Chapter 17.

Modelling microstructural evolution under irradiation

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Abstract

Microstructural evolution of materials under irradiation is characterised by some unique features that are not typically present in other application environments. While much understanding has been achieved by experimental studies, the ability to model this microstructural evolution for complex materials states and environmental conditions not only enhances understanding, it also enables prediction of materials behaviour under conditions that are difficult to duplicate experimentally. Furthermore, reliable models enable designing materials for improved engineering performance for their respective applications. Thus, development and application of mesoscale microstructural model are important for advancing nuclear materials technologies. In this chapter, the application of the Potts model to nuclear materials will be reviewed and demonstrated, as an example of microstructural evolution processes.

Introduction

Microstructural evolution of nuclear fuels and claddings under irradiation is characterised by some unique features that are not typically present in other application environments. A very wide range of irradiation conditions, radiation with many different particles over a large range of energies, lead to formation of defects in crystalline materials. These defects can interact in many different ways with each other and existing defects such as grain boundaries to give rise to microstructural evolution not observed in other applications. These radiation-induced defects can alter the kinetics by enhancing diffusion. They can have more substantial effects such as void formation due to aggregation of vacancies. Under some conditions, radiation can create a large density of defects causing the crystalline material to transform to an amorphous state.

Swelling is another common consequence of radiation in many materials. The aggregation of vacancies to form voids is observed in many materials including some fuel rod claddings. The production of extra atoms by fission in nuclear fuel can strain the

lattice leading to swelling, albeit to a lesser extent. Nuclear fuels can also swell due to precipitation of fission gas (primarily Xe and Kr) into nanosized intragranular bubbles and sub-micron intergranular bubbles. The creation of extra atoms by fission or transmutation of atoms alters the chemistry of the fuel (see the next section for a detailed discussion) and results in microstructural evolution that is unique to nuclear materials.

Another feature that is unique to some nuclear materials is the large temperature gradient present in these materials that leads to different microstructural evolution in the different regions and segregation of components. Restructuring of fast reactor fuels to form an axial pore along the central axis of the fuel pellet is an example of this. Another unique feature of nuclear fuels is the accumulation of radiation damage at the outer rim of the fuels, which, in turn, drives recrystallisation in this region. Recrystallisation is virtually non-existent in most ceramics making this phenomenon most interesting in itself, but is of great importance for fuel performance. Finally, radiation-induced segregation of components in two or more component materials occurs in many materials.

All these processes unique to irradiated materials drive a number of microstructural evolution processes, which are not observed in other materials. The ability to simulate these evolution processes at the microstructural scale would enhance our ability to predict their behaviour and hence design them at the microstructural scale for optimal engineering performance. In this section, the application of Potts models to simulate microstructural evolution nuclear materials will be reviewed.

Potts kinetic Monte Carlo model

The Potts kinetic Monte Carlo (kMC) is a statistical-mechanical model that populates a lattice with an ensemble of discrete particles to represent and evolve the microstructure. The Potts kMC used for mesoscale simulations is distinct from other kinetic Monte Carlo models used for simulation of atomistic, chemical, neutronic and other materials simulations. In the following sections, the term kMC is used to refer to the Potts kMC model. The particles in the Potts kMC model represent a discrete quantity of material that is much larger than an atom, thus all atomistic information about the material system is aggregated into mesoscale model parameters. In kMC, the particles evolve in a variety of ways to simulate microstructural changes due short- and long-range diffusive processes. kMC methods have proven themselves to be versatile, robust and capable of simulating various microstructural evolution processes. They have the great advantage of being simple and intuitive, while still being a rigorous method that can incorporate all the thermodynamic, kinetic and topological characteristics to simulate complex processes. They are easy to code, readily extendable from 2D to 3D and can simulate the underlying physics of many materials evolution processes based on the statistical-mechanical nature of the model. These processes include curvature-driven grain growth [1,2], anisotropic grain growth [3], recrystallisation [4], grain growth in the presence of a pinning phase [5,6], Ostwald ripening [7], and sintering [8-10].

