m^{Total} d\Omega \right)_{y_B} = \\ &= \left(\frac{\partial G_m^{Total}}{\partial y_A} \right)_{y_B} - \nabla \cdot \left(\frac{\partial G_m^{Total}}{\partial \nabla y_A} \right)_{y_B}, \end{aligned} \quad (19)$$

where y_B is treated as the dependent variable and Ω is the integration volume. Eqs. 19 follows the same approach as in phase field models. As an example, application of Eq. 19 to Eq. 8 (for simplicity the interaction parameters and gradient energy terms are not shown) gives:

$$\begin{aligned} \mu_{Xe_{U_2O}} - (\mu_{Xe_{UO}} + \mu_{V_U}) &= G_B^{Xe_{U_2O}} + \\ k_B T (\ln y_{Xe_{U_2O}} - \ln y_{Xe_{UO}} - \ln y_{V_U}), \end{aligned} \quad (20)$$

where $G_B^{Xe_{U_2O}} = {}^oG_{Xe_{U_2O}}^{UO_2} - {}^oG_{Xe_{UO}}^{UO_2} - {}^oG_{V_U}^{UO_2}$ is the binding energy of the cluster. This implies that the steady state solution to Eq. 8 simplifies to the standard mass action law in the dilute limit. The other reaction rate equations abide by similar relations.

The remaining parameters K_{V_U} , K_{U_I} , $k_{V_U}^2$, $k_{V_{U_2}}^2$ and $k_{U_I}^2$ were estimated from experimental data [8, 26] or treated as free parameters. Typical values are listed in Table 1. For irradiated UO_2 small intragranular fission gas bubbles or voids constitute the leading sink contribution.

2.4. Simulation methodology

The diffusion and reaction rate equations (Eqs. 2, 4, 5, 6, 8, 9, 11, 12, 13 and 14) were solved with the MARMOT phase field code [44], which is based on the MOOSE finite element framework [45, 46]. The simulations used adaptive time-stepping and adaptive meshing. In order to avoid numerical instabilities for very low concentrations, logarithmic terms and their derivatives were Taylor expanded below a certain threshold value (10^{-12}).

Formation energies	${}^oH_s^{UO_2}$ (eV)	${}^oS_s^{UO_2}$ (k_B)
${}^oG_{UO_2}^{UO_2}$	0.00	0.00
${}^oG_{UO_2}^{UO_2}$	-0.19	-16.35
${}^oG_{UO_2}^{UO_2}$	-0.68	-25.51
${}^oG_{UO_2}^{UO_2}$	x	y
${}^oG_{XeUO}^{UO_2}$	$x - 2.01$	$y - 14.38$
${}^oG_{XeU_2O}^{UO_2}$	0.00	0.00
${}^oG_{U_I}^{UO_2}$	13.39	16.35
Regular solution parameters	${}^0L_{s_1,s_2}^0$ (eV)	${}^0L_{s_1,s_2}^1$ (k_B)
${}^0L_{XeUO,V_U}$	-10.92	0.00
${}^0L_{U_U,V_U}$	1.80	0.00
${}^0L_{XeUO,U_U}$	9.12	0.00
${}^0L_{XeUO,V_U}$	5.04	0.00
${}^0L_{XeU_2O,V_U}$	-6.55	0.00
${}^0L_{XeU_2O,XeU}$	-7.73	0.00
${}^0L_{XeUO,V_{U_2}}$	-9.51	0.00
${}^0L_{XeU_2O,V_{U_2}}$	16.49	0.00
${}^0L_{U_U,V_{U_2}}$	4.80	0.00
${}^0L_{V_U,V_{U_2}}$	-3.34	0.00
Kinetic parameters	D_0 (nm ² /s)	E_m (eV)
D_{XeU_2O}	$1.48 \cdot 10^{13}$	4.94
D_{V_U}	$7.12 \cdot 10^{11}$	4.72
$D_{V_{U_2}}$	$5.45 \cdot 10^{13}$	2.84
D_{U_I}	$1.20 \cdot 10^{12}$	4.70
Other parameters		
Z	1.0	
K (defects/U atom s)	$4.05 \cdot 10^{-6}$	
$k_{U_I}^2$ (1/nm ²)	0.013	
$k_{V_U}^2$ (1/nm ²)	0.013	
$k_{V_{U_2}}^2$ (1/nm ²)	0.013	

