

Multiscale modeling for high burnup structure formation and associated pulverization

Technical Report

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Abstract

This report summarizes the lower length scale modeling work performed in fiscal year 2023 under the Nuclear Energy Advanced Modeling and Simulation (NEAMS) program to capture the microstrutural evolution and associated pulverization criteria in the high burnup regions of UO₂ nuclear fuel. This year, the resolution mechanisms within the cluster dynamics code has been updated and its influence on the bubble growth in HBS regions at the mesoscale is studied. To improve the accuracy of phase-field models of fission gas bubble growth, a new Helmholtz free energy for high-density Xe gas is derived from a virial equation of state. Two previously used strategies for representing net vacancy production in phase-field models of fission gas bubble growth are compared with each other and with analytical models of bubble growth. The vacancy source only model is found to be more convenient to parameterize realistically compared with the vacancy source+sink model. Furthermore, the phase-field-fracture simulation have been performed using MD-informed failure stress values and realistic HBS structure obtained from the phase-field simulations. We also present the uncertainty bands on prediction of the critical stress to account for the effect of the lower length scale variabilities on the failure criteria at the mesoscale. It is observed that pulverization may occur in partially restructured regions with restructuring fraction as low as 17%. In light of this, an update to the BISON's pulverization criteria is recommended. Page intentionally left blank

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1. INTRODUCTION

To improve the economics of commercial nuclear reactors, U.S. nuclear industries are seeking approval for the increased burnup usage of the existing nuclear fleet past the current regulatory limit of 62 MWd/kgU up to 75 MWd/kgU. However, at higher burnups, nuclear fuels undergo significant restructuring which poses the risks of potential fuel fragmentation, relocation, and dispersal (FFRD) during a loss-of-coolant accident (LOCA). Specifically, the regions exposed to high burnup and low temperatures exhibit a fine-grained microstructure with large bubbles known as a high-burnup structure (HBS) [1], which has been correlated to the diminished performance of the fuel, leading to an accelerated fission gas release, as well as fuel fragmentation and pulverization during transient and accidental conditions. Therefore, it is paramount to understand the mechanisms for HBS formation along with its impact on the properties and performance of nuclear fuels.

HBS has been observed in various types of nuclear fuels, including ceramics and metals [2, 3, 4]. The key characteristics of the HBS region include the (1) accumulation of dislocations, creating of large dislocation networks, (2) formation of new defect-free subgrains, (3) depletion of intra-granular fission gas concentration, and (4) development of large spherical inter-granular bubbles. There is a lack of consensus among researchers regarding the mechanisms that lead to the restructuring observed in HBS. Grain subdivision due to polygonization versus recrystallization, continuous versus discrete recrystallization occurring in tandem or conjunction, etc., have been proposed and debated. In general, it is hypothesized that defect accumulation and dislocation interaction within the grains cause the realignment of dislocations into grain boundaries (GBs), leading to the new subgrain formation, which over time transforms into new grains. Experimentally, advanced characterization techniques have been used on irradiated samples to study the grain structure in the partially and fully restructured HBS regions. In HBS fuels, both low-angle grain boundaries (LAGB) and high-angle grain boundaries (HAGB) were observed in different fractions at different fission densities. The low-angle character of boundaries between the subdivided grains disappeared in the fully developed HBS. Experimentally, pulverization has been observed in both fully-formed and partially restructured HBS regions. Hence, we study the onset of the fracture behavior as the HBS structure forms.

This report provides the details of the lower length scale modeling work that has been performed in fiscal year 2023 under NEAMS to capture the microstrutural evolution in the HBS regions and associated pulverization. This year, we updated the resolution mechanisms within the cluster dynamics code and evaluated how it influences the bubble growth in HBS regions at the mesoscale. To further improve the accuracy of phase-field models of fission gas bubble growth, a new Helmholtz free energy for high-density Xe gas is derived from a virial equation of state. Two previously used strategies for representing net vacancy production in phase-field models of fission gas bubble

growth are compared with each other and with analytical models of bubble growth. Finally, we present the phase-field-fracture simulation performed using MD-informed failure stress values and realistic HBS structure obtained from the phase-field simulations.

2. HBS FORMATION AND BUBBLE GROWTH

2.1 Bubble evolution in the fully formed HBS region

In previous years, a multiscale model coupling the phase-field model with a cluster-dynamics simulations has been developed to simulate the HBS formation and associated bubble growth. It was demonstrated that the coupled model can realistically capture the convex bubble shapes typically observed in the HBS regions. However, the growth rate of these bubbles was slower than experiments. In fiscal year 23, the cluster dynamics code Xolotl implemented a new re-solution model that switches from partial to full re-solution within the grain. As a result, more Xe atoms are released from the intragranular Xe clusters and accumulated within the intergranular bubbles. In light of this, we reevaluate the bubble growth in the HBS region with the changes to the re-solution model. In this section, we briefly describe the coupled approach and present the results for the bubble evolution in fully formed HBS.

2.1.1 Description of the coupled cluster-dynamics and phase-field model

The HBS bubble growth model presented in this section was formulated by following the grand-potential-based multiorder parameter, multi-component phase-field model. This model can concurrently capture the evolution of multiple phases, grains, and chemical species. Here, the microstructure consists of two primary crystallographic features: the solid matrix and the bubble phases. Within the matrix, multiple grains are represented with different order parameters, $\eta_{m0}, \eta_{m1}, \dots, \eta_{mi}, \dots, \eta_{mn}$, while the bubbles are represented by a single order parameter, η_b . Additionally, local concentrations of various defect species such as vacancies and fission gases are represented as chemical components, the number densities of which are represented by ρ_v and ρ_g , respectively.

The evolution of the order parameters is captured using the Allen-Cahn equations derived from the grand potential functional, such that:

$$\frac{\partial \eta_{mi}}{\partial t} = -L_m \frac{\delta \Omega}{\delta \eta_{mi}}$$

$$\frac{\partial \eta_b}{\partial t} = -L_b \frac{\delta \Omega}{\delta \eta_b},$$
(2.1)

where L_m and L_b are the kinetic mobility of the order parameters, and $\frac{\delta\Omega}{\delta\eta_{mi}}$ and $\frac{\delta\Omega}{\delta\eta_b}$ are the variational derivatives of the grand potential Ω with respect to the order parameters η_{mi} and η_b , respectively. The total grand potential of the

system, Ω , is derived from the local grand-potential density as:

$$\Omega = \int_{V} \left(\omega_{bulk} + \omega_{grad} + \omega_{chem} + \omega_{d} \right) \mathrm{d}V \,, \tag{2.2}$$

where ω_{bulk} accounts for the bulk free energy density term, ω_{grad} adds the gradient energy contribution, and ω_{chem} incorporates the appropriate grand-potential densities for each phase, and ω_d is the deformation energy generated due to dislocations. Each of these components is defined as follows:

$$\omega_{bulk} = \alpha \left[\left(\frac{\eta_b^4}{4} - \frac{\eta_b^2}{2} \right) + \sum_{i=1}^{n_m} \left(\frac{\eta_{mi}^4}{4} - \frac{\eta_{mi}^2}{2} \right) + \left(\gamma_{bm} \eta_b^2 \sum_i \eta_{mi}^2 + \sum_i^{n_m} \sum_{j \neq i}^{n_m} \frac{\gamma_{mm}}{2} \eta_{mi}^2 \eta_{mj}^2 \right) + \frac{1}{4} \right],$$
(2.3)

$$\omega_{grad} = \frac{\kappa}{2} \left(|\eta_b|^2 + \sum_{i=1}^{n_m} |\nabla \eta_{mi}|^2 \right), \qquad (2.4)$$

and

$$\omega_{chem} = h_b \omega_b + h_m \omega_m \,, \tag{2.5}$$

where *m* and *b* represent the matrix and bubble phases, *i* and *j* are indices for the grains, n_m is the total number of grains, and α is a constant free energy barrier coefficient. γ_{mb} and γ_{mm} are constant parameters that allow adjustment of interfacial energies between phases and grains. ω_m and ω_b represent the local grand-potential density of the matrix and bubble phases, respectively, and h_m and h_b are the switching functions used for interpolating the grand-potential density between the phases. For the matrix and bubble phases, the switching functions are:

$$h_m = \frac{\sum_{i=1}^{n_m} \eta_{mi}^2}{\eta_b^2 + \sum_{i=1}^{n_m} \eta_{mi}^2}$$
(2.6)

and

$$h_b = \frac{\eta_b^2}{\eta_b^2 + \sum_{i=1}^{n_m} \eta_{mi}^2},$$
(2.7)

respectively. Additionally, the dislocation energy density is added to capture the its contribution on the recrystallization behavior such that

$$\omega_d = \frac{1}{2} G \, b_g^2 \, d_{eff} \,, \tag{2.8}$$

where G is the shear modulus of the material, b_g is the Burgers vector, and d_{eff} is the effective dislocation density [5].

The evolution of the vacancies and gas atoms is expressed in terms of the chemical potentials μ_v and μ_g , such that:

$$\frac{\partial \mu_g}{\partial t} = \frac{1}{\chi_g} \left[\nabla \cdot \left(D_g \chi_g \nabla \mu_g \right) + s_g - \frac{\partial \rho_g}{\partial \eta_b} \frac{\partial \eta_b}{\partial t} - \sum_{i=1}^{n_m} \frac{\partial \rho_g}{\partial \eta_{mi}} \frac{\partial \eta_{mi}}{\partial t} \right]$$
(2.9)

and

$$\frac{\partial \mu_{v}}{\partial t} = \frac{1}{\chi_{v}} \left[\nabla \cdot \left(D_{v} \chi_{v} \nabla \mu_{v} \right) + s_{v} - \frac{\partial \rho_{v}}{\partial \eta_{b}} \frac{\partial \eta_{b}}{\partial t} - \sum_{\alpha} \sum_{i=1}^{p_{\alpha}} \frac{\partial \rho_{v}}{\partial \eta_{\alpha i}} \frac{\partial \eta_{\alpha i}}{\partial t} \right], \qquad (2.10)$$

where D_g and D_v are the diffusion coefficients, and s_g and s_v are the source terms for the production of Xe atoms and U site vacancies, respectively. χ_g and χ_v are the susceptibilities defined as:

$$\chi_g = h_m \frac{1}{V_a^2 k_g^m} + h_b \frac{1}{V_a^2 k_g^b}$$
(2.11)

and

$$\chi_{\nu} = h_m \frac{1}{V_a^2 k_{\nu}^m} + h_b \frac{1}{V_a^2 k_{\nu}^b},$$
(2.12)

respectively. The grand-potential density for each phase is given by:

$$\omega_m = f_m - \mu_g \rho_g - \mu_v \rho_v \tag{2.13}$$

and

$$\omega_b = f_b - \mu_g \rho_g - \mu_v \rho_v, \qquad (2.14)$$

where f_m and f_b are the Helmholtz free energies of each phase and μ_g and μ_v are the chemical potentials of the gas atoms and vacancies. The free energy of both phases are approximated as parabolic functions of vacancy and gas concentration, such that:

$$f_m = \frac{1}{2}k_v^m (c_v - c_v^{m,eq})^2 + \frac{1}{2}k_g^m (c_g - c_g^{m,eq})^2$$
(2.15)

and

$$f_b = \frac{1}{2}k_v^b(c_v - c_v^{b,eq})^2 + \frac{1}{2}k_g^b(c_g - c_g^{b,eq})^2,$$
(2.16)

where k_v^m and k_g^m are the curvatures of the parabolas and $c_v^{m,eq}$ and $c_g^{m,eq}$ represent the equilibrium concentration of vacancies and gas atoms in the UO₂ matrix, respectively. The curvatures of these parabolic functions were derived from the equivalency of the ideal energy form for the respective phases. Details on this approach including the details of the recrystallization model are provided in [6].

