LA-UR-14-24304

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Intended for: Report

Issued: 2014-11-26 (rev.1)

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Effective fission gas diffusivity study using First Passage Monte Carlo

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(Dated: June 2, 2014)

I. INTRODUCTION AND REVIEW

A key challenge in the development of high burn-up generation IV reactor technologies is understanding the fission gas behavior in uranium dioxide fuel. The size and spatial distributions of fission gas bubbles are key parameters in determining the gas transport properties and the fuel performance. Fission gas retention can adversely influence the thermal and mechanical properties of reactor fuels, depending on the size of the bubbles, while release of gaseous species from the fuel can lead to cladding failure at high burn-up.

In previous studies we have investigated the diffusion process of Xe fission gas atoms in bulk $\text{UO}_{2\pm x}$ based on density functional theory (DFT) and empirical potential calculations [1, 2]. Models for the Xe diffusivity were developed for both intrinsic and irradiation conditions. These studies [1, 2] addressed the first of three steps in the fission gas release process, namely 1) diffusion of individual fission gas atoms from the grain interior to grain boundaries. However, the description of Xe bulk diffusion in Refs. [1, 2] does not provide a complete picture of step 1), since fission gas diffusion is also affected by the formation of small fission gas bubbles in the grain interior, acting as sinks for the diffusing fission gas atoms. Under irradiation these bubbles do not grow beyond the nanometer range in size due to resolution by fission fragments [3–5]. Moreover, these intragranular bubbles are usually assumed to be stationary for in-pile conditions (under irradiation) and thus act as sinks rather than contribute to mass transport, though bubble growth and migration are both possible for out-of-pile conditions (no irradiation) as well as for transients [6–9]. The intergranular fission gas bubbles may reach dimensions of several micrometers.

Intragranular fission gas bubbles are continuously resolved during reactor operation. Schwen and Averbeck have reviewed the main mechanisms for the resolution of fission gas atoms by fission fragments [5]. The available bubble population models build on two generally accepted fundamental mechanisms for re-resolution of gas atoms from bubbles. One, proposed by Nelson [10] and later termed homogeneous re-resolution, constitutes the interaction of the fission fragments (ff) with fission gas bubbles through energetic collision cascades. Individual fission gas atoms are ejected from bubbles by this mechanism through singular binary collision recoil events. A threshold energy for gas atoms to leave the bubbles is postulated in an ad hoc manner. The other, termed heterogeneous re-resolution, and proposed by Turnbull [11], is an unspecified interaction of the fission fragments with entire bubbles, leading to the instantaneous total or partial re-resolution of the contained fission gas in the UO_2 matrix. A comprehensive discussion of analytical bubble population models has been presented by Tucker and White [3] and more recently by Olander and Wongsawaeng [12]. Of particular interest for the study by Schwen and Averbeck [5] were models based on the homogeneous re-resolution, such as Ronchi and Matzkes [13], as well as models that do not explicitly specify the re-resolution mechanism, e.g. Lösönens work [8].

The fact that the intragranular fission gas bubbles act as sinks implies that they reduce the effective fission gas diffusivity. The bubbles themselves are usually considered immobile, however that conclusion depends on the size distribution of the bubbles (the mobility is expected to decrease with size). Rate theory models have been developed to express the effective fission gas diffusivity (D') in terms of the Xe bulk diffusivity (D) and the trapping (g) and resolution rates (b') [14]:

$$D' = \frac{Db'}{b' + g}. \quad (1)$$

In Ref. [2] this equation was applied to transform the DFT/empirical potential data for the bulk diffusivity D into D' , which is the parameter used in most fuel performance fission gas release models [15, 16]. Standard literature values were used for b' and g [14–16]. In order to deliver a complete mechanistic fission gas release model, these two parameters should be investigated and derived from lower length scale simulations that account for mechanistic aspects of the fission gas behavior in the fuel, similar to the approach in Ref. [2]. However, due to the time and length scale limitations of DFT and molecular dynamics simulations, they are not well suitable to address this problem as stand-alone applications. To solve this problem, Schwen *et al.* have developed hybrid molecular dynamics and Monte Carlo techniques as well as a first passage Monte Carlo simulation methodology to study the properties of intragranular fission gas bubbles [4, 5]. The focus of the work in Ref. [5] is the homogeneous re-resolution mechanism, and the feasibility of using computer simulations to obtain quantitative data on the re-resolution of Xe atoms. A hybrid approach was employed whereby Monte Carlo (MC) simulations are used to obtain the full recoil energy spectrum of

the Xe atoms in intragranular bubbles under fission fragment irradiation, and molecular dynamics (MD) simulations are used to build a library of re-solution events for these energies. While the MC simulations themselves provide re-solution information, Ref. [5] chose to verify the data by running full MD simulations within a selected recoil energy window. The lower energy bound coincides with recoils that have a very low re-solution probability, and are therefore unimportant. The upper energy boundary is set by the practicality of running MD simulations. For recoils above this cut-off, and there are only 2% such recoils, binary collision MC simulation are again employed. As the study shows, this introduces negligible error in the calculations. The second study by Schwen *et al.* [4] introduces a first passage based Monte Carlo algorithm to investigate the population evolution of Xe fission gas bubbles in UO_2 fuels. Growth laws were obtained for homogeneous and heterogeneous re-solution models for a wide range of gas and bubble diffusivities. Under certain irradiation conditions, bubble populations find dynamic steady states. Homogeneous re-solution is included using a Monte Carlo binary collision model, while heterogeneous re-solution is modeled as the ad hoc destruction of bubbles. Examples of their results is shown in Figure 1.

