Modeling thermal spike driven reactions at low temperature and application to zirconium carbide radiation damage

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ABSTRACT

The development of TEM-visible damage in materials under irradiation at cryogenic temperatures cannot be explained using classical rate theory modeling with thermally activated reactions since at low temperatures thermal reaction rates are too low. Although point defect mobility approaches zero at low temperature, the thermal spikes induced by displacement cascades enable some atom mobility as it cools. In this work a model is developed to calculate "athermal" reaction rates from the atomic mobility within the irradiation-induced thermal spikes, including both displacement cascades and electronic stopping. The athermal reaction rates are added to a simple rate theory cluster dynamics model to allow for the simulation of microstructure evolution during irradiation at cryogenic temperatures. The rate theory model is applied to in-situ irradiation of ZrC and compares well at cryogenic temperatures. The results show that the addition of the thermal spike model makes it possible to rationalize microstructure evolution in the low temperature regime.

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1. Introduction

The degradation of material properties is one of several limiting factors in nuclear reactor performance. This process occurs, in part, by microstructural and microchemical changes induced by irradiation, and prediction of microstructure evolution is necessary as part of an accurate prediction of future material performance in a reactor environment. Rate theory is a method by which microstructure evolution under irradiation is modeled [1–3]. Similar to chemical rate theory, systems of equations involving species' concentrations and reaction rates are solved to yield defect cluster concentrations. Reactions are generally controlled by diffusion of the reactants and are, as such, dependent on temperature.

A simple rate theory approach is to consider the equal production of interstitials and vacancies with the only allowable reaction being the mutual annihilation of those species by recombination. In that regime $C_i = C_v = C$ and the governing equation for this system is

$$\frac{\partial C}{\partial t} = G - RC^2 \tag{1}$$

where C is the concentration of interstitials and vacancies, G is the rate of production of interstitials and vacancies, and R is the rate

constant for recombination with the term RC^2 being the rate of recombination. The analytical solution for this equation is

$$C(t) = \sqrt{\frac{G}{R}} \tanh\left(\sqrt{GR}t\right) \tag{2}$$

and describes a system in which the concentrations of interstitials and vacancies increase until being limited by mutual recombination at $C = \sqrt{G/R}$ after a time $t = 1/\sqrt{GR}$. This system is referred to as recombination-dominated.

Reactions in the rate theory framework are typically diffusion-controlled. The rate constant R is therefore proportional to the diffusion coefficients of the reactants. Because of this, as the temperature decreases, so do the diffusion coefficients which causes the steady-state defect concentration, $C = \sqrt{G/R}$, to increase. For the rate constant R defined as in Eq. (17), and for reasonable values of the relevant properties in ZrC, the steady-state atomic concentration of interstitials and vacancies is on the order of 10^{-5} at 300 K. For the same parameters at 50 K, however, the concentration of defects is unphysically $\gg 1$, indicating that the high temperature model is no longer valid. The defect concentration at room temperature, while high, is within reason, but the concentration at 50 K is completely non-physical.

This demonstrates a fundamental limitation of the typical rate theory approach: classical rate theory does not model the microstructure evolution at low temperatures in any meaningful

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way. The same is true for more complex systems where individual defects can agglomerate into defect clusters, such as dislocation loops and voids. At very low temperatures, the slow diffusion controlled reactions would inhibit the nucleation and growth of defect clusters in the rate theory framework.

In-situ irradiation of ZrC was previously performed at temperatures ranging from 20 K to 1073 K [4]. The observed microstructure evolution did not vary greatly over the temperature range of 20 K to room temperature; small "black-dot" defects appeared after an incubation dose and their density increased until saturation without growing to form distinct dislocation loops. The black-dot defects are clusters with size estimated on the order of tens of individual defects. The presence of an incubation dose indicates that the defects resolvable by transmission electron microscopy (TEM) were not produced *directly* in single displacement cascades but, rather, formed over time during irradiation. At 20 K, a slow accumulation of defects into larger aggregates by thermal diffusion is not viable given the low defect diffusion coefficient at these temperatures [5], thus another process is required to explain these results.

In this work, we present an addition to rate theory which relies on the defect mobility within displacement cascades. In particular, the thermal spike model of Vineyard [6] is used to calculate an "athermal", radiation-driven component for each reaction rate that is effective even at cryogenic temperatures. This baseline irradiation response can then be added to the usual thermally activated processes to model the reactions at all temperatures. The new reactions are applied to basic ZrC rate theory for evaluation, and these results are reviewed in the context of the experimental measurements of average defect diameter and density as functions of dose. Further recommendations for improving the model are provided.

2. Athermal reaction rates

Atomic collisions with energetic ions transfer energy to lattice atoms during ion irradiation. In this model, this deposited energy drives reactions even at low ambient temperature through defect mobility within the cascade, as put forward by Vineyard [6]. Following Vineyard, the initial collision is considered as an instantaneous point-source of heat. The heat then thermally diffuses outwardly in the radial direction of a spherically symmetric system. The local temperature increase due to the addition of heat by the collision results in a number of atomic jumps which cause reactions that would not otherwise occur at these temperatures. For ion irradiation, additional electronic stopping is considered as an instantaneous line-source of heat. This heat instead diffuses outwardly in the radial direction of a cylindrically symmetric system.