The cluster-dynamics code Xolotl captures the evolution of the intra-granular fission gases [11]. It considers Xe as the primary fission gas present in the system and does not explicitly model vacancy evolution. The evolution of the Xe cluster is represented by:

$$\frac{\partial C_n}{\partial t} = \dot{F} y_n + D_n \nabla^2 C_n - Q(C_n), \qquad (2.17)$$

where C_n is the concentration of the cluster containing *n* Xe atoms, \dot{F} is the fission rate, y_n is the fission yield of the Xe atoms, and D_n is the diffusion coefficient of a given cluster. The time evolution of the clusters consists of the production of new Xe, the diffusion of a single Xe atom, the clustering of Xe to form intra-granular bubbles, and the re-solution of Xe monomers. In this model, only single Xe atoms (i.e., Xe monomers) are considered mobile. The general reaction

Parameter	Formulation	Value	Source
Т		1200 K	
V _a		0.04092 nm ³	[7]
E_f^v		3 eV	[8]
E_f^g		3 eV	[8]
$c_{v/g}^{m,eq}$	$\exp\left(-\frac{E_v^f}{k_BT}\right)$	2.515×10^{-13}	[6]
k_v^m	$7335 \text{ eV/nm}^3 - 0.9682 T \text{ eV/nm}^3/\text{K}$	6173.17 eV/nm ³	[6]
k_g^m	$3667.5 \mathrm{eV/nm^3} - 0.41 T \mathrm{eV/nm^3/K}$	3175.5 eV/nm ³	[6]
$c_v^{b,eq}$		0.562	[6]
$c_{g}^{b,eq}$		0.438	[6]
$k_{v/g}^{b}$	$0.2328 T \text{ eV/nm}^3/\text{K} - 30.723 \text{ eV/nm}^3$	245 eV/nm ³	[6]
l _{int}		10 nm	
σ_{mm}		$1.5 \text{ J/m}^2 \text{ or } 9.363 \text{ eV/nm}^2$	
κ	$\frac{3}{4}\sigma_{mm}l_{int}$	1.125×10^{-8} J/m or 70.2 eV/nm	[6]
α	$\frac{\delta\sigma_{mm}}{l_{int}}$	9×10^8 J/m ³ or 5.62 eV/nm ³	[6]
G	111	64.1 GPa	[9]
M _{GB}	$9.21 \times 10^{-9} \exp\left(-\frac{3.01}{k_B T}\right) \text{m}^4/\text{Js}$	$3.43 \times 10^{-4} \text{ nm}^{4}/\text{eV/s}$	[6]
L _{GB}	$\frac{4M_{GB}}{3l_{int}}$	$4.58 \times 10^{-5} \text{ nm}^{3}/\text{eV/s}$	[6]
L_b	10L	$4.58 \times 10^{-4} \text{ nm}^{3}/\text{eV/s}$	[10]
S_v	$1.2S_g$		[10]
D_g^m		0.0175 nm ² /s	[10]
D_g^b	$10000 D_g^m$	175 nm ² /s	[10]
D_g^s	$1000 D_g^m$	17.5 nm ² /s	[10]
D_g^{GB}	$10000 \stackrel{\bullet}{D}{}_{g}^{m}$	175 nm ² /s	[10]
D_v^m	$D_{v_{II}} = 2 \times 10^{-3} \exp(-2.4/k_B T) \text{ cm}^2/\text{s}$	16.65 nm ² /s	[10]
D_v^b	$100 D_g^m$	1665.27 nm ² /s	[10]
D_v^s	$10 D_g^m$	166.527 nm ² /s	[10]
D_v^{GB}	$100 \tilde{D}_g^m$	1665.27 nm ² /s	[10]

Table 2.1. Parameters used for phase-field simulations of bubble evolution in HBS.

term for a cluster of size $n \ge 2$ is:

$$Q(C_n) = k_n C_n C_1 - k_{k-1} C_{n-1} C_1 + k_n^{emit} C_n - k_{n+1}^{emit} C_{n+1} + k_n^{reso} C_n - k_{n+1}^{reso} C_{n+1},$$
(2.18)

with the following reaction rates:

$$k_n = 4\pi D_1(r_1 + r_n), (2.19)$$

$$k_{n+1}^{emit} = \frac{k_n}{V_a} \exp\left(\frac{-E_b}{k_B T}\right),$$
(2.20)

$$k_n^{reso} = \left(a_1 \exp\left(-b_1 r_n\right) + \frac{y(0) - a_1}{1 + cr_n^2} \exp\left(-b_2 r_n^2\right)\right) 10^4 \dot{F}.$$
 (2.21)

Here, D_1 is the single Xe diffusion coefficient, r_n is the reaction radius for a bubble consisting of *n* Xe atoms, V_a is the atomic volume, E_b is the binding energy of Xe_{*n*+1}, k_B is the Boltzmann constant, and *T* is the temperature. For the full resolution model, the resolution rate is defined as,

$$k_n^{reso} = 2\pi\mu_f \left(R + R_f\right) F. \tag{2.22}$$

where, μ_f and R_f are the average length and radius of the fission spike, respectively. The reaction term for a single Xe atom sums the contributions from each reaction, such that:

$$Q(C_1) = \sum_{n \ge 2} \left[k_n C_n C_1 - k_{n+1}^{emit} C_{n+1} \right] + 2k_1 C_1^2 - k_2^{emit} C_2 - 2k_2^{reso} C_2.$$
(2.23)

A schematic of the coupling approach is presented in Figure 2.1.



Figure 2.1. Schematic of the coupled approach: (a) transfer of physical quantities, and (b) strategy for transferring data between the applications [11].

2.2 Bubble evolution in HBS

Bubble evolution for different initial bubbles and temperatures are presented here. Three initial conditions considered for the simulations are presented in Figure 2.2.



Figure 2.2. Sample initial HBS structure created via a Voronoi tessellation with (a) 100, (b) 150, and (c) 200 nm bubbles.

To benchmark, first we compare the bubble evolution within a fully formed HBS without any initial Xe supersaturation of the matrix. Figure 2.3 shows the time evolution of the 100 nm bubble. It is observed that the bubble growth rate is higher than what was observed previously. Due to switching to the full resolution model, the intragranular Xolotl clusters release more Xe monomers that make their way to the GBs and eventually to the intergranular bubbles.



Figure 2.3. Evolution of a 100 nm bubble in HBS at time approximately a) 2.34×10^5 b) 2.74×10^6 without initial Xe supersaturation in the matrix.

For the next case, we generate the initial Xe supersaturation in the matrix using 1D cluster dynamics calculations. The 1D model also considers the clustering and full-resolution. Figure 2.4 presents the time evolution of the 100 nm bubble with initial Xe supersaturation in the matrix. The existing bubbles grow faster than the previous case. Additionally, due to accumulation of Xe monomers and vacancies, more new bubbles are formed at various triple junctions. This is consistent with the porous structure typically observed around the rim region of the UO_2 fuel within LWRs. The model captures certain grain growth, towards later stage. This is because no new grains are introduced in the simulations and it is considered that the HBS region is exposed to steady 1200K temperature for the duration of the simulation.



Figure 2.4. Evolution of an initial 100 nm bubble in HBS at time a) 6.0×10^5 b) 4.5×10^6 with initial Xe supersaturation in the matrix.

Figure 2.5a captures the porosity evolution over time for different initial bubble sizes with initial supersaturation generated for 1200K. In all the cases, growth of existing bubbles and formation of new triple-junction bubbles are observed. Additionally, the growth rate of the bubbles decreases with increase in the initial bubble sizes.



Figure 2.5. Evolution of the bubbles observed with initial bubbles sizes of a) 100 nm at 2.6×10^6 sec, b) 150 nm at 5.8×10^5 sec, c) 200 nm at 9.4×10^5 sec.

2.3 HBS formation model

In this section we present the HBS formation model that captures the formation of new grains from the initial damaged grains. Figure 2.6 depicts the different stages of HBS formation at 1100 K temperature. Determining the volume fraction of the restructured HBS fuel is important for evaluating the performance of the fuel after restructuring (i.e., the fission gas release behavior and pulverization criteria of the restructured fuel).



Figure 2.6. Different stages of HBS formation at 1100 K temperature.

Figure 2.7 compares the intermediate stages of HBS formation at 1100 K and 1200 K temperature. The HBS formation happens in stages, where formation of the new grains is followed by a coarsening stage.



Figure 2.7. Restructuring leading to HBS formation at 1100 K (left) and 1200 K (right) temperatures.

As observed here, the rate of restructuring and average grain size vary with the temperature [12]. In general, the HBS volume fraction can be calculated using the Kolmogorov-Johnson-Mehl-Avrami (KJMA) correlation for phase transformations such that [13]:

$$\alpha = 1 - \exp\left(-k \, b u_{eff}^n\right) \tag{2.24}$$

where α is the volume fraction of the new grains, k is the transformation rate constant, bu_{eff} is the effective burnup, and n is the Avrami constant.

Figure 2.8 compares the mesoscale data with the existing BISON model. The mesoscale data follows the KJMA correlation. However, the slope of the curve is different from what the current BISON model uses. Moreover, the mesoscale simulations shows that the slope of the curve and the time to achieve a complete restructuring varies with temperature, as well as nucleation rate. Thus, the slope of the model (k) should be a function of temperature. The mesoscale observations do not support the assumption of the current BISON model that the slope of the curve remains constant below a threshold temperature which determines whether restructuring has occurred or not. Therefore, the BISON model needs to be updated based on the mesoscale data for a more accurate prediction of the HBS volume fraction in the fuel. Further investigation of the HBS formation model will be done in the following year. It is also worth mentioning that the current grain nucleation model at the mesoscale has some numerical limitation which prevents us from evaluating HBS formation at even lower temperatures. This will be investigated in the following year.



Figure 2.8. Variation of the volume fraction of the restructured HBS region with the effective burnup.