In this study, we have explored the possibility of using extended versions of the two approaches developed by Schwen *et al.* [4, 5] for calculating values of b' and g or, if deemed appropriate, deriving new models to represent the effective fission gas diffusivity.

Above we have outlined the various aspects of the first step in fission gas release and the physical processes that impact the rate at which this occurs. The remaining two steps in the fission gas release process are 2) nucleation, growth and interconnection of fission gas bubbles at the grain boundaries and 3) percolation of these intergranular bubbles, which connects them to free surfaces and subsequently leads to venting of the fission gas [3, 17]. The Monte Carlo methods developed in this work are able to simulate the interaction between fission gas atoms and sinks, in particular grain boundaries. This provides an opportunity for, not only using the first passage Monte Carlo simulation methodology to study the intragranular bubbles population, but also how they interact with grain boundaries. This includes resolution of large intergranular bubbles, which will provide important understanding of the second fission gas release step.

II. RESULTS AND DISCUSSION

Progress has been made towards determining effective diffusion coefficients of intragranular fission gas in the presence of sinks such as grain boundaries. For the simulation of dilute fission gas loaded UO_2 fuel systems we utilize a first passage Monte Carlo approach [4]. In this subclass of object Monte Carlo algorithms the fission gas atoms and bubbles are represented by Brownian walkers. We chose a surface diffusion based size dependent mobility for the walkers in the simulation. Reactions between walkers are implemented to facilitate bubble growth and coalescence. Resolution is implemented through coupling to a binary collision Monte Carlo code [5].

Typical fission gas concentrations are less than 1%. The small concentration of walkers in this system results in a sparseness of walker interactions. For significant amounts of time the diffusing gas atoms and bubbles occupy disjoint regions of space. First passage Monte Carlo offers a way to replace most of the eventless diffusion jumps by a vastly reduced number of super-jumps. It does so by partitioning the sample volume into non-overlapping sub volumes (protective zones), with each containing only one diffusing walker. The super-jump is given by the direct move of the walker from its original location to the edge of its protective zone. The time associated with this super-jump is the time it takes the walker to reach the edge of the protective zone for the first time, hence *first* passage. This first passage time can be calculated analytically for certain geometries of protective zones. In particular the sphere is a natural choice, as the probability density for the super-jump to go to any point on its surface is uniform in the case of isotropic diffusion. It should be noted that the random walk processes of individual diffusion jumps and the first passage super-jumps are statistically equivalent.

First passage Monte Carlo can offer speed-ups of several orders of magnitude in dilute systems, and thus it enables simulation times up to several years. In contrast to mean field theories, local fluctuations and spatial correlations are included. The model provides simple access to a multitude of statistical data on the simulated systems. The size evolution of individual bubbles can be tracked, average lifetimes computed, individual knockouts can be followed and return probabilities calculated as a function of precipitate size. Our approach offers flexibility to change or switch out underlying mechanisms allowing direct access to the influence of each input parameter and every sub-process in the population evolution. A limitation of the method is the assumption of isotropic material properties within the protective zones.

An effort has to be made to treat the interactions between particles, which cannot be separated into non-overlapping volumes at the time of interaction. We handle this by falling back to individual jumps as long as two particles are within a minimum distance of each other.

The presence of grain boundaries constitutes a further break in symmetry that has to be taken into account when constructing the bounding volumes for the walkers. Care must be taken to not have the bounding volumes intersect

FIG. 1: Both a) and b) as well as the captions are taken from Ref. [4]. a) Volume averaged bubble radius as a function of time, for two different re-resolution mechanisms and various diffusion constants. Fission gas is added at a constant rate of Xe/s. The growth law depends strongly on the re-resolution mechanism, yielding a $t^{1/6}$ dependence for the heterogeneous re-resolution case and $t^{1/3}$ as well as $t^{1/4}$ dependencies for the homogeneous re-resolution case. The curve labeled r_{max} denotes the maximum possible bubble size attainable in the simulation volume by aggregating all available Xe atoms into a single bubble. The scaling of the diffusion constants, which is related to the sample temperature, is reflected in a scaling of the volume-averaged bubble radius. b) Bubble size distributions for the homogeneous and heterogeneous re-resolution cases as a function diffusion constant. All histograms were taken at $t=3 \times 10^6$ s. The size distributions for the heterogeneous re-resolution runs (gray curves) are clearly peaked around an average radius, as opposed to the histograms of homogeneous re-resolution runs (black curves) which exhibit a maximum at the single gas atom radius. The amount of single gas atoms in solution is comparable for both re-resolution mechanisms at the same diffusivities. Both a) and b) as well as the captions are taken from [4].

with the grain boundaries to uphold the assumption of isotropic properties within the bounding volume. For walker grain boundary interactions a scheme similar to walker-walker interactions is being implemented. This augmentation of the existing first passage code is a significant undertaking that is still in progress.