Table 1: Bulk thermodynamic and kinetic parameters for defects in UO_2 used in the present model. The values denoted x and y for ${}^oG_{XeUO}^{UO_2}$ do not explicitly enter the present model and they are consequently not specified.

2.5. Simulation of effective Xe and U diffusivities in UO_2

Both Xe and U diffusivities are functions of the vacancy concentration, which in thermodynamic equilibrium is expressed in terms of the vacancy formation energy. Ref. [26] performed this analysis for UO_2 based on the same data from DFT and empirical potentials as applied in the present study (see Table 1). They predicted an activation energy of 2.93 eV and a pre-exponential factor of $8.32 \cdot 10^{-12} \text{ m}^2/\text{s}$ for Xe diffusion in stoichiometric UO_2 . Effective diffusivities may be calculated from our model by imposing flux boundary conditions at the left and right ends of a rectangular simulation cell and zero flux conditions at the top and bottom. By measuring the steady state concentration gradient, the effective diffusivity is obtained as:

$$D_X = -\frac{J_X}{\nabla y_X}. \quad (21)$$

By performing simulations at a number of different temperatures, the activation energy and pre-exponential factor, $D_X = D_0 \exp\left(-\frac{E_a}{k_B T}\right)$, can be extracted. The same result may be obtained by weighting the Xe_{U_2O} diffusivity by the concentration of this cluster. The results are plotted in Fig. 1a) and both $D_0 = 8.71 \cdot 10^{-12} \text{ m}^2/\text{s}$ and $E_a = 2.94 \text{ eV}$ agree well with the analytical results from Ref. [26]. As concluded in this reference, the activation energy is in good agreement with experiments while the pre-exponential factor is lower than obtained from experimental data [9]. At the lower end of the temperature range, cluster formation starts to become controlling (i.e. most Xe atoms exist as Xe_{U_2O}) and the diffusivity tends towards that predicted for the mobile Xe cluster (Xe_{U_2O}). The same type of simulation can be performed for the flux of U ions, which corresponds to a tracer diffusion experiment. In this simulation we only considered the contribution from single U vacancies. The results in Fig. 1b) gives $D_0 = 5.718 \cdot 10^{-14} \text{ m}^2/\text{s}$ and $E_a = 4.55 \text{ eV}$, which agrees well with the analytical solution of $D_0 = 5.61 \cdot 10^{-14} \text{ m}^2/\text{s}$ and $E_a = 4.53 \text{ eV}$ derived from the data in Ref. [26] and the experimental activation energy of 4.4 eV [51]. The pre-exponential factor is underestimated compared to experiments (the experimental value is $D_0 = 8.54 \cdot 10^{-11} \text{ m}^2/\text{s}$) [51].

Figure 1: The Xe diffusivity (a) and U (tracer) diffusivity (b) as function of temperature under intrinsic conditions calculated from MARMOT simulations (Calc., MARMOT) and compared to experimental data from Davies and Long [9], Miekeley *et al.* [52] and Sabioni *et al.* [51]. The intrinsic analytical and Xe_{U_2O} cluster model predictions were taken from Ref. [26].