3. HELMHOLTZ FREE ENERGY OF VIRIAL EQUA-TION OF STATE FOR XENON GAS BUBBLES IN URANIUM DIOXIDE

An important parameter needed for phase-field modeling of fission gas bubbles in UO₂ nuclear fuel is the chemical free energy of the bubble phase. In past work, the bubble phase has been treated as a mixture of U-site vacancies and Xe atoms, and the chemical free energy was given by the Helmholtz free energy of Xe using the van der Waals equation of state [14]. Alternatively, a parabolic approximation to the Helmholtz free energy has been used in phase-field modeling to improve numerical performance [8]. In the van der Waals equation of state (EOS), it is assumed that the gas atoms have a hard-sphere volume b_{Xe} which is incompressible. In this EOS, the relationship between gas pressure P_g and Xe gas atom density ρ_g (number of gas atoms per unit volume) is given by

$$P_g = \frac{kT}{\frac{1}{\rho_g} - b_{Xe}}$$
(3.1)

where k is the Boltzmann constant and T is the temperature.

Recently, molecular dynamics simulations have been used to determine a more accurate equation of state for Xe atoms at high pressures [15] where the hard-sphere assumption of the van der Waals equation of state is not valid. The pressure-volume relationship was found to be described well by the virial EOS:

$$P_g = \rho_g kT \left[1 + B \frac{\rho_g}{\rho_c} + C \left(\frac{\rho_g}{\rho_c} \right)^2 + E \left(\frac{\rho_g}{\rho_c} \right)^4 \right]$$
(3.2)

where *B*, *C*, and *E* are temperature-dependent coefficients and $\rho_c = 5.06 \text{ nm}^{-3}$ is the density of Xe atoms at the critical point.

The Xe gas pressure for these EOSs is plotted in Figure 3.1 as a function of the Xe gas atom dimensionless concentration c_g , which is related to the number density ρ_g and U-site density ρ_U using $c_g = \frac{\rho_g}{\rho_U}$. Significant deviation between the van der Waals and virial EOS begins for $c_g > 0.2$, where pressures are of the order of a few hundred MPa.

Because of the breakdown of the van der Waals EOS at these pressures, it is expected that the Helmholtz free energy derived from the van der Waals EOS will also be inaccurate at such pressures, which could result in errors in phase-field



Figure 3.1. Comparison of pressure-concentration relationship for the virial EOS [15] with the van der Waals EOS.

simulations that use this Helmholtz free energy. Therefore, in this section, we determine the Helmholtz free energy from the virial EOS by performing thermodynamic integration of the EOS. We also develop a parabolic approximation to the Helmholtz free energy for use in phase-field models that require it, or where it is desired for improved numerical performance.

For N_g moles of Xe gas atoms, the bulk Helmholtz free energy density f_g (J/m³) is given in terms of the molar density of gas atoms N_g (mol/volume) as

$$f_g = N_g F_g^\circ + N_g \Delta F_g^{EOS} \tag{3.3}$$

where F_g° is the reference Helmholtz free energy of Xe per mole at reference molar volume v_g° , and ΔF_g^{EOS} is the change in the Helmholtz free energy per mole due to change in gas molar volume. Equation 3.3 can be expressed in terms of c_g using $N_g = \frac{c_g}{v}$, where $v_m = 2.53 \times 10^{-5} \text{ m}^3/\text{mol}$ is the molar volume of U sites in the solid:

$$f_g = c_g \frac{F_g^\circ}{v_m} + c_g \frac{\Delta F_g^{EOS}}{v_m}$$
(3.4)

 F_g° can be determined from the thermodynamic relation $F_g^{\circ} = (G_g^{\circ} - H_{298}^{\circ}) - P_g^{\circ} v_g^{\circ}$ [16]. The quantity $(G_g^{\circ} - H_{298}^{\circ})$ is available at a range of temperatures from thermodynamic tables in the form $-(G_g^{\circ} - H_{298}^{\circ})/T$ [17]. The reference state pressure $P_g^{\circ} = 10^5$ Pa. The reference state molar volume at this pressure is given by the ideal gas law as $v_g^{\circ} = RT/P$. ΔF_g^{EOS} can be determined by integrating the EOS with respect to the gas molar volume v_g starting from the reference molar volume v_g° :

$$\Delta F_g^{EOS} = -\int_{v_g^\circ}^{v_g} P_g dv_g \tag{3.5}$$

To perform thermodynamic integration of the virial EOS, it is convenient to first express it in terms of the molar volume of the Xe gas, v_g , using $v_g = \frac{N_a}{\rho_g}$, where N_a is Avogadro's number:

$$P_g = \frac{RT}{v_g} \left[1 + \frac{B}{\rho_c} \frac{N_a}{v_g} + \frac{C}{\rho_c^2} \left(\frac{N_a}{v_g} \right)^2 + \frac{E}{\rho_c^4} \left(\frac{N_a}{v_g} \right)^4 \right]$$
(3.6)

where $R = N_a k$. Substituting Equation 3.6 into 3.5 and integrating analytically, we obtain

$$\Delta F_{g}^{EOS} = RT \left[\ln \left(\frac{c_{g}}{c_{g}^{\circ}} \right) + \frac{B}{v_{m}} \frac{N_{a}}{\rho_{c}} (c_{g} - c_{g}^{\circ}) + \frac{C}{2v_{m}^{2}} \left(\frac{N_{a}}{\rho_{c}} \right)^{2} (c_{g}^{2} - c_{g}^{\circ 2}) + \frac{E}{4v_{m}^{4}} \left(\frac{N_{a}}{\rho_{c}} \right)^{4} (c_{g}^{4} - c_{g}^{\circ 4}) \right]$$
(3.7)

where $c_g^{\circ} = v_m / v_g$. Substituting Equation 3.7 in to 3.4,

$$f_{g} = c_{g} f_{g}^{\circ} + c_{g} \frac{kT}{V_{a}} \left[\ln\left(\frac{c_{g}}{c_{g}^{\circ}}\right) + \frac{B}{v_{m}} \frac{N_{a}}{\rho_{c}} (c_{g} - c_{g}^{\circ}) + \frac{C}{2v_{m}^{2}} \left(\frac{N_{a}}{\rho_{c}}\right)^{2} (c_{g}^{2} - c_{g}^{\circ2}) + \frac{E}{4v_{m}^{4}} \left(\frac{N_{a}}{\rho_{c}}\right)^{4} (c_{g}^{4} - c_{g}^{\circ4}) \right]$$
(3.8)

where $f_g^{\circ} = F_g^{\circ}/v_m$. The Helmholtz free energy density for Xe using the virial equation of state in plotted in Figure 3.2 at T = 700 K, along with the same quantity using the van der Waals equation of state. For convenience in phase-field modeling, a parabolic approximation to the virial EOS was fit at 700 K:

$$f_g^p = \frac{1}{2} k_{virial} (c - c_{virial}^{min})^2 + f_0$$
(3.9)

From the fit, $k_{virial} = 4.96 \times 10^9 \text{ J/m}^3$, $c_{virial}^{min} = 0.967$, and $f_0 = -2.23 \times 10^9 \text{ J/m}^3$. The parabolic expression with these parameters is also shown in Figure 3.2.



Figure 3.2. Helmholtz free energy density as a function of gas concentration c_g for the virial equation of state of Xe in UO₂ [15] at T = 700 K. A parabolic fit to the Helmholtz free energy from the virial EOS at this temperature is also shown, along with the Helmholtz free energy of a van der Waals gas at 700 K for comparison.

4. COMPARISON OF NET VACANCY PRODUCTION APPROXIMATIONS

In this chapter, we compare two different approaches to approximate the net production of vacancies in phase-field modeling of fission gas bubbles in nuclear fuel. During reactor operation, energetic fission fragments are ejected from nuclei undergoing fission, leading to collision cascades that produces pairs of interstitials and vacancies (Frenkel pairs). Although many Frenkel pairs rapidly recombine in the aftermath of collision cascades, some remain as free species that can diffuse to sinks such as voids and dislocations. Because interstitials are preferentially absorbed at dislocation sinks, a net excess of vacancies remains that can contribute to fission gas bubble or void growth. Although it would be preferable to track both vacancies and interstitial species in phase-field models, including their production, recombination, and absorption at sinks, interstitials usually diffuse much more rapidly than vacancies. This makes it computationally challenging to simulate experimentally relevant times, because the simulation time step is limited to be small enough to resolve the transport of the faster-diffusing interstitial species.

Due to this challenge, many phase-field models of nuclear fuel have not included interstitials, and have approximated the net production of vacancies by various methods. One of the most common approaches has been the use of a source term for vacancy production, similar to the source term required to simulate the production of insoluble fission gas atoms [8, 18]. For convenience, this approach will be referred to as source-only (SO). One disadvantage of this approach is that it is not known what the appropriate value of the source term should be to correctly represent the net vacancy production rate. The rate of Frenkel pair production during fission is several orders of magnitude greater than the fission rate [19], but rapid recombination in the aftermath of collision cascades should reduce the net production rate significantly. Thus, net vacancy production rates of 5-20 times the Xe production rates have been used, and the effect of this range was studied parameterically [8]. Another approach was to introduce both a vacancy source term and a sink term proportional to the vacancy concentration [14]. This approach will be referred to as source+sink (SS). The SS approach results in a vacancy concentration that is in steady-state and constant in the bulk of the fuel far from bubbles, as is expected from rate theory models. The value of the effective sink term was calculated [14] so that steady-state vacancy concentration, c_n^{ss} , matched the value predicted from cluster dynamics simulations [20]. Capturing the steadystate vacancy concentration correctly improves the SS model's fidelity to one aspect of the full vacancy-interstitial model, but it has not been determined how growth rate of the SO or SS models compare to the full vacancy-interstitial model.

Although computational models using techniques such as the phase-field method can simulate a far wider variety

of microstructures than is possible with an analytical model, there are advantages of analytical models in gaining qualitative and even quantitative understanding. Therefore, in this chapter, we compare the growth rates and vacancy concentrations of the SO and SS models to analytical models to gain understanding of what factors control growth rates in the SO and SS models, and how they compare to an analytical model of growth rates derived for the full interstitial-vacancy picture. To simplify the comparison as much as possible, we consider vacancies only, and do not include any fission gas species. This can be considered as representative of ion irradiation, with parameters chosen to match fission-driven defect production. In Section 4.1, we review existing models of growth for the SO model and an analytical model of the growth rate for the full vacancy-interstitial picture, and derive a new analytical model for the growth rate for the SS model. In Section 4.2, we describe a phase-field model used to simulate bubble growth in these conditions. In Section 4.3, we simulate growth using the phase-field model and compare the results to the analytical models.