Representation of microstructure

The microstructure consists of an ensemble of particles that occupy a regular lattice. Recently, some kMC models have started to use non-regular or non-lattice based methods. However, the vast majority of kMC models use regular lattices and for the purpose of this

work, we will confine our discussion to regular lattices. The particles can be considered to be a discrete amount of material that is much larger than an atom; thus all atomistic characteristics are aggregated into discrete extensive thermodynamic quantities such as mass and energy for each particle. For the simplest case of grain growth, the microstructure is represented by particles identified by an integer value signifying membership in a particular grain. This membership integer value is simply a distinct degenerate state identifying each particle as belonging to a certain grain with no other physical significance. In a two-phase system such as a porous material, the solid material can be assigned one set of spins and all the porosity a single distinct membership value. In a two-phase system consisting of two solid components such as a eutectic material, each phase can be represented by a set of membership integer values. Lattices can be two-dimensional triangular or square, three-dimensional cubic or face-centered cubic or other geometries. The most commonly used geometries are two-dimensional square and three-dimensional cubic lattices.

Energy and thermodynamics

Since kMC uses a discrete ensemble of particles to represent the microstructure, it follows that the total volumetric energy is the sum of energies of each particle. In addition, interfacial energies must also be included in the calculation of the total free energy of the system. Interfaces in kMC are defined by neighbouring particles with unlike membership. Different types of interfaces with different energies can be defined. Neighbouring particles belonging to two different grains would define a grain boundary or grain particles forming an interface with pore particles would define a pore surface. Each of these can be given its own energy value. The total interfacial energy of the system is then the length in 2D or area in 3D of each interface multiplied by its interfacial energy per unit length or area. Thus, the sum of all unlike neighbour interaction energies of all the particles is E_{int}.

$$E_{int} = \sum_{i=1}^{N} \sum_{j=1}^{n} J_{qi,qj}$$

where i is each particle, N is the total number of particles, j is the neighbouring particle, n is the total number of neighbours being considered, qi is the spin of particle i and J is the interaction energy between particles i and j of spins qi and qj. The bulk energy of the system is the sum of the inherent energy of each particle and does not depend on its neighbours.

$$E_{vol} = \sum_{i=1}^{N} V_i$$

where V_i is the volumetric energy of particle i. Examples of volumetric energy may be the volumetric chemical free energy, elastic strain energy or the irradiation damage energy stored in the nuclear fuel. The interfacial and volumetric energies are very versatile and can be formulated to match virtually any energy that is characteristic of real materials. They can be functions of microstructure or materials, so that as the system evolves due to changing chemistry or accumulation of irradiation or other damage, the particle energies can reflect their current thermodynamic state. This ability to easily tailor particle energies

makes kMC models highly versatile and widely applicable to many materials evolution processes.

Evolution and kinetics

kMC models have been shown to correctly simulate complex path-dependent evolutionary processes. They yield images with great detail of the microstructure and its evolution in response to a given set of starting conditions and applied conditions. The microstructure evolves in response to local conditions such as curvature, radiation damage, temperature, etc. These local conditions may also be changing with time and position. The basic mechanisms for change in a kMC model are the changes in membership of particles from one grain or phase to another or transport of the particles to a different lattice positions by exchanging places with neighbouring particles. These types of changes can be used to simulate many types of transport mechanisms such as grain boundary motion, surface and bulk diffusion, dissolution and precipitation and other mechanisms. The spin change event frequencies are determined using the standard Metropolis algorithm with Boltzmann statistics. A spin change event is identified. The change in total energy of a spin change event is calculated using the equation of state described in the previous section. The probability of this change is:

$$P = 1 \qquad \Delta E \leq 0$$

$$P = \exp\frac{-\Delta E}{k_B T} \qquad \Delta E > 0$$

where k_B is the Boltzmann constant, and T is the simulation temperature. The change is performed with this probability by choosing a random number R, uniformly distributed from 0 to 1. If $R < P$, then the event is accepted and a change is made. If not then no change is made, and the original spin is restored. kMC models reduce the total free energy of the system and, when implemented correctly, reduce free energy along the correct kinetic path of microstructural evolution. These characteristics make the Potts model well suited for studying microstructural evolution in nuclear materials.