In the next step we perform the same type of simulation, but introduce damage via the K_{V_U} and K_{U_I} parameters. Fig. 2 plots the Xe diffusivity as function of temperature. The analytical models derived in Ref. [26] capture the diffusivity at the lowest and highest temperatures, but within the intermediate temperature range the calculated diffusivity exceeds the analytical prediction from both the intrinsic and radiation-enhanced models in Ref. [26]. We have also investigated the effect of varying the sink strengths, defect production rates and the concentration of fission gas atoms, see Fig. 3. As expected, increasing the damage rate and decreasing the sink strength both lead to higher diffusivity in the intermediate temperature range and also extension of the radiation-enhanced range to higher temperatures. The opposite conclusion

applies to decreasing damage rates and increasing sink strengths. Interestingly, the diffusivity decreases with increasing irradiation below the temperature where cluster diffusion starts to become dominant. Cluster diffusion means the diffusivity is controlled by the migration properties of the Xe_{U_2O} cluster only, instead of a combination of the migration properties and the fraction of Xe atoms in mobile clusters (Xe_{U_2O}) governed by the vacancy concentration and the binding energy to the Xe trap site [26]. This occurs when a majority of Xe atoms exist as Xe_{U_2O} rather than Xe_{UO} [26]. The decrease in diffusivity for increasing irradiation can be explained by irradiation induced interstitials recombining with the Xe_{U_2O} cluster, which results in decreasing concentration with increasing damage rate due to the higher concentration of interstitials. The diffusivity is largely independent of the concentration of Xe atoms at high temperature, but below 2000 K the diffusivity exhibits small variations as function of the Xe concentration, see inset in Fig. 3. This is a consequence of increased clustering between vacancies and Xe atoms at low Xe concentrations. In the microstructure simulations in Sec. 3.3 we treat the Xe diffusivity as independent of the concentration.

The calculated Xe diffusivity under irradiation differs from that obtained in experiments [8], see Fig. 2. The experimental data is interpreted as being controlled by intrinsic diffusion at high temperature and enhanced at low temperature by increased concentration of vacancies due to irradiation [8]. However, the simulations indicate that at low temperature the diffusivity is controlled by the mobility of the Xe_{U_2O} cluster and increasing the vacancy concentration has limited effect. However, at intermediate temperature the simulations predict increased diffusivity due to irradiation and only at very high temperature are the intrinsic properties recovered (too high to be of practical relevance). Even though the parameters used in the present model involve uncertainties, we do not believe that these uncertainties are sufficient to explain the discrepancy between theory and experiments. Rather, our results suggest that other mechanisms, for example involving larger clusters of Xe atoms and vacancies, also contribute to diffusion. This possibility will be further investigated in a future work.

Figure 2: The Xe diffusivity under irradiation conditions compared to the intrinsic diffusivity (Calc., MARMOT), the corresponding analytical expressions derived in Ref. [26] and experimental data [9, 52].

Figure 3: a) The result of increasing and decreasing the defect production by factors of 10 compared to the reference case. The inset shows how the effective Xe diffusivity depends on the concentration of Xe atoms, measured in factors of 10 compared to the reference case. b) The result of increasing and decreasing the sink strength by factors of 10 compared to the reference case. All results were obtained from MARMOT simulations. The analytical results for the intrinsic diffusivity and the Xe_{U_2O} cluster diffusivity are shown as reference.

3. Xe segregation to grain boundaries

3.1. Segregation data

The interaction between Xe atoms and the UO_2 fuel microstructure is a critical component of fission gas release. In order to simulate redistribution of fission gas atoms to microstructure sinks, the interaction between fission gas atoms and those sinks must first be determined and then formulated in a model suitable for coupling to the diffusion and reaction rate models developed in Sec. 2. We have investigated segregation of Xe atoms to three different grain boundary types, $\Sigma 5$ tilt, $\Sigma 5$ twist and a high angle random boundary. This particular selection of grain boundaries was based on electron backscatter diffraction (EBSD) measurements of the grain boundary distribution in sintered UO_2 samples [53]. The structure of the grain boundaries in the present study follows the modeling work performed in Ref. [53]. Nerikar *et al.* calculated Xe grain boundary segregation energies in UO_2 for this particular set of boundaries using atomistic simulations with the interatomic interactions described by empirical potentials [42]. They provided data on the segregation energy as a function of the distance from the boundary as well as the distribution of segregation sites at the boundary. The segregation energy is defined as the energy difference between a Xe atom occupying a bulk position far away from the grain boundary and a Xe atom positioned within the grain boundary. The assumption that Xe atoms reside in a single U vacancy ignores the fact that Xe atoms occupy trap sites consisting of one U vacancy and either one or two additional O vacancies in stoichiometric UO_2 [25, 30, 54]. Nevertheless, the relative energies obtained from this assumption should capture the segregation trends correctly, which was also confirmed by performing a limited number of calculations for Xe occupying a bound Schottky defect (one U and two O vacancies).