4.1 Analytical models for growth

4.1.1 Source-only model

In the source-only model, the growth of a bubble of instantaneous radius R is considered. Radial coordinates with spherical symmetry are used, in a simulation domain of radius R. The variable r describes the distance from the center of the domain. The bubble phase is within the region $0 < r \le R$, and the solid UO₂ matrix phase is within the region $R < r \le R$. The diffusion equation describing the non-dimensional concentration (mole fraction) of vacancies, c_v , within the solid in spherical coordinates is

$$\frac{\partial c_v}{\partial t} = \frac{D_v}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial c_v}{\partial r} \right) + S_v \tag{4.1}$$

Although an analytical solution to the time-dependent Equation 4.1 is not available, if the rate of change in the bubble size is slow relative to the relaxation time of the diffusion field, the concentration profile of c_v will be near a steady state at a particular time *t*. This is known as the quasi-steady state approximation, and the diffusion equation in this case is

$$\frac{\partial c_v}{\partial t} \approx 0 \approx \frac{D_v}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial c_v}{\partial r} \right) + S_v \tag{4.2}$$

The quasi-steady state diffusion Equation 4.2 can be solved given appropriate boundary conditions. As described previously, it is expected that far from the bubble, a steady-state vacancy concentration is reached; therefore, c_v should be constant with respect to changes in *r* at the simulation domain boundary, leading to the boundary condition $\frac{\partial c_v}{\partial r}\Big|_{r=\mathcal{R}} = 0$. The vacancy concentration in the matrix at the bubble-matrix interface, $c_R = c_v(r = R)$, can be calculated using the Gibbs-Thomson equation and represents the other necessary boundary condition:

$$c_R = c_{m,0} + \frac{2\sigma_{int}}{Rk_v(c_{v,0} - c_{m,0})}$$
(4.3)

where $c_{m,0}$ is the equilibrium concentration of vacancies in the bulk solid far from a curved interface (assumed to be 0 here), σ_{int} is the interfacial energy of the bubble-solid interface, k_m is the curvature of the free energy versus composition in the matrix phase, and $c_{v,0} = 1$ is the equilibrium concentration of vacancies in the void.

Subject to these boundary conditions, the solution to Equation 4.2 in the solid is given by [19]

$$c_{v}(r) = c_{R} + \frac{S_{v}}{6D_{v}} \left[\frac{2\mathcal{R}^{3}(r-R)}{rR} - (r^{2} - R^{2}) \right]$$
(4.4)

If $\mathcal{R} \gg R$, Equation 4.4 can be approximated as [19]

$$c_{\nu}(r) \approx c_R + \frac{S_{\nu} \mathcal{R}^3}{3D_{\nu} R} \left(1 - \frac{R}{r}\right)$$
(4.5)

The growth rate of the bubble using the source-only model can be derived by equating the time rate of change of the bubble volume V to the flux of vacancies J across the boundary at R, which has area $4\pi R^2$:

$$\frac{dV}{\partial t} = 4\pi\Omega R^2 J \tag{4.6}$$

where Ω is the atomic volume. Since $V = \frac{4}{3}\pi R^3$, $\frac{dV}{dt} = 4\pi R^2 \frac{dR}{dt}$. Substituting in to Equation 4.6,

$$\frac{dR}{dt} = \Omega J \tag{4.7}$$

Flux J at the bubble-matrix interface is given by

$$J(R) = -D_v \left(\frac{\partial (c_v / \Omega)}{\partial r} \right) \bigg|_{r=R} = -\frac{D_v}{\Omega} \left(\frac{\partial c_v}{\partial r} \right) \bigg|_{r=R}$$
(4.8)

Thus,

$$\left. \frac{dR}{dt} = -D_v \left(\frac{\partial c_v}{\partial r} \right) \right|_{r=R} \tag{4.9}$$

Substituting Equation 4.5 and taking the derivative,

$$\frac{dR}{dt} = \frac{S_v \mathcal{R}^3}{3R^2} \tag{4.10}$$

4.1.2 Source+sink model

In this section, we derive a quasi-steady state solution for the SS model. The quasi-steady state diffusion equation for this case is

$$\frac{\partial c_v}{\partial t} \approx 0 \approx \frac{D_v}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial c_v}{\partial r} \right) + S_v - K_v c_v \tag{4.11}$$

This can be rewritten by dividing through by D_v and taking all c_v dependent terms to one side:

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial c_v}{\partial r}\right) - \frac{K_v}{D_v}c_v = -\frac{S_v}{Dv}$$
(4.12)

Following the theory of differential equations, the equation can be split into homogeneous and particular solutions, c_h and c_p , such that $c_v = c_h + c_p$. The solution to the homogeneous part can be found by solving

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial c_h}{\partial r}\right) - \frac{K_v}{D_v}c_h = 0$$
(4.13)

Expanding the first term and multiplying through by r^2 ,

$$r^2 \frac{\partial^2 c_h}{\partial r^2} + 2r \frac{\partial c_h}{\partial r} - \frac{K_v}{D_v} c_h r^2 = 0$$
(4.14)

This is the modified spherical Bessel differential equation with n = 0 [21]. Solutions are of the form

$$c_h = c_1 i_0 + c_2 k_0 \tag{4.15}$$

where c_1 and c_2 are constants to be determined, and i_0 and k_0 are the modified spherical Bessel functions of the first and second kind, respectively, for n = 0:

$$i_{0} = \frac{\sinh\left(\sqrt{\frac{K_{v}}{D_{v}}}r\right)}{\sqrt{\frac{K_{v}}{D_{v}}}r}$$
(4.16)

$$k_{0} = \frac{\exp\left(-\sqrt{\frac{K_{v}}{D_{v}}}r\right)}{\sqrt{\frac{K_{v}}{D_{v}}}r}$$
(4.17)

To find the particular solution, based on the fact that the particular term of the differential equation, S_v/D_v , is a constant, we try $c_p = A$, where A a constant. Substituting to the particular form of the differential equation.

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial A}{\partial r}\right) + \frac{S_v}{D_v} - \frac{K_v}{D_v}A = 0$$
(4.18)

Which results in

$$A = \frac{S_v}{K_v} = c_p \tag{4.19}$$

Combining Equation 4.15 and 4.19, we obtain

$$c_v = c_h + c_p = c_1 i_0 + c_2 k_0 + \frac{S_v}{K_v}$$
(4.20)

Now the boundary conditions must be used to determine c_1 and c_2 . Because $i_0 \to \infty$ as $r \to \infty$, but $c_v \to c_v^{ss}$ as $r \to \infty$, this requires that $c_1 = 0$. We can determine c_2 from the fact that at r = R, $c_v(R) = c_R$, as determined from the Gibbs-Thomson condition of Equation 4.3. Defining $\lambda = \sqrt{S_v/K_v}$ for convenience,

$$c_{v} = c_{2}k_{0} + \frac{S_{v}}{K_{v}} = c_{2}\frac{e^{-\lambda r}}{\lambda r} + \frac{S_{v}}{K_{v}}$$
(4.21)

Evaluating at r = R,

$$c_v(r=R) = c_R = c_2 \frac{e^{-\lambda R}}{\lambda R} + \frac{S_v}{K_v}$$
(4.22)

This allows us to solve for c_2 :

$$c_2 = \frac{\lambda R}{e^{-\lambda R}} \left(c_R - \frac{S_v}{K_v} \right) \tag{4.23}$$

Substituting Equation 4.23 into 4.21, we obtain the vacancy concentration as a function of position in the solid for the SS model:

$$c_{v} = \left(c_{R} - \frac{S_{v}}{K_{v}}\right) \frac{\lambda R}{e^{-\lambda R}} \frac{e^{-\lambda r}}{\lambda r} + \frac{S_{v}}{K_{v}}$$
(4.24)

The growth rate can be obtained by using Equation 4.24 in 4.9:

$$\frac{dR}{dt} = D_v \left(\frac{S_v}{K_v} - c_R\right) \left(\sqrt{\frac{K_v}{D_v}} + \frac{1}{R}\right)$$
(4.25)

4.1.3 Chemical stress model

Accounting for the presence of both vacancies and interstitials, an approximation for the growth rate of bubbles due to the supersaturation of irradiation-produced defects can be obtained [22]:

$$\frac{dR}{dt} = \frac{D_v}{R} \left(c_v^{ss} - c_R \right) \left(1 - \frac{Z_v}{Z_i} \right)$$
(4.26)

where Z_v and Z_i are capture rates of the point defects by sinks such as dislocations [22]. The growth rate resulting from the supersaturation of defects has been referred to as a "chemical stress" because it produces bubble growth like a mechanical force.

4.2 Phase-field model formulation

The model for UO₂ bubbles uses the approach developed by Kim et al. [23], typically referred to as the "KKS" formulation. For the SO and SS models, the formulation tracks the normalized concentration (site fraction) of uranium site vacancies, c_v . The bubble or void phase is represented as composed entirely of vacancies, $c_v = 1$. The model also indicates the difference between matrix (solid) and bubble phases with a non-conserved order parameter, η , that varies continuously from 0 in the matrix phase to 1 in the void/bubble phase. (Since there are no fission gas atoms in the current phase-field model, it may be more typical to refer to the bubble regions as voids. However, to avoid potential confusion with the subscript v used for vacancies, we maintain the use of the term bubbles and the subscript b to refer to regions composed entirely of vacancies throughout.)

The total free energy F of the system is given by

$$F = \int_{V} \left[f_{chem} + Wg(\eta) + \frac{\kappa}{2} |\nabla \eta|^2 \right] \, \mathrm{d}V, \tag{4.27}$$

where f_{chem} is the chemical contribution to the free energy density, $g(\eta) = \eta^2 (1 - \eta)^2$ is a double-well function, W is the height of the double well, and κ is the gradient energy coefficient.

4.2.1 Chemical free energy density

The chemical free energy density is interpolated from the chemical free energy densities of the matrix and bubble phases:

$$f_{chem} = [1 - h(\eta)] f_{chem}^{m}(c_{v}^{m}) + h(\eta) f_{chem}^{b}(c_{v}^{b})$$
(4.28)

where f_{chem}^{m} is the chemical free energy density of the matrix phase; f_{chem}^{b} is the chemical free energy density of the bubble phase; c_{v}^{m} is the concentration of vacancies in the matrix phase; and c_{v}^{b} is the concentrations of vacancies in the bubble phase. $h(\eta) = \eta^{3}(6\eta^{2} - 15\eta + 10)$ is an interpolation function that varies smoothly from h(0) = 0 to h(1) = 1. Parabolic approximations are used for the dependence of chemical free energies on defect concentrations:

$$f_{chem}^{m} = \frac{k_{v}}{2} (c_{v}^{m} - c_{v}^{m,min})^{2}$$
(4.29)

$$f_{chem}^{b} = \frac{k_{v}}{2} (c_{v}^{b} - c_{v}^{b,min})^{2}$$
(4.30)

where $k_v = 6.4 \times 10^{11} \text{ J/m}^3$ (the same order of magnitude as used in previous phase-field simulations of fission gas bubble growth [8]), $c_v^{m,min} = 0$, and $c_v^{b,min} = 1$.

4.2.2 KKS system constraints

The physical concentrations are defined in terms of the phase concentrations as [23]

$$c_v = [1 - h(\eta)]c_v^m + h(\eta)c_v^b$$
(4.31)

In addition, the KKS model requires that the local chemical potentials of a component be equal to each other in each phase [23]:

$$\mu_{v} = \frac{df_{chem}^{b}}{dc_{v}^{b}} = \frac{df_{chem}^{m}}{dc_{v}^{m}}$$
(4.32)

where μ_v is the chemical potential of vacancies.