Application of kMC model to nuclear materials

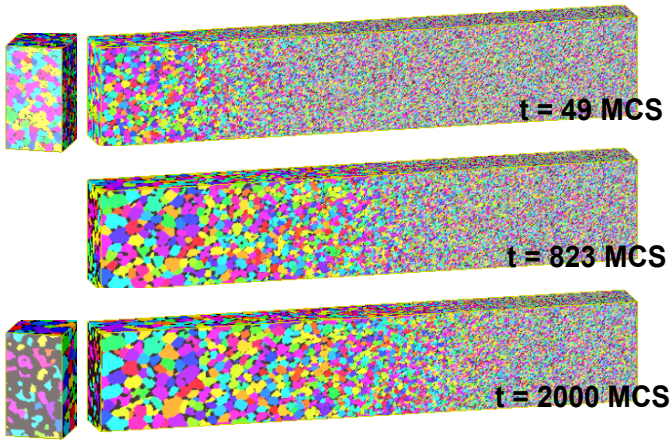
The kMC model has been applied to a variety of processes that are relevant to the simulation of nuclear fuel, clads and other materials. Grain growth was the first and has been the most extensively studied microstructural evolution process. It has been shown that this model simulates curvature-driven grain growth with the expected kinetics of $R^2 - R_o^2 = kt$, where R is the average grain radius and R_o is the average grain radius at time $t = 0$ and k is a kinetic constant related to grain boundary diffusivity. Grain growth in systems with immobile, mobile and evolving pinning phases are important processes for nuclear fuels.

Nuclear fuels are often porous at the start of their service and become more so as fission gases are produced during in-reactor service. This porosity can move and coarsen as the matrix coarsens as well. Solid fission products often segregate to grain boundaries and pin them to effectively reduce or stop grain growth. This process has been extensively studied using the kMC model. Other fission products can segregate to grain boundaries

and pin them so that grain growth is suppressed even at high temperatures. This two-phase pinning model is described in detail elsewhere [6] and shown to incorporate all the processes necessary to simulate coarsening in a two-phase system such as that found in nuclear fuels. These processes include curvature driven grain growth mediated by pore drag on the grain boundaries, which leads to different grain boundary motion behaviours: slower grain boundary motion due to pore drag, grain boundary break away from very slow pores or complete stagnation of the grain boundary by pores.

In materials that have temperature gradients, particularly the large gradients seen in nuclear materials, microstructural evolution in different regions can vary greatly depending on the local temperature. Thermally activated processes such as grain boundary motion, and surface and bulk diffusion, occur at a faster rate at higher temperatures with the temperature-dependent rate or mobility M(T) given by the Arrhenius relationship $M = M_o \exp\left(\frac{-Q_A}{k_B T}\right)$ where Mo is a pre-exponential constant and QA is the activation energy for that process. In nuclear fuels and clads, most processes are indeed thermally activated, although a few are enhanced by radiation-induced defects as well. The thermally activated processes are treated in the kMC model by varying their mobility as a function of the local temperature. For example, grain growth. The grain boundary velocity v is proportional to the driving force (curvature) and mobility as $v = M\kappa$ where κ is the grain boundary curvature. This mobility term is introduced very easily in the kinetic equation as PM = M(T)P where PM is the temperature-dependent probability term and P is the original probability. It has been shown by Garcia et al. [11] that under continuously varying temperature gradients, the kinetics and topology of the grain growth are locally normal. The local grain size and grain size distribution are the same in the temperature gradient as they would be at the same temperature in an isothermal grain growth simulation. This method for simulation of temperature gradients is correct as long as the mechanism for microstructural evolution and the corresponding activation energy remain constant over the entire temperature range. In two-phase systems, the Soret effect that segregates phases is important. This, too, can be simulated in the Potts model by introducing a heat of transport term, Q^* into the energy of the system. An example that combines all the processes described above has been combined in one simulation for illustrating the model capability. Coarsening in a two-phase system with a thermal gradient applied is shown in Figure 1. Curvature-driven grain growth with a mobile pinning phase, in this case gas, is evolving in a temperature gradient. The gas pockets coarsen by coalescence and move by surface diffusion. As can be seen, coarsening is much faster at the high temperature region and the gas preferentially diffuses to the higher temperature region as this lowers the total free energy of the system.