The segregation properties are unique for each type of grain boundary, as illustrated in Fig. 4. This conclusion refers to both the maximum sink strength (see Table 2), i.e. the most negative segregation energy, and the distribution of segregation sites as function of distance from the centre of the grain boundary. The random boundary is the strongest Xe sink, followed by the $\Sigma 5$ tilt and $\Sigma 5$ twist boundaries. Segregation of large atoms such as Xe is often described in terms of elastic interactions, i.e. the extra volume found at the grain boundary attracts the large Xe atoms by reducing the total strain of the system. This approach was, for example, applied in phase field simulations by Hu *et al.* [13]. Near the boundary core this description is expected to become less accurate. Nerikar *et al.* attempted to map the Xe segregation properties onto the strain obtained from atomistic simulations, but, although some correlation was found, it was difficult

to quantitatively predict the segregation energy from the local strain [42]. This may be related to the importance of electrostatic effects in these systems [55].

Fig. 5 plots the (relative) segregation energy as function of the Xe fraction in the boundary region. This quantity was derived by independently filling available Xe trap sites, starting from the most favorable one, up to a certain site fraction and the segregation energy for this concentration is then defined as the segregation energy of the next empty Xe site. Fig. 5 illustrates that the segregation energy first increases rapidly for increasing x , after which it levels out up to $x \approx 0.9$ where the segregation energy starts rising almost exponentially. The segregation model neglects any explicit Xe-Xe interactions. The interactions are rather assumed to be the same as in the bulk. Obviously, this model is of qualitative nature and only valid for low concentrations of Xe. For example, at a concentration of $x \approx 0.9$ a Xe fission gas bubble would have nucleated and rendered the present model non-applicable. Inspection of the segregation energy in Table 2 and the concentration dependence in Fig. 5 shows that above a certain Xe concentration the segregation energy reaches positive values. The reason for this behavior is that the molecular dynamics calculations predict a range of energies for the segregation sites at grain boundaries, some of them are lower than the bulk energy and some are higher [42]. However, the concentrations at which the crossover occurs are above the level where the assumption of low Xe concentration is valid.

3.2. Analytical segregation model

For application in continuum models, the atomistic segregation data summarized in Figs. 4 and 5 are represented by fits to appropriate functions. The following equation was applied for the concentration dependent Xe segregation energy density, $E_m^{Xe,gb}(y_{Xe}^{TOT}, r)$:

$$\frac{E_m^{Xe,gb}(y_{Xe}^{TOT}, \vec{r})}{N_A} = \sum_{i,j} \int_0^{y_{Xe}^{TOT}} 2(C_i - g_i(y'_X)) f_{ij}(r_{ij}) dy'_X, \quad (22)$$

where

$$f_{ij}(r_{ij}) = \frac{1}{1 + \exp(-r_{ij}^2/k_i^2)} - 1 \quad (23)$$

and

$$g_i(y_{Xe}^{TOT}) = m_i \ln \left(100 y_{Xe}^{TOT} + \exp \left(-\frac{b_i}{m_i} \right) \right) + b_i. \quad (24)$$