4.2.3 Interfacial parameters parameterization

The interfacial energy γ of the matrix-bubble interface is estimated to be 1.17 J/m² [14]. In the KKS model, the interfacial energy and interface thickness 2*l* are related to the gradient energy coefficient and double-well potential height via the following analytical expressions:

$$\gamma = \frac{\sqrt{\kappa W}}{3\sqrt{2}} \tag{4.33}$$

$$2l = 2.2\sqrt{2}\sqrt{\frac{\kappa}{W}} \tag{4.34}$$

where the interface thickness 2*l* is defined as the distance between $\eta = 0.1$ and $\eta = 0.9$. 2*l* was chosen to be 10 nm, such that bubbles with radii from tens to hundreds can be adequately resolved. With γ and 2*l* specified, Equations (4.33) and (4.34) can be rearranged to obtain the required values of $\kappa = 1.60 \times 10^{-8}$ J/m and $W = 1.54 \times 10^9$ J/m³.

4.2.4 Evolution equations

The order parameter η evolves by the Allen-Cahn equation as

$$\frac{\partial \eta}{\partial t} = -L\left(\frac{\delta F}{\delta \eta}\right) \tag{4.35}$$

where L is the order parameter mobility for η . Using Equations (27) and (28) of Reference [23], this can be written as

$$\frac{\partial \eta}{\partial t} = L \left[\frac{dh}{d\eta} \left[(f_{chem}^m - f_{chem}^b) - \mu_v (c_v^m - c_v^b) \right] - W \frac{dg}{d\eta} + \kappa \nabla^2 \eta \right]$$
(4.36)

In the SO model, the evolution equation for vacancies is

$$\frac{\partial c_v}{\partial t} = \nabla \cdot M_v \nabla \mu_v + S_v [1 - h(\eta)]$$
(4.37)

while in the SS model, the vacancy evolution equation is

$$\frac{\partial c_v}{\partial t} = \nabla \cdot M_v \nabla \mu_v + S_v [1 - h(\eta)] - K_v c_v^m$$
(4.38)

where M_v is the vacancy mobility, and the function $[1 - h(\eta)]$ limits defect production to the matrix phase only. The values of S_v and K_v are varied parameterically in both models to determine their effect on growth rate. The purpose of the effective sink term $-K_v c_v^m$ is to maintain the vacancy concentration in the matrix at steady-state conditions far from any large bubbles at $c_v^{ss} \approx 8 \times 10^{-3}$ based on cluster dynamics simulations for UO₂ under irradiation at temperatures less than 1300 K [24]. At steady-state in the bulk solid far from any bubbles, the vacancy concentration is constant both time and position, so $\frac{\partial c_v}{\partial t} = 0$ and $\nabla \mu_v = 0$. Under these conditions, from Equation (4.38),

$$K_v = \frac{S_v}{c_v^{ss}} \tag{4.39}$$

Parameter	Value	Source
$c_v^{m,min}$	0	Section 4.2.1
$c_v^{b,min}$	1	Section 4.2.1
k _v	$6.4 \times 10^{11} \text{ J/m}^3$	Section 4.2.1
κ	1.60×10^{-8} J/m	Section 4.2.3
W	$1.54 \times 10^9 \text{ J/m}^3$	Section 4.2.3
D_v^m	0.96 nm ² /s	[14]
L	$1.56 \times 10^{-10} \text{ m}^3/\text{J/s}$	Section 4.2.4

Table 4.1. Parameters used for phase-field simulations of bubble growth.

The defect mobility was calculated from the diffusion coefficients and second derivatives of free energies for each phase as in Equation (18) of Reference [23]:

$$M_{v} = \frac{D_{g}(\phi)}{f_{c_{v}c_{v}}} = \frac{hD_{v}^{b} + (1-h)D_{v}^{m}}{f_{c_{v}c_{v}}}$$
(4.40)

where $f_{c_n c_n}$ is as defined in Equation (29) of Reference [23]:

$$f_{c_v c_v} = \frac{\frac{d^2 f_{chem}^m}{dc_v^2} \frac{d^2 f_{chem}^b}{dc_v^2}}{[1 - h(\eta)] \frac{d^2 f_{chem}^b}{dc_v^2}} + h(\eta) \frac{d^2 f_{chem}^m}{dc_v^2}}{dc_v^2} = k_v$$
(4.41)

The vacancy diffusion coefficient in the matrix $D_v^m = 0.96 \text{ nm}^2/\text{s}$ [14], and D_v^b was set to $10^3 D_v^m$. The Allen-Cahn mobility L was set sufficiently high that interface motion was controlled by defect diffusion, resulting in $L = 1.56 \times 10^{-10} \text{ m}^3/\text{J/s}$.

The evolution equations were non-dimensionalized using the characteristic energy scale $E^* = 64 \times 10^9$ J/m³, length scale $l^* = 1$ nm, and time scale $\tau^* = 1$ s, and discretized using the finite element method as implemented in the MOOSE framework [25]. Since the simulations have spherical symmetry, the problem is solved in spherical coordinates, with symmetry allowing the problem to be solved in 1D as a function of the radial coordinate *r* only. The simulation domain size $\mathcal{R} = 500$ nm in each case, and 1D elements are used with linear Lagrange shape functions, with a mesh size $\Delta r = 1$ nm.

Natural boundary conditions are used, resulting in no-flux boundary conditions for chemical species and a zerogradient condition for η . Time integration uses the second-order backward differentiation formula. The evolution equations are solved at each time step using the preconditioned Jacobian-Free Newton-Krylov method. Adaptive time stepping is used with the IterationAdaptiveDT algorithm as implemented in the MOOSE framework [26].

4.3 Simulations of bubble growth and comparison to analytical models

4.3.1 Source-only model simulations

The growth of a bubble with initial radius of 30 nm was simulated with the source-only model (Equation 4.37). The initial concentration of vacancies in the void and matrix phases was adjusted 1.0001214 and 1.214×10^{-4} , respectively, to account for the Gibbs-Thomson shift in composition as per Equation 4.3. The source term was set to $S_n = 4.092 \times$ 10^{-10} s⁻¹. This is approximately 5 times larger than the Xe source term for typical light-water reactor conditions [14], which is within the range considered in past parametric studies of source term strength [8]. The bubble radius as a function of time (as determined by the position where $\eta = 0.5$ by interpolation of the finite element shape functions at each time step) is shown in Figure 4.1a, showing that the bubble grows to a radius of approximately 100 nm at the end of the simulation time of 2×10^7 s. The rate of change in bubble size $\frac{dR}{dt}$ was calculated using backward finite differences of the interface position at each time step (the relatively fine mesh size of $\Delta r = 1$ relative to 2l = 10 nm was used to reduce noise in the calculation of dR/dt). $\frac{dR}{dt}$ from the simulation is plotted as a function of R in Figure 4.1b, along with the predicted value of $\frac{dR}{dt}$ from the quasi-steady state model from Equation 4.10. The simulated $\frac{dR}{dt}$ starts at 0 and begins to increase as vacancies build up as they are created by the source term. The growth rate predicted by the quasi-steady state approximation starts much higher because it assumes the vacancy concentration profile is already in steady-state and thus does not account for the time required for vacancies to build up to the steady-state profile. At $R \approx 40$ nm, the simulated growth rate reaches a maximum and then becomes to decrease as the vacancy concentration approaches its steady-state profile. At this point the simulated rate approaches the quasi-steady state approximation. The simulated growth rate closely matches the quasi-steady state approximation for R > 65 nm. The vacancy concentration profile as a function of r at time $t = 1.4 \times 10^7$ s is shown in Figure 4.1c for both the simulation and quasi-steady state approximation. Although the simulated c_v profile is slightly lower in magnitude than the analytical expression, the slope is approximately the same near the bubble-matrix interface, meaning that the flux and therefore $\frac{dR}{dt}$ is very nearly the same by this time.

The effect of significantly increasing the vacancy source term is shown in Figure 4.2. The value of S_v was increased by a factor of 10^2 to $S_v = 4.092 \times 10^{-8} \text{ s}^{-1}$. As expected, the bubble size grew much faster, reaching a radius of over 160 nm after a much shorter simulation time of 1×10^6 s compared with Figure 4.1. The simulated $\frac{dR}{dt}$ is shown in Figure 4.2b and compared to the analytical steady-state approximation. The bubble size increases much more significantly before there is good agreement between the simulation results and the analytical solution. This is because the bubble growth rate is significantly higher, meaning that the quasi-steady state approximation breaks down. Only toward the later times in the simulation, when $\frac{dR}{dt}$ has decreased significantly, does the simulation come into reasonable agreement with the analytical solution. The vacancy concentration profile c_v versus r is shown in Figure 4.2c at $t = 5 \times 10^5$ s, where R = 110 nm. The slope of the simulated c_v profile is steeper than the analytical solution, meaning that the growth rate is slightly larger in simulation at this time, as seen in Figure 4.2b.

The effect of changes in the diffusion coefficient D_v are shown in Figure 4.3, where growth of the 30 nm bubble was simulated with $S_v = 4.092 \times 10^{-8} \text{ s}^{-1}$, $D_v = 0.48 \text{ nm}^2/\text{s}$. The quasi-steady state analytical solution of Equation 4.10 predicts that $\frac{dR}{dt}$ is independent of D_v . However, Figure 4.3a shows that the total growth is somewhat less than the case with $D_v = 0.96 \text{ nm}^2/\text{s}$ that was shown in Figure 4.2a. This is because there is greater difference between the



Figure 4.1. Simulations with vacancy source only (SO) and comparison to quasi-steady state approximation. $S_v = 4.092 \times 10^{-10} \text{ s}^{-1}$, $D_v = 0.96 \text{ nm}^2/\text{s}$. (a) Void radius R, (b) void growth rate dR/dt, (c) vacancy concentration as a function of radius at $t = 1.4 \times 10^7 \text{ s}$.



(c)

Figure 4.2. Simulations with vacancy source only (SO) and comparison to quasi-steady state approximation for increased vacancy source term. $S_v = 4.092 \times 10^{-8} \text{ s}^{-1}$, $D_v = 0.96 \text{ nm}^2/\text{s}$. (a) Void radius *R*, (b) void growth rate dR/dt, (c) vacancy concentration as a function of radius at $t = 5 \times 10^5 \text{ s}$.

simulated $\frac{dR}{dt}$ and the quasi-steady state analytical solution. This means that there is some dependence of the growth rate in the source-only model D_v at high source strength, although the dependence is relatively weak. The vacancy concentration profile c_v versus r is shown in Figure 4.3c. The slope is larger than the higher-diffusivity case that was shown in Figure 4.3c, but the lower value of D_v means the growth rate $\frac{dR}{dt}$ does not change significantly.