The thermal spike model is applied to diffusion controlled reactions. Being diffusion controlled, the reaction rate density takes the form

$$(\text{rate})_{\text{diff}} = A \exp(-E/(k_B T)) \tag{3}$$

where A is a constant, E is the energy barrier, k_B is the Boltzmann constant, and T is the temperature. For a homogeneous medium with constant thermal conductivity and heat capacity, the heat equation is solved with solutions [6]

$$T_s(r,t) = \left(\frac{qC^{1/2}}{(4\pi\kappa t)^{3/2}}\right) \exp\left(\frac{-Cr^2}{4\kappa t}\right) \tag{4}$$

for the spherical thermal spike and

$$T_c(r,t) = \left(\frac{\epsilon}{4\pi\kappa t}\right) \exp\left(\frac{-Cr^2}{4\kappa t}\right) \tag{5}$$

for the cylindrical thermal spike, where r is the radial distance from the center of the thermal spike, t is the time from the initiation of the thermal spike, q is the energy of the spherical thermal spike, ϵ is the energy deposited per unit line length in the cylindrical thermal spike, κ is the thermal conductivity of the material, and C is the heat capacity of the material. The total number of reactions resulting from the thermal spikes, η, is calculated by integrating the reaction rate density over the whole thermal spike with

$$\eta_s = \int_0^\infty 4\pi r^2 dr \int_0^\infty A\exp(-E/(k_B T))dt = A\left(\frac{\sqrt{3/5}\,\Gamma(5/3)q^{5/3}}{10\pi\kappa C^{2/3}(E/k_B)^{5/3}}\right) \tag{6}$$

for spherical thermal spikes and

$$\eta_c = \int_0^\infty 2\pi r dr \int_0^\infty A\exp(-E/(k_B T))dt = A\left(\frac{\epsilon^2}{8\pi\kappa C(E/k_B)^2}\right) \tag{7}$$

for cylindrical thermal spikes, where $\Gamma(5/3)$ is the gamma function evaluated at 5/3.

The rate of reactions resulting from thermal spikes is then calculated from the results of Eqs. (6) and (7). The number of reactions resulting from a spherical cascade is calculated using the average collision energy, the result of which is then multiplied by the number of collisions per unit volume and time, φ. The number of reactions per unit line length is calculated using the average electronic stopping power and is then multiplied by the ion flux, ϕ. The average spherical thermal spike energy is calculated as the average of all SRIM cascade energies weighted to the 5/3 power, and the average cylindrical thermal spike energy is the electronic stopping power averaged over the thickness of the thin-foil. The final result for the thermal spike reaction rate density follows as

$$(\text{rate})_{\text{spike}} = \eta_s\varphi + \eta_c\phi = A\left[\frac{\sqrt{3/5}\,\Gamma(5/3)\overline{q^{5/3}}\varphi}{10\pi\kappa C^{2/3}(E/k_B)^{5/3}} + \frac{\overline{\epsilon^2}\phi}{8\pi\kappa C(E/k_B)^2}\right] \tag{8}$$

such that the temperature-dependent exponential term of Eq. (3) is replaced by a term evaluated using a combination of material properties and irradiation parameters.

The material properties needed to evaluate Eq. (8) are found in the literature, and the irradiation parameters were specifically evaluated for this work. The Stopping and Range of Ions in Matter (SRIM) [7] is a Monte Carlo program commonly used to simulate ion irradiation, and it was used while planning the in-situ irradiation experiments of ZrC to find the relationship between damage level in displacements-per-atom (dpa) and ion fluence. In this simulation, the average displacement cascade energy was found to be 9361 eV, and the number of cascades per ion was extracted from the text-based collision details. These parameters are used to define the spherical thermal spikes. The average electronic stopping power, 1100 eV nm^{-1}, was estimated from the SRIM graphical user interface ionization plot. This is used to define the cylindrical thermal spike.

The total reaction rate is defined as the sum of the thermal diffusion reaction rate and the thermal spike reaction rate.

$$(\text{rate}) = (\text{rate})_{\text{diff}} + (\text{rate})_{\text{spike}}$$
$$= A\left[\exp(-E/(k_B T)) + \frac{\sqrt{3/5}\,\Gamma(5/3)\overline{q^{5/3}}\varphi}{10\pi\kappa C^{2/3}(E/k_B)^{5/3}} + \frac{\overline{\epsilon^2}\phi}{8\pi\kappa C(E/k_B)^2}\right] \tag{9}$$

The behavior of this new formula is easily understood from inspection. At very low temperatures, $T \ll (E/k_B)$, the thermal diffusion term approaches zero and only the thermal spike reaction rate remains. At higher temperatures, both the thermal diffusion