$E_m^{Xe,gb}(y_{Xe}^{TOT}, \vec{r})$ is the total or integrated segregation energy as function of the (projected) distance from the grain boundary (r_{ij}) and the local (total) Xe concentration y_{Xe}^{TOT} on the cation sublattice. The i index covers different types of sinks (e.g. different types of grain boundaries) and the j index covers all sinks of a specific type i (e.g. $\Sigma 5$ tilt boundaries). C_i measures the dilute limit sink strength, g_i its concentration dependence and f_{ij} its spatial interaction range. The function $f_{ij}(r_{ij})$ describes the (normalized) segregation energy in the dilute limit, which is defined by the most negative segregation energy among all the grain boundary segregation sites available at a certain distance from the centre of the boundary, see Fig. 4. The most negative segregation energy is used for normalization (note that the normalization constant is in fact twice the lowest segregation energy, $2C_i$). In Eq. 23 the parameter k_i determines the slope of the Xe grain boundary interaction range. For each type of grain boundary the k_i parameter was fitted to the data in Fig. 4. The $g_i(y_{Xe}^{TOT})$ term (Eq. 24) describes the concentration dependence (y_{Xe}^{TOT}) of the segregation energy and the b_i and m_i parameters were fitted to the atomistic data in Fig. 5. The integral in Eq. 22 measures the total segregation energy as function of the Xe fraction rather than the incremental change expressed by $g_i(y_{Xe})$ alone. Any contributions that originate from entropy differences between bulk and grain boundaries are presently ignored. The segregation energy is assumed to be independent of temperature, which ignores the statistical distribution between segregation sites expected at high temperature.

Table 2 summarizes the fitted k_i , b_i and m_i values as well as the direct calculation of C_i for each grain boundary type. The quality of the $f_{ij}(r_{ij})$ and $g_i(y_{Xe})$ fits is illustrated in Figs. 4 and 5. For $\Sigma 5$ tilt

boundaries the deviation between data points and the fitted curve may originate from the presence of an electrostatic field [42, 56] that would require a different functional form of the f_{ij} interaction range or explicit calculation of electrostatic interactions to give optimal results. Improved representation could in principle be achieved by changing the r_{ij} exponent from 2 to 1 or some non-integer value in Eq. 23. The $g_i(y_{Xe})$ fits were performed for data points up to the concentration level where the calculated data points turn quickly to higher energies ($x \approx 0.85$). Ignoring this upturn has no influence on our simulation results, because the present description still captures the saturation point for the local concentration field in our simulations and, in particular, once fission gas bubble or void formation is incorporated, this process will be initiated well before reaching the local concentration limit.

In our simulations the grain boundary network is represented by a phase field model in which each grain i is described by an order parameter ϕ_i . $\phi_i = 1$ within this grain and zero in all other grains [57]. It varies continuously from one to zero over the boundary. At a point on a boundary, several order parameters have values between zero and one. In the phase field description the sum in Eq. 22 is over the number of possible pairings between order parameters with values greater than zero. The index i denotes the properties of the grain boundary type defined by the current order parameter pair. The spatial interaction is defined as $f_{ij} = 8\Phi_{ij}$ (representing Eq. 23), where $\Phi_{ij} = \phi_i^2\phi_j^2$. Here ϕ_i and ϕ_j are the current order parameter pair of type i . The width of the grain boundaries were chosen to best represent f_{ij} as defined by Eq. 23 and the fitted parameters in Table 2.

Grain boundary triple junctions require special attention, since direct application of the above model would render them weaker sinks than regular grain boundaries. The correct properties are recovered by scaling the phase field variables by $\phi_i + \phi_j$ whenever more than two phase field variables have non-zero values.

The thermodynamic model for Xe segregation to grain boundaries in UO_2 is obtained as the sum of Eqs. 15 and 22. The segregation dynamics is determined by calculating the driving forces or differences in chemical potentials from the sum of Eqs. 15 and 22 rather than Eq. 15 alone.