4.3.2 Source+sink model simulations

Growth of a 30 nm bubble was simulated using the SS model using Equation 4.38. The vacancy source term was set to 10^4 times greater than the fission rate in typical light water reactor conditions [19], resulting in $S_v = 4.092 \times 10^{-6}$ s⁻¹ [14]. The sink term was set to maintain $c_v^{ss} = 0.008$, resulting in $K_{iv} = 5.114 \times 10^{-4}$ s⁻¹. Simulation results are shown in Figure 4.4. The growth rate of the bubble is greater than the high S_v cases considered for the SO model, reaching a final radius of 319 nm at the end of the simulation time of 10^6 s (Figure 4.4a). The growth rate in the simulation is compared to the quasi-steady state analytical model of Equation 4.25 in Figure 4.4b. The general trends of the simulation and analytical model are consistent. During the initial stages of growth, the 1/R term in Equation 4.25 is comparable to the $\sqrt{K_v/D_v}$ term, and as *R* increases, the growth rate goes down. As *R* increases past 150 nm, the 1/R term becomes small compared to the $\sqrt{K_v/D_v}$ term and the growth rate is somewhat larger, indicating that the growth rate is high enough that analytical model has begun to break down. Nonetheless, the analytical model provides useful qualitative understanding of the reasons for the trend in growth rate with changing radius. The vacancy concentration profile versus radius from simulation is shown in Figure 4.4c at time $t = 2 \times 10^5$ s and compared to the analytical expression of Equation 4.24. Agreement between simulation and the analytical model is good and the vacancy concentration reaches the expected value of $c_v^{ss} = 0.008$ far from the bubble.

The effect of changing the source and effective sink terms is studied next. Qualitatively, it might be expected that the growth rate should remain constant as long as c_v^{ss} in the matrix far from the bubbles is maintained at the same value. The growth rate predicted by the chemical stress model, Equation 4.26, is consistent with this intuition. To test whether the SS model shows this behavior, the vacancy source and effective sink were doubled from the values considered in Figure 4.4, resulting in $S_v = 8.184 \times 10^{-6} \text{ s}^{-1}$ and $K_v = 1.0228 \times 10^{-3} \text{ s}^{-1}$, which maintains $c_v^{ss} = 0.008$. Figure 4.5a shows that the growth rate increases significantly compared to Figure 4.4a, even though c_v^{ss} is the same between the two models. This counter-intuitive result can fairly be called a disadvantage of the SS model. The growth rate from the simulation is compared to the quasi-steady state analytical model in Figure 4.5b. The analytical model correctly predicts the trend of increased growth rate relative to the previous case of $S_v = 4.092 \times 10^{-6} \text{ s}^{-1}$, $K_v = 5.114 \times 10^{-4} \text{ s}^{-1}$. From Equation 4.25, the $\sqrt{K_v/D_v}$ term is larger than considered in Figure 4.4b, resulting in the larger growth rate. The vacancy concentration profile versus radius for this case is shown in Figure 4.5c at $t = 2 \times 10^5$ s, showing good agreement between the simulation results and the analytical model.

The effect of vacancy diffusivity is next considered in the SS model. To clarify its expected impact, Equation 4.25 can be rewritten as

$$\frac{dR}{dt} = \left(\frac{S_v}{K_v} - c_R\right) \left(\sqrt{K_v D_v} + \frac{D_v}{R}\right)$$
(4.42)

Thus, a decrease in D_v is expected to decrease the growth rate at all times. Figures 4.6a and 4.6b show that this is



(c)

Figure 4.3. Simulations with vacancy source only (SO) and comparison to quasi-steady state approximation for increased vacancy source term and lower diffusivity. $S_v = 4.092 \times 10^{-8} \text{ s}^{-1}$, $D_v = 0.48 \text{ nm}^2/\text{s}$. (a) Void radius *R*, (b) void growth rate dR/dt, (c) vacancy concentration as a function of radius at $t = 7 \times 10^5 \text{ s}$.



(c)

Figure 4.4. Simulations with vacancy source and effective sink (SS) and comparison to quasi-steady state approximation. $S_v = 4.092 \times 10^{-6} \text{ s}^{-1}$, $K_v = 5.114 \times 10^{-4} \text{ s}^{-1}$, $D_v = 0.96 \text{ nm}^2/\text{s}$. (a) Void radius *R*, (b) void growth rate dR/dt, (c) vacancy concentration as a function of radius at $t = 2 \times 10^5 \text{ s}$.



Figure 4.5. Simulations with vacancy source and effective sink (SS) and comparison to quasi-steady state approximation for increased S_v and K_v , maintaining the same vacancy concentration far from the bubble in the matrix, $c_v^{ss} = 0.008$. $S_v = 8.184 \times 10^{-6} \text{ s}^{-1}$, $K_v = 1.0228 \times 10^{-3} \text{ s}^{-1}$, $D_v = 0.96 \text{ nm}^2/\text{s}$. (a) Void radius R, (b) void growth rate dR/dt, (c) vacancy concentration as a function of radius at $t = 2 \times 10^5 \text{ s}$.

indeed the case. Agreement between the simulated vacancy concentration profile and the quasi-steady state analytical model is again relatively good, as shown in Figure 4.6c at $t = 2 \times 10^5$ s.

4.3.3 Comparison to chemical stress model

In this section, simulations are compared to the chemical stress model of growth rate (Equation 4.26). The chemical stress model includes the effect of interstitial and vacancy production, recombination, and sink absorption, and thus provides a more complete physical picture of bubble growth for this simplified geometry, although several approximations are needed to reach the analytical expression of Equation 4.26. Thus, one potential strategy for parameterizing vacancy-only phase-field models is to set the phase-field model parameters so that they best match the growth rates of the chemical stress model.

The SO phase-field model can be parameterized to match the chemical stress model using Equation 4.10 and 4.26, resulting in

$$S_{v} = \frac{3D_{v}R}{\mathcal{R}^{3}} \left(1 - \frac{Z_{v}}{Z_{i}}\right) \left(c_{v}^{ss} - c_{R}\right)$$

$$(4.43)$$

This is only valid at one particular value of R. The SS phase-field model, while appealing in that it allows the physical value of c_v^{ss} to be maintained in the bulk of the matrix, is more difficult to parameterize to match the chemical stress model. By Equation 4.25, in addition to S_v , D_v and K_v also impact the growth rate. Although S_v and K_v may be considered as effective parameters whose values do not necessarily need to match physical constants, D_v is an important physical parameter whose value controls the rates of other processes such as coarsening, and adjusting it to an arbitrary value could unphysically affect the rates of these other processes. Thus, when trying to match a growth rate from a more physical model, the SO approach is more suitable.

The SO phase field model was parameterized using Equation 4.43. Since the exact values of Z_v are Z_i are not important here, only their ratio, and Z_i is typically greater than Z_v by a few percent [19], we choose $Z_v = 1$ and $Z_i = 1.1$, resulting in $S_v = 5.03 \times 10^{-10} \text{ s}^{-1}$ for the initial bubble radius of R = 30 nm. This is 5.23 times greater than the Xe production rate in typical light water reactor operation [14], and thus within the range of effective vacancy production rates considered in previous parametric study [8]. In Figure 4.7, the simulated bubble growth rate using the SO model with $S_v = 5.03 \times 10^{-10} \text{ s}^{-1}$ is compared to the quasi-steady state analytical growth rate for the SO model and the chemical stress model. The analytical model matches the chemical stress model at R = 30, but decreases more rapidly with increasing R than the chemical stress model. This is because the SO case analytical model depends on $1/R^2$, while the chemical stress model depends on 1/R. The growth rate in simulation is significantly below both analytical models during the initial stages of growth, due to the time required for the vacancies to build up to the steadystate vacancy concentration profile. The simulated growth rate eventually matches the quasi-steady analytical model well, but remains lower than in the chemical stress model.

4.4 Discussion

The quasi-steady state analytical models described in this chapter provide useful insight into how phase-field models that do not include interstitials can more effectively capture the behavior of the full picture of vacancy-interstitial



(c)

Figure 4.6. Simulations with vacancy source and effective sink (SS) and comparison to quasi-steady state approximation for decreased D_v . $S_v = 4.092 \times 10^{-6} \text{ s}^{-1}$, $K_v = 5.114 \times 10^{-4} \text{ s}^{-1}$, $D_v = 0.48 \text{ nm}^2/\text{s}$. (a) Void radius R, (b) void growth rate dR/dt, (c) vacancy concentration as a function of radius at $t = 2 \times 10^5 \text{ s}$.



Figure 4.7. Comparison of growth rates using vacancy source only (SO), with $S_v = 5.03 \times 10^{-10} \text{ s}^{-1}$ to match initial growth rate of chemical stress growth model from Equation 4.26, along with growth rate from chemical stress model.

production, recombination, and sink absorption. The analytical models were shown to describe the behavior of phasefield models well, especially when the bubble growth rate is small. The growth rate in the SO phase-field model has only a very weak dependence on diffusivity, consistent with the analytical model, which predicts no dependence on diffusivity. The initial growth rate of the SO model is significantly lower than that predicted by the analytical model, due to the fact that some time is required for the vacancy concentration to build up to its quasi-steady state value. In future work, this discrepancy could be alleviated by initializing the vacancy concentration field in the phase-field model based on the analytical solution (if appropriate for the physical problem being simulated).

The SS model produces growth rates much larger than the chemical stress model using physically motivated parameters for diffusivity, vacancy source, and effective sink terms. Surprisingly, the growth rate of bubbles was different for different choices of source and effective sink terms, even though these choices maintained the same value of steady-state vacancy concentration. Compared with the SO model, the growth rate of the SS model is a much more complicated function of model parameters, making it more difficult to parameterize to match predictions of the chemical stress model.

Bubble growth rate with the SO model was compared to the chemical stress model. Although the growth rate can be matched between the two models for a given bubble radius, the growth rate in the SO model decreases more rapidly with radius than the chemical stress model, making it impossible to match the growth rate at all times. In future work, rather than setting the vacancy source strength by matching the growth rates at one particular bubble radius *R*, the source strength could be determined by fitting such that the difference between growth rates between the SO and chemical stress models is minimized for some chosen range of bubble sizes.