With the grain boundaries available and as logical extension also support for point line sinks, we can study the effect of the spatial distribution of the fission gas within the grain on bubble coarsening and gas trapping, and the resulting change in effective diffusivity. In particular we will be able to measure the Booth flux of fission gas onto the grain boundaries. This flux is an important input parameter for studying the formation of intergranular fission gas bubbles, which impact the fission gas release from nuclear fuel.

Preliminary support for free surfaces on the rectangular simulation volume has been implemented. The terminating surfaces in either of the three cardinal directions can be set to either periodic or free boundary conditions. If any walker touches a periodic boundary it reenters the simulation cell on the opposite side, effectively generating an infinite array of replicated simulation cells. Any walker that touches a free boundary is removed from the simulation cell.

Figure 2 shows the change in fission gas concentration in a thin film with a thickness of 50 nm over time. This geometry is implemented by setting up a simulation cell of dimensions 50 nm $\times$ 15 nm $\times$ 15 nm and setting the boundary condition in the x direction to *free* while the boundaries in y and z direction are kept periodic. Gas can thus be released through the front and back surfaces in x direction. The two simulation scenarios compared are the release of Xe gas with all walker-walker interactions turned off (blue curve) and the release of Xe gas taking bubble formation and the resulting reduction in mobility into account (red curve). The gas release is slowed down by orders of magnitude as bubbles nucleate and coarsen, causing the red curve diverge from the blue curve further over time.

FIG. 2: Fission gas concentration change over time in a thin film with a thickness of 50 nm. Xe can leave the film through the front and back surfaces. The blue curve illustrated the release of non-interacting Xe atoms, while the red curve takes bubble formation and the resulting reduction in diffusivity into account.

III. CONCLUSIONS AND OUTLOOK

The effect of bubble formation on the effective mobility is apparent and warrants further investigation. Future work will study the mobility change in the presence of ongoing resolution and imperfect sinks. Resolution of gas from intragranular bubbles is expected to increase the effective mobility. The grain boundary description will have to be changed from simple free boundary conditions which remove gas from the simulation volume to sinks that can be loaded with gas, and track the amount of gas contained. This will allow for resolution from grain boundaries into the grain interior to occur. Furthermore tracking the gas loading of grain boundaries over time will give insight into the formation of intergranular fission gas bubbles and may help determine the timescales needed to grow a percolated bubble network which can lead to rapid release of fission gas.

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- [1] Andersson, D. A., Uberuaga, B. P., Nerikar, P. V., Unal, C., and Stanek, C. R., Phys. Rev. B 84, (2011) 054105.
 - [2] Andersson, D.A., Garcia, P., Liu, X.-Y., Pastore, G., Tonks, M., Millett, P., Dorado, B., Gaston, D.R., Andrs, D., Williamson, R.L., Martineau, R.C., Uberuaga, B.P., and Stanek, C.R., J. Nucl. Mater. 451 (2014) 225.
 - [3] White, R. J., and Tucker, M. O., J. Nucl. Mater. 118 (1983) 1-38.
 - [4] Schwen, Daniel, and R.S. Averback, J. Nucl. Mater. 402 (2010) 116-23.
 - [5] Schwen, D., M. Huang, P. Bellon, and R. S. Averback, J. Nucl. Mater. 392 (2009) 35-39.
 - [6] Kashibe, S., Une, K., and Nogita, K., J. Nucl. Mater. 206 (1993) 22-34.
 - [7] Löfönen, P., J. Nucl. Mater. 280 (2000) 56-72.
 - [8] Löfönen, P., J. Nucl. Mater. 304 (2002) 29-49.
 - [9] Mac Innes, D. A., and Brearley, I. R., J. Nucl. Mater. 107 (1982) 123-132.
 - [10] Nelson, R.S., J. Nucl. Mater. 31 (1969) 153.
 - [11] Turnbull, J., J. Nucl. Mater. 38 (1971) 203.
 - [12] Olander, D.R., Wongsawaeng, D., J. Nucl. Mater. 354 (2006) 94.
 - [13] Ronchi, C., Matzke, H.J., J. Nucl. Mater. 45 (1972/73) 15.
 - [14] Speight, M. V., Nucl. Sci. Eng. 37 (1969) 180-185.
 - [15] Forsberg, K., Massih, A. R., J. Nucl. Mater. 135 (1985) 140-148.

- [16] Forsberg, K., Massih, A. R., J. Nucl. Mater. 127 (1985) 141-145.
- [17] White, R. J., J. Nucl. Mater. 325 (2004) 61-77.