In order to describe the complete diffusion problem we should also treat segregation of U vacancies and interstitials. However, we will simplify our model by assuming that these concentrations are given by the steady state solution to the reaction rate equations. This is supported by the fact that, unlike Xe atoms, the interstitial and vacancy defects will quickly be annihilated at the boundary and resolving these processes in detail would complicate the simulation of Xe diffusion. Also, even though single U vacancies or interstitials do not diffuse much faster than Xe atoms, U divacancies do, which sets the time-scale for vacancy segregation. If all species are treated explicitly, the disparate time-scales of U divacancies and Xe atoms make the segregation simulations numerically challenging. There are however cases where the steady state assumption for U vacancies and interstitials may not be adequate.

Figure 4: The normalized (by $2C_i$, see Table 2) Xe segregation energy calculated using molecular dynamics simulations as function of the distance from the centre of the grain boundary for three different boundary types, $\Sigma 5$ tilt, $\Sigma 5$ twist and a high angle grain boundary classified as random (blue symbols). The solid red lines illustrate Eq. 22 without the $g(y_{Xe})$ term (no concentration dependence) fitted to the lowest segregation energy as function of distance from the boundary.

3.3. Simulation of Xe segregation to grain boundaries in UO_2

Xe redistribution was simulated for bicrystal microstructures, with a $\Sigma 5$ twist, $\Sigma 5$ tilt and random grain boundary, respectively. Instead of solving the full set of diffusion equations describing segregation of

Figure 5: The concentration dependence of the Xe segregation energies calculated using molecular dynamics simulations (blue symbols). The solid red lines illustrate Eq. 24 fitted to the calculated data.

Grain boundary type	C_i (eV)	k_i (nm)	b_i	m_i
Σ5 tilt	3.55	0.610	-0.444	0.872
Σ5 twist	0.64	0.680	-0.278	0.346
Random	4.79	0.600	1.485	0.954

Table 2: Fitted (k_i , b_i and m_i) or calculated (C_i) parameters for Xe segregation to different grain boundary types.

Xe, interstitials and vacancy clusters, only Xe atoms are treated according to Eqs. 1 (diffusion) and 22 (segregation). The diffusivity in Eq. 1 is obtained by first calculating the effective diffusivity for the relevant condition according to Sec. 2.5 and the mobility in Eq. 22 is obtained from the diffusivity as

$$M = \frac{D}{k_B T}. \quad (25)$$

First simulations are performed with the Xe-U (or equivalently Xe-Xe) interaction parameter set to zero. The Xe-U interaction parameter (0L) refers to the regular solution parameter (see Eq. 15) for the simplified binary Xe-U system. The steady-state distributions for intrinsic conditions with initial homogeneous Xe concentration of $y_{Xe} = 0.001$ at 2000 K are shown in Fig. 6. The grain size was 40 nm and the simulations were performed in a 1D configuration. Fig. 7 plots the highest Xe concentration at the core of each grain boundary as function of time for both intrinsic and radiation-enhanced conditions at 2000 K and at 1600 K. The unique behavior of the different grain boundary types is obvious in both Figs. 6 and 7. As expected, irradiation increases the rate of Xe segregation, but the difference compared to the intrinsic case is not very significant. The highest Xe concentration is reached for the Σ5 tilt and random boundaries, followed by the Σ5 twist boundary. The latter has much lower maximum concentration. The Σ5 tilt boundary thus seems to be a stronger sink than the random boundary, despite having a lower segregation energy (see Table 2). For very short times the random boundary attracts more Xe, but due to the slower (with respect to y_{Xe}) increase in the concentration term, $g_i(y_{Xe})$, the Σ5 tilt boundary eventually attracts the most Xe. The sink strength balance between these two grain boundaries is a function of the concentration of Xe.

Simulations were also performed for the DFT calculated value of ${}^0L = 9.12$ eV for the Xe-U interaction parameter, which corresponds to ${}^0L_{XeUO,UU}$ in Table 1. These results are illustrated in Fig. 8. It is clear that for all boundaries segregation is increased for ${}^0L = 9.12$ eV, which is understood in terms of the positive interaction parameters favoring Xe rich and poor regions. The concentrations in our simulations are too low to give rise to nucleation of Xe bubbles.