5. MULTISCALE MODELING OF UO₂ HBS PUL-VERIZATION

5.1 Phase-field fracture model

The phase-field fracture model is formulated based on the mechanics minimization problem that is regularized and approximated using the phase-field variable *c*, as per:

$$\{\boldsymbol{u}, \boldsymbol{c}\} = \underset{\boldsymbol{u}, \boldsymbol{c}}{\arg\min} \Psi(\boldsymbol{u}, \nabla \boldsymbol{u}, \boldsymbol{c}, \nabla \boldsymbol{c}), \tag{5.1a}$$

subject to
$$\boldsymbol{u} = \boldsymbol{g}, \quad \forall \boldsymbol{x} \in \partial \Omega_D,$$
 (5.1b)

$$\dot{c} \ge 0, \quad \forall x \in \Omega,$$
 (5.1c)

where *u* is the displacement vector. Eq. (5.1c) represents the irreversibility condition equivalent to the "no healing" condition on the permanent crack set. The objective function $\Psi(\boldsymbol{u}, \nabla \boldsymbol{u}, c, \nabla c)$ is defined as:

$$\Psi(\boldsymbol{u}, \boldsymbol{\nabla}\boldsymbol{u}, c, \boldsymbol{\nabla}c) = \Psi_{\text{elastic}}(\boldsymbol{\nabla}\boldsymbol{u}, g(c)) + \Psi_{\text{fracture}}^{l}(c, \boldsymbol{\nabla}c) - \Psi_{\text{dissipation}}(c) - \Psi_{\text{external}}^{\text{traction}}(\boldsymbol{u}) - \widetilde{\Psi}_{\text{external}}^{\text{pressure}}(\boldsymbol{u}, c, \boldsymbol{\nabla}c),$$
(5.2a)

$$\Psi_{\text{elastic}}(\nabla \boldsymbol{u}, g(c)) = \int_{\Omega} g(c) \psi_{\text{elastic}}^{\langle A \rangle}(\nabla \boldsymbol{u}) \, \mathrm{d}V + \int_{\Omega} \psi_{\text{elastic}}^{\langle I \rangle}(\nabla \boldsymbol{u}) \, \mathrm{d}V,$$
(5.2b)

$$\Psi_{\text{fracture}}^{l}(c, \nabla c) = \int_{\Omega} \mathcal{G}_{c} \gamma_{l}(c, \nabla c) \, \mathrm{d}V, \qquad (5.2c)$$

$$\dot{\Psi}_{\text{dissipation}}(\dot{c}) = \int_{\Omega} \frac{1}{2} \eta \dot{c}^2 \, \mathrm{d}V, \qquad (5.2d)$$

$$\Psi_{\text{external}}^{\text{traction}}(\boldsymbol{u}) = \int_{\partial\Omega_N} \boldsymbol{\tau} \cdot \boldsymbol{u} \, \mathrm{d}\boldsymbol{A}, \tag{5.2e}$$

$$\widetilde{\Psi}_{\text{external}}^{\text{pressure}}(\boldsymbol{u}, \boldsymbol{c}, \boldsymbol{\nabla} \boldsymbol{c}) = -\int_{\Omega} p \boldsymbol{\nabla} \boldsymbol{c} \cdot \boldsymbol{u} \boldsymbol{I}'(\boldsymbol{c}) \, \mathrm{d} \boldsymbol{V}.$$
(5.2f)

It considers the energy contribution due to deformation ($\Psi_{elastic}$), fracture ($\Psi_{fracture}^{l}$, internal dissipation ($\Psi_{dissipation}$), and external pressure ($\Psi_{external}^{traction}$, $\widetilde{\Psi}_{external}^{pressure}$). Let us define the trial spaces:

$$\mathcal{U} = \left\{ \boldsymbol{u} | \boldsymbol{u} \in \mathcal{H}^{1}(\Omega)^{d}, \boldsymbol{u} = \boldsymbol{g}, \forall \boldsymbol{x} \in \partial \Omega \right\}, \quad \mathcal{C} = \left\{ c | c \in \mathcal{H}^{1}(\Omega), \dot{c} \ge 0, \forall \boldsymbol{x} \in \Omega \right\},$$
(5.3)

along with their corresponding weighting spaces:

$$\mathcal{V} = \left\{ \delta \boldsymbol{u} | \delta \boldsymbol{u} \in \mathcal{H}^1(\Omega)^d, \boldsymbol{u} = \boldsymbol{0}, \forall \boldsymbol{x} \in \partial \Omega \right\}, \quad \mathcal{Q} = \left\{ \delta c | \delta c \in \mathcal{H}^1(\Omega), \delta c \ge 0, \forall \boldsymbol{x} \in \Omega \right\}.$$
(5.4)

The optimality conditions for \boldsymbol{u} follow from the functional derivative of the objective function Ψ , as per:

$$\int_{\Omega} \nabla \cdot \frac{\partial \psi_{\text{elastic}}(\nabla u, g(c))}{\partial \nabla u} \, \mathrm{d}V - \int_{\partial \Omega_N} \frac{\partial \psi_{\text{elastic}}(\nabla u, g(c))}{\partial \nabla u} n \, \mathrm{d}A$$
$$+ \int_{\partial \Omega_N} \frac{\partial \psi_{\text{external}}^{\text{traction}}(u)}{\partial u} \, \mathrm{d}A + \int_{\Omega} \frac{\partial \widetilde{\psi}_{\text{external}}^{\text{pressure}}(u, c, \nabla c)}{\partial u} \, \mathrm{d}V = 0, \quad \forall \Omega' \subseteq \Omega, \forall \partial \Omega'_N \subseteq \partial \Omega_N.$$
(5.5)

Substituting (5.2) yields:

$$\nabla \cdot \boldsymbol{\sigma} - pI'(c)\nabla c = \boldsymbol{0}, \quad \forall \boldsymbol{x} \in \Omega,$$
(5.6a)

$$\sigma n = \tau, \quad \forall x \in \Omega_N, \tag{5.6b}$$

where $\sigma = \frac{\partial \psi_{\text{elastic}}}{\partial \nabla u}$ is the stress-strain constitutive relation. The optimality conditions for *c* that are subject to the irreversibility constraint (5.1c) also follow from the functional derivative (with respect to the rate of the objective function) and recover the Karush–Kuhn–Tucker conditions, such that:

$$\int_{\Omega} \frac{\partial \psi_{\text{elastic}}(\nabla \boldsymbol{u}, \boldsymbol{g}(c))}{\partial c} \dot{c} \, dV - \int_{\Omega} \nabla \cdot \frac{\partial \psi_{\text{fracture}}^{l}(c, \nabla c)}{\partial \nabla c} \dot{c} \, dV + \int_{\partial\Omega} \frac{\partial \psi_{\text{fracture}}^{l}(c, \nabla c)}{\partial \nabla c} \cdot \boldsymbol{n} \dot{c} \, dA$$
$$+ \int_{\Omega} \frac{\partial \psi_{\text{fracture}}^{l}(c, \nabla c)}{\partial c} \dot{c} \, dV + \int_{\Omega} \nabla \cdot \frac{\partial \widetilde{\psi}_{\text{external}}^{\text{pressure}}(c, \nabla c)}{\partial \nabla c} \dot{c} \, dV - \int_{\partial\Omega} \frac{\partial \widetilde{\psi}_{\text{external}}^{\text{pressure}}(c, \nabla c)}{\partial \nabla c} \cdot \boldsymbol{n} \dot{c} \, dA \tag{5.7}$$
$$+ \int_{\Omega} \frac{\partial \widetilde{\psi}_{\text{external}}^{\text{pressure}}(c, \nabla c)}{\partial c} \dot{c} \, dV + \int_{\Omega} \frac{\partial \psi_{\text{dissipation}}(\dot{c})}{\partial \dot{c}} \dot{c} \, dV = 0, \quad \forall \Omega' \subseteq \Omega, \forall \partial \Omega'_N \subseteq \partial \Omega_N.$$

Again, substituting (5.2) yields:

$$\phi^{f} \ge 0, \quad \dot{c} \ge 0, \quad \phi^{f} \dot{c} = 0,$$
with $\phi^{f} = \begin{cases} \eta \dot{c} - \nabla \cdot \boldsymbol{\xi} + \frac{G_{c}}{c_{0}l} \alpha'(c) - Y, & \forall \boldsymbol{x} \in \Omega, \\ \boldsymbol{\xi} \cdot \boldsymbol{n} + pI'(c)\boldsymbol{u} \cdot \boldsymbol{n}, & \forall \boldsymbol{x} \in \partial\Omega \end{cases}$
(5.8)

where $\xi = \frac{\partial \psi_{\text{fracture}}^l}{\partial \nabla c} = \frac{2\mathcal{G}_c l}{c_0} \nabla c$ is the thermodynamic conjugate to ∇c , and Y is the generalized fracture driving force consisting of contributions from the active elastic energy density as well as work done by pressure:

$$Y = -g'(c)\psi_{\text{elastic}}^{\langle A \rangle} + pI'(c)\nabla \cdot \boldsymbol{u}.$$
(5.9)

With a view toward the solution strategy, using a variational inequality solver (e.g., a primal-dual active set algorithm) to enforce the irreversibility constraint requires discretization of the fracture envelope ϕ^f only on the inactive sets $\dot{c} > 0$ and $\phi^f = 0$. Hence, only the weak form in the case of $\phi^f = 0$ is outlined below:

Given g, τ , and c_0 , find $u \in \mathcal{U}$ and $c \in \mathcal{C}$, such that $\forall \delta u \in \mathcal{V}$ and $\forall \delta c \in Q$:

$$\int \boldsymbol{\sigma} : \boldsymbol{\nabla} \delta \boldsymbol{u} \, \mathrm{d}V + \int_{\Omega} p I'(c) \boldsymbol{\nabla} c \cdot \delta \boldsymbol{u} \, \mathrm{d}V - \int_{\partial \Omega_N} \boldsymbol{\tau} \cdot \delta \boldsymbol{u} \, \mathrm{d}A = 0, \qquad (5.10a)$$

$$\int_{\Omega} \eta \dot{c} \delta c \, \mathrm{d}V + \int_{\Omega} \boldsymbol{\xi} \cdot \boldsymbol{\nabla} \delta c \, \mathrm{d}V + \int_{\Omega} \frac{\mathcal{G}_c}{c_0 l} \alpha'(c) \delta c \, \mathrm{d}V - \int_{\Omega} Y \delta c \, \mathrm{d}V + \int_{\partial\Omega} p I'(c) \boldsymbol{u} \cdot \boldsymbol{n} \delta c \, \mathrm{d}A = 0.$$
(5.10b)

Furthermore, the macro-scale pulverization behavior is approximated by using periodic boundary conditions (PBCs). PBCs are useful for avoiding the boundary effects caused by finite size, and for making the system deform like an infinite one. In MOOSE, the global strain system was implemented to enforce the PBC [27]. The global strain system can capture the deformation with applied loads while still maintaining the periodic strains.

5.2 MD simulations of grain boundary fracture with nm-sized bubbles

In a NEAMS milestone investigating fracture criteria of HBS using atomistic and meso-scale simulations by Galvin et al. [28], molecular dynamics (MD) simulations were conducted to predict the amount of stress needed to cause GB failure in UO₂ containing a Xe bubble. This was investigated as a function of temperature, bubble pressure (given by the Xe:Schottky Defect (SD) ratio for a given temperature) and at different bubble separations. $\Sigma 5$ tilt GB structures in a slab geometry were used, containing a bubble of different sizes of either a cylindrical (representing a sphere) or a lenticular shape (see figure 5.1).

The GB bubble structures were run for different temperature ramps and then stress-strain MD simulations were carried out using the bubble structures from the temperature ramps where the GB did not fail, to predict failure stresses at the grain boundary. For this the structure was elongated in the direction normal to the grain boundary (x-direction) until a strain of 5% was achieved. During this procedure the stress increases until a maximum stress (failure stress) is reached, after which the stress decreases. The predicted failure stresses of the GB as a function of temperature are presented in Figure 5.2.

It is observed that for an increase in temperature there is a decrease in the failure stress. This is due to the thermal expansion of the bubble which assists in driving fracture. Moreover, an increase in the Xe:SD ratio (increase in bubble density) also causes a lower failure stress, as does a decrease in the bubble separation. It is also seen in figure 5.2 that the bubble shape does not greatly influence the failure stress. For both the cylindrical and lenticular cases at a similar



Figure 5.1. A 5 nm cylindrical Xe bubble shown by green spheres in a Σ 5 tilt GB of UO₂ where the U atoms are shown by blue spheres and the O atoms by red spheres.