Figure 1. Coarsening of grains and pores in a thermal gradient



Grains and pores coarsen more quickly at higher temperatures. Pores migrate to the high temperature end due to the Soret effect as shown by the difference in pore volume at the high-temperature edge between time t = 49 and 2,000 MCS.

Recrystallisation is an important phenomenon observed in LWR and some other fuels. Rollet et al. [12] developed a recrystallisation model and later used it to study abnormal growth [13]. Further evolution of this model was used to study dynamic recrystallisation [14]. A preliminary application of kMC model to study recrystallisation in the high burn-up rim region of LWR fuels was recently presented by Oh [15] and more developed by Madison et al. [16]. Another very important microstructural evolution process is swelling. This mechanism is very similar to densification during sintering of crystalline materials. A validated kMC model for sintering has been demonstrated by comparison to detailed experimental three-dimensional images of microstructural evolution in Cu powder compacts [17]. While almost all the basic microstructural evolution processes at the mesoscale have been simulated to varying degrees using kMC methods, their application to nuclear fuel and cladding is in its infancy. In order to make significant advances, the models have to be adapted to the specific application conditions of nuclear fuels and coupled so that many different processes (i.e., fission gas generation, diffusion, bubble formation accompanied by swelling and recrystallisation) can occur simultaneously. The adaptation of kMC models to the specific processes relevant to nuclear materials and development of coupled models is not trivial. However, the previous use of kMC models to correctly simulate various processes including coupled processes suggests that kMC is a powerful and useful method for modelling microstructural evolution in nuclear materials.

Current trends and future development of Potts models

Continued model development of the kMC model has taken the form of developing hybrid models that couple multiple materials physics that the kMC model cannot inherently treat. One of the early examples of this type of modelling was a sintering model that treated all the processes active during solid state sintering, except densification by annihilation using kMC. Densification, however, was simulated by a unique method of addressing global shrinkage based on the local microstructural configuration [17]. This is another example for simulation of recrystallisation. Application of the Potts model alone

with a volumetric free energy modified to include the strain energy density of dislocations in the metal could not simulate the kinetics of recrystallisation correctly. Rollett and Raabe [18] showed that a hybrid Potts cellular automaton model correctly simulated the kinetics of recrystallisation and Madison et al. [19] extended this model and applied it to simulate dynamic recrystallisation in the high-burn-up rim region of UO_2 fuels. In contrast, the phase-field model has remained essentially the same model. Its development has been in the form of introducing new phase fields to represent new physics. The numerical implementation of additional coupled fields has limited the advancement of phase-field models. Coupling phase fields which introduce additional physics is difficult as the development of free energy functionals that are numerically stable and converge to the correct solution is difficult. The evolution of the phase-field model is improved in numerical techniques to enable larger simulations with more coupling of the physics. Adaptation and use of advanced numerical solver that converges to solutions with less computation has been a large effort to improve phase-field model performance. Development of adaptive meshes that reduces computation in stable non-evolving areas away from the interfaces has been the focus of model improvement. Another is reassignment of degenerate grain orientation locally to both reduce the number of phase fields required and to prevent the artefacts introduced by having a limited number of grain orientations. An exciting development in mesoscale modelling has been the introduction of a hybrid model that couples phase-field with Potts model [20].

This type of hybrid combines the inherent efficiency and stability of the Potts model with the ability to treat continuously varying materials characteristics such as composition in the phase-field model to enable simulation of microstructural evolution in a new class of materials. One area of microstructural evolution problems has remained challenging. Models that can simulate microstructural evolution that is driven partially by mechanical stresses are the focus of much research. While, some solutions have been found under a limited set of conditions, the development of modelling techniques that would enable simulation microstructural evolution that is partially driving by mechanical stresses has not been achieved. The problems of interest to nuclear materials are swelling in nuclear fuels due to fission gas bubble formation, interactions between clad and pellet, hydride reorientation in cladding during long-term storage and many others.

Acknowledgements

Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the US Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

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