Figure 6: Steady-state Xe distribution in a bicrystal containing a $\Sigma 5$ tilt, $\Sigma 5$ twist or random grain boundary. The domain size is 40×5 nm, but only visualized in the x direction. The simulations were performed for intrinsic conditions at 2000 K. The initial state was a homogeneous distribution of Xe ($y_{Xe} = 0.001$). The grain boundary is centered at the 40 nm coordinate.

Figure 7: The highest Xe concentration at the core of the grain boundary as function of time for both intrinsic and radiation-enhanced conditions. The initial state was a homogeneous distribution of Xe ($y_{Xe} = 0.001$). a) The simulation temperature was 2000 K and b) 1600 K.

Figure 8: The highest Xe concentration at the core of the grain boundary as function of time for intrinsic condition with the ${}^0L = 0.0$ eV and ${}^0L = 9.12$ eV (interaction). a) The simulation temperature was 2000 K and b) 1600 K.

In order to demonstrate the importance of considering the grain boundary character, we performed simulations on a simplified 2D nanocrystalline microstructure consisting of hexagonal grains with a distribution of different grain boundary types. The simulation was performed at 2000 K for an initial concentration of $y_{Xe} = 0.001$. The size of the simulation domain is 75×65 nm and periodic boundary conditions were imposed. Fig. 9 shows the steady state solution for ${}^0L = 0.0$ eV. The difference between the grain boundary types follow the same trend as for the bicrystal simulations. The drastic difference in the Xe concentration between the tilt and twist grain boundaries may result in preferential bubble nucleation and growth. Future work will expand this model to include bubble nucleation and growth, and investigate this effect in more detail.

Figure 9: Xe distribution for a microstructure composed of random, $\Sigma 5$ tilt and $\Sigma 5$ twist grain boundaries. The Xe-Xe interaction parameter was set to 0 (${}^0L=0.0$ eV, ideal solution). The domain size is 75×65 nm and the initial state was a homogeneous distribution of Xe ($y_{Xe} = 0.001$).

4. Conclusions

Models for diffusion of xenon (Xe), uranium (U) vacancies and U interstitials in UO_2 were derived for both intrinsic conditions and under irradiation. The mechanistic diffusion models were based on results from density functional theory (DFT) and empirical potential calculations [26], which were also used for determining the model parameters. The diffusion models were implemented in the MARMOT phase field code. Effective Xe diffusivities were calculated for a range of irradiation and microstructure conditions by solving the complete set of diffusion and rate equations. Radiation-enhanced diffusion occurs at intermediate temperature ($1785 < T < 2860$ K), while at low and high temperatures the diffusivity is given by the intrinsic values. At low temperature ($T < 1785$ K) cluster formation governs the diffusivity for both intrinsic and irradiation conditions. Comparison to experimental data indicate that the Xe vacancy diffusion mechanism included in the present model (the Xe_{U_2O} cluster) may not be sufficient to explain the radiation-enhanced diffusivity observed at low temperature. Overall, the predicted Xe diffusivity is lower than reported in experimental studies.

Segregation of Xe to grain boundaries was simulated by combining the bulk diffusion model with a model for the interaction between Xe atoms and three different grain boundaries in UO_2 ($\Sigma 5$ tilt, $\Sigma 5$ twist and a high angle random boundary), as derived from empirical potential calculations. The simulations capture the segregation of Xe to grain boundaries and the unique characteristics of different boundary types clearly emerge from these simulations. For short time scales the random boundary is the strongest Xe sink, but when the local Xe concentration increases the $\Sigma 5$ tilt boundary overtakes the random boundary as the strongest

sink. The $\Sigma 5$ twist boundary attracts significantly less Xe than the other two cases. These segregation properties may result in different nucleation rates of fission gas bubbles.

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