Figure 5.2. Failure stresses for a grain boundary containing a bubble at different temperatures, different pressures (Xe:SD) and for different bubble separations.

	0			
Shape	Separation (Å)	Xe:SD	m	С
Lenticular	85	1:1	-2.21x10-3	4.13
Lenticular	155	1:1	-1.88x10-3	4.61
Cylindrical	157	1:1	-1.97x10-3	4.78
Lenticular	189	1:1	-1.82x10-3	4.89
Lenticular	85	1.2:1	-2.58x10-3	2.92
Lenticular	155	1.2:1	-2.60x10-3	4.04
Cylindrical	157	1.2:1	-3.18x10-3	4.47
Lenticular	189	1.2:1	-2.52x10-3	4.39
Lenticular	155	1.4:1	-2.47x10-3	2.58
Cylindrical	157	1.4:1	-4.62x10-3	3.70
Lenticular	189	1.4:1	-2.91x10-3	3.67

Table 5.1. Fitting parameters for the different cases considered in the MD simulations

bubble separation (155 Å for the lenticular bubble and 157 Å for the cylindrical) the failure stresses are almost identical across the temperature range and for the different Xe:SD cases. The fits describing the failure stresses (σ_c) in figure 5.2 are described by the linear equation:

$$\sigma_c = mT + C \tag{5.11}$$

where m and C are fitting coefficients given in Table 5.1.

In addition to the cases presented in Table 5.1, a Xe:SD ratio 2.0 case has been considered where the fracture pressure changes as a function of temperature such that,

$$\sigma_c = 9.056 \times 10^{-4} T^2 + 3.346T + 3075, \tag{5.12}$$

where, σ_c is the fracture stress in MPa and T is the temperature in K. It is noteworthy that fracture stress decreases with increase in Xe:SD ratios and temperature.

5.3 Multiscale Model Description

This year, the phase-field fracture approach is extended to utilize a multiscale approach to have better prediction of the pulverization criteria. In this section we present several adjustments that were made to the phase-field fracture simulations to update the pulverization criteria. First of all, the fracture simulation utilize the realistic HBS structure and bubble geometry generated from the phase-field-based simulations presented in Chapter 2. This is done to realistically capture the impact of the large convex bubbles on the pulverization criteria. Furthermore, the temperature effect is included in the simulations. A typical LOCA test usually ramps the temperature at a rate of 5 K/sec. In this case to reduce the computational cost, we use a temperature ramp of 10 K/sec rate. This speeds up the simulations without affecting the critical stress at which the fracture occurs. The effect of thermal strain is added to the model using the eigenstrain approach such that the strain value is updated:

$$\varepsilon_{total} = \varepsilon - \varepsilon_{thermal} \tag{5.13}$$

The bubble pressure is ramped in accordance with the temperature ramping using a linear relationship starting from an initial pressure close to 100 MPa. An evolution of bubbles pressure as a function of temperature can be obtained from the phase-field simulation to make the model prediction more accurate. Furthermore, for the multiscale simulations, the critical stress values for the mesoscale simulations are obtained from the MD calculations described in Section 5.2.

5.4 Pulverization in partially restructured regions

Figure 5.3 shows the crack propagation captured using the phase-field fracture simulations performed on 30% and 60% restructured HBS regions with single 100 nm bubble. Similar crack growth pattern is observed in both the structures. Moreover, the critical bubble pressure and temperature at which pulverization occurs are also similar for both the cases. For the 30% restructured region, failure occurs at 201 MPa pressure and 1228 K temperature. For the 60% case, critical pressure and temperature for failure are 202 MPa and 1235 K, respectively. This indicates that the pulverization is primarily governed by the operating conditions and bubble pressure, rather than restructuring fraction. Formation of new GBs due to grain subdivision weakens the material and creates a GB network which facilitates crack propagation leading to pulverization. Figure 5.4 shows the degradation of failure stress and increase in bubble pressure as a function of temperature during LOCA conditions. It is noteworthy that the rate of temperature and pressure ramping does not seem to influence the critical bubble pressure at which pulverization occurs.



Figure 5.3. Fracture behavior in partially restructured HBS with a) 30%, and b) 60% restructuring with single 100 nm bubble.



Figure 5.4. Ramping of the bubble pressure with temperature during LOCA until failure occurs

Next we consider another HBS region with two bubbles to investigate the effect of bubble density on the pulverization. Three partially restructured regions with a fraction of 17%, 30%, and 45% has been considered in this case. It is observed that the pulverization can occur at a restructuring fraction as low as 17%. It is also noticeable that for all the cases, the fracture occurs at similar bubble pressure and temperatures. Hence, crack initiation is primarily governed by the bubble pressure, while the propagation is dictated by the weakened grain boundaries. The critical pressure at which the crack initiates is 208 MPa for the 17% and 30% restructuring case. The temperature at failure is 1272 K for both the cases. For the 45% restructured region, the critical pressure is 205 MPa, and failure occurs at 1252.5 K temperature. Currently, BISON assumes that pulverization only occurs after 50% restructuring. However, the mesoscale analysis presented here indicates that the value is conservative and pulverization may occur at even lower restructuring fraction. This supports the experimental observation where pulverization has been noticed in partially restructured regions.



Figure 5.5. Fracture behavior in partially restructured HBS with a) 17%, and b) 30%, c) 45% restructuring with two bubbles.

5.5 Uncertainty quantification of the model predictions

In this section we present the fracture analysis within fully formed HBS structures. The initial HBS structures are obtained from the phase-field simulations presented in Section 2. Three geometries with varying bubble sizes considered for this study are shown in figure 5.6. Additionally, another HBS structure with two bubbles has also been studied to observe the effect of structural variations and bubble interactions on the pulverization criteria. These simulations take into account a realistic bubble shape compared to previous years when only spherical bubbles were considered. Figure 5.7 shows the crack propagation path and corresponding maximum principal stress. In this case, the pulverization occurs at critical bubble pressure of 202 MPa and at 1234 K temperature.



Figure 5.6. Initial HBS structures used in the multiscale fracture simulations.



Figure 5.7. Crack propagation in fully restructured HBS. Pulverization occurs at critical bubble pressure of 202 MPa and at 1234 K temperature.

A statistical analysis is done for quantifying the uncertainties in the model prediction based on variation in bubble number densities and material properties. In computational models uncertainties may originate from several sources including, but not limited to, input parameters, material properties, etc.. Additionally, numerical aspects of a model can also introduce uncertainty in its predictions. Here, we assume that the variation in Xe:SD ratio, bubble spacing, and bubble geometry in MD simulations are the uncertainty parameters for the mesoscale simulations. They introduce the uncertainty in the prediction of critical bubble pressure at which pulverization occurs. For each of the initial conditions presented in Figure 5.6, the fracture stress is varied following the data presented in Section 5.2. The critical

bubble pressure for pulverization obtained for different applied stresses corresponding to a single MD case and the mean across different cases are presented in Figure 5.8. It is observed that the critical pressure for failure decreases with increase in porosity. In addition, the critical pressure increases with increase in applied external pressure. This is consistent with what has been observed during experiments [29]. It is noticeable that the effect of porosity and external loading is slightly less pronounced on the mean values than the individual case. This is because the effect of bubble geometry and corresponding failure stress is not explicitly captured when the critical pressure values are averaged across different scenarios. Figure 5.9 shows the prediction uncertainties for the three cases with different external pressures. Uncertainty bands are presented in the form of 1 standard deviation values. In all the cases, the standard deviation is less than 10%.



Figure 5.8. Variation of critical pressure for pulverization under the influence of different external pressures corresponding to a) a single MD case, b) mean value across different cases.



Figure 5.9. Uncertainty quantification of the critical bubble pressure for failure corresponding to the values for applied stress a) 0 MPa, b) 30 MPa, and c) 60 MPa. Uncertainty bands represent 1 standard deviation.

6. OVERALL CONCLUSIONS AND FUTURE WORK

In conclusion, this report summarizes the advancements made to the existing phase-field-based multiscale model to improve the prediction of bubble growth in the HBS regions. In Chapter 2 we present the effect of the intragranular fission gas evolution mechanisms on the growth of the intergranular bubbles. Compared to previous years, this model represents more realistic bubble growth rate. We also utilize the coupled model to capture the HBS formation using grain nucleation type algorithm. The evolution of the restructuring fraction is compared against the analytical HBS formation model available in BISON. It is demonstrated that the current BISON model does not include the effect of temperature on the restructuring. Hence, a mesoscale-informed mechanistic model for restructuring needs to be implemented in BISON to improve its robustness. This will be pursued in the following year.

The Helmholtz free energy of high-density Xe gas in UO_2 was developed from thermodynamic integration of a recently developed virial equation of state. The equation of state and Helmholtz free energy differ significantly from the commonly used van der Waals equation of state at high Xe densities. The newly developed free energy is most relevant for nano-sized gas bubbles such as found in the intragranular regions of UO_2 , where pressures are very high. A parabolic approximation to the Helmholtz free energy was determined for convenience in future phase-field modeling. This improved free energy will significantly improve the accuracy of phase-field models when simulating nano-sized fission gas bubbles.

Two different approaches to incorporating net vacancy production in phase-field models were compared: the sourceonly (SO) approach and source+sink (SS) approach. An analytical model for the SS approach was derived, and the SO approach was compared to an existing analytical model. Good agreement was found between the analytical models and phase-field simulations, especially for lower bubble growth rates. The SO approach can more easily be parameterized to match growth rates of the chemical stress model that considers a more physically realistic picture of interstitials and vacancies. However, the growth rate in the SO model cannot match the chemical stress model for all simulation times. In future work, the effective vacancy source term in the SO can be more accurately determined by fitting the growth rate of the SO model to the chemical stress model for a range of bubble sizes. This will have broad applicability to make phase-field simulations of bubble growth more accurate.

Finally, the pulverization criteria in HBS region has been evaluated using a multiscale modeling approach. The phase-field fracture model, in this case, incorporates the fracture properties obtained from MD calculations and HBS structure generated from phase-field simulations presented in Chapter 2. The onset of pulverization in partially restructured regions has also been evaluated. It is observed that pulverization may occur at a lower restructured fraction that what is currently used by BISON. Findings from the mesoscale simulation indicates that pulverization can occur at a

restructuring fraction as low as 17%. This is consistent with the experimental observation of fragmentation in partially formed HBS structures. In light of this, it is recommended that BISON's restructuring criteria for fission gas release and FFRD be updated.

In the following years, the phase-field-based restructuring model will be extended to include the role of dislocation interaction and grain orientation to distinguish between different types of grain boundaries to better understand the restructuring that occurs both within the rim region and at the dark region closer to the fuel center. The BISON restructuring fraction model will be updated based on the mesoscale observations. Such updates are necessary to evaluate the fuel performance as a function of radial location.

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