FROM MOLECULAR DYNAMICS TO KINETIC RATE THEORY: A SIMPLE EXAMPLE OF MULTISCALE MODELING

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From Molecular Dynamics to Kinetic Rate Theory: A Simple Example of Multiscale Modeling

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ABSTRACT

Radiation damage formation in iron has been investigated using the method of molecular dynamics simulation. The MD simulations have been used to determine primary defect production parameters for cascade energies up to 50 keV at temperatures from 100 to 900K. The energy dependence of these parameters has been used to determine appropriate neutron-energy-spectrum averaged damage production cross sections for various irradiation environments. Two applications of these effective cross sections are discussed. The first is an evaluation of neutron energy spectrum effects in commercial fission reactor pressure vessels. The second example deals with the use of these cross sections in the source term of a kinetic model used to predict void swelling and microstructural evolution. The simulation of the primary damage event by MD involves times less than 100 ps and a size scale of a few tens of nm, while the kinetic simulation encompasses several years and macroscopic sizes. This use of the MD results to develop an improved source term for rate theory modeling provides a simple example of multiscale modeling.

INTRODUCTION

Models based on reaction rate theory have been broadly and successfully applied to simulate radiation-induced microstructural evolution.¹⁻⁴ Typically, the use of these models involves the simultaneous solution of a modest number of differential equations to predict phenomena such as void swelling, irradiation creep, or embrittlement. The time scale of interest for these processes is determined by atomic diffusion rates and the desired in-service lifetime of irradiated components. The rate theory is well suited to span this time range from seconds to years, and a size scale from micro-meters to macroscopic dimensions. However, the source term in the rate equations is dictated by atomic displacement cascades, events that occur on a time scale of a few tens of pico-seconds and a few tens of nano-meters in space. The method of molecular dynamics (MD) is an appropriate tool for simulating these displacement cascades.

MD has seen extensive application in simulating displacement cascades in irradiated materials,⁵⁻¹² and recent advances in computing have enabled researchers to examine higher energy events with their requirement for larger blocks of atoms. These same computing resources have permitted cascade simulations to be completed in sufficient numbers to allow for statistically meaningful trends to be determined as a function of simulation energy and irradiation temperature. For example, the comparison of iron and copper contained in Ref. 9 is based on a database of over 600 cascades with energies from 60 eV to 10 keV and irradiation temperatures of 100, 600, and 900 K. The results used in this work represent an extension of the collaborative study presented in Ref. 9, with the peak cascade energy increased to 50 keV.^{13,14}

The analysis of displacement cascade simulations provides useful information on point defect formation at specific cascade energies. However, integral damage parameters that account for the energy dependence of the primary knockon atom (PKA) spectra are needed for more

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general applications in radiation damage modeling. Since the energy range accessible by MD simulations now includes the domain of cascades produced by high energy neutrons, it is appropriate to use the MD results to develop these integral parameters for different neutron irradiation environments. The integral parameters can be used to compare the effects of neutron energy spectrum as well as providing improved estimates for the average atomic displacement rate in these environments. The use of the MD-based parameters in kinetic radiation damage models represents one simple example of multiscale modeling.

MD SIMULATION METHOD

The details of the MOLDY code and the interatomic potential used are discussed in detail elsewhere.^{7,9,15,16} The interatomic potential used was a many-body type, originally developed by Finnis and Sinclair for α -iron¹⁶ and subsequently modified by Calder and Bacon⁷ in order to permit its use in dynamic simulations. The original version of this potential was fitted to a number of physical parameters; the primary modification of Calder and Bacon was to the repulsive pair term in order to fit the pressure-volume relationship and to reproduce the displacement threshold surface.⁷ The simulations were carried out using an atom block with periodic boundary conditions and at constant pressure. Since the boundary atoms were not damped to remove heat, the initiation of a cascade event led to some lattice heating. The primary impact of the temperature increase (up to 300 K at 1 ps) is to extend the lifetime of the thermal spike; it has no impact on the ballistic phase of the cascade. In addition, the temperature increase does not appear to influence defect survival since this has been shown to exhibit very little temperature dependence.^{7,9}

Prior to conducting the cascade simulations, a block of atoms is thermally equilibrated for about 10 ps to establish thermal equilibrium. This equilibrated atom block is then used as the starting point for the subsequent cascade simulations, with the largest atom block used in this work being 2.25 million atoms for the 50 keV cascades. The simulations are initiated by giving one of the lattice atoms a defined amount of kinetic energy and a specific direction. Multiple cascades are differentiated by changing the location of the initial PKA or further equilibrating the block. As discussed in Ref. 9, the initial kinetic energy is analogous to the damage energy in the standard NRT displacement model.¹⁷ In the terminology of the NRT model, a 50 keV cascade simulation energy (or damage energy) corresponds to a PKA energy of 78.7 keV.^{9,17} This is the average PKA energy in an elastic collision between a 2.3 MeV neutron and an iron atom. The difference between the PKA and damage energy is the kinetic energy lost to electronic excitation.

RESULTS OBTAINED FROM MD CASCADE SIMULATIONS

Building on the work published in Refs. 7 and 9, iron cascade simulations up to 50 keV have been completed and used in this analysis. Three parameters have been extracted from the analysis because of their relevance to radiation damage simulation: the total number of surviving point defects, the total fraction of surviving interstitials in clusters, and the fraction of interstitials in clusters containing 10 or more interstitials. At each energy, an average value was obtained from several cascades (typically 8 to 10). In order to provide a standard basis of comparison, the averages were divided by the number of displacements calculated from the NRT model.¹⁷ These normalized values are shown in Figs. 1 (a-c), where the standard deviation about the average is included on the higher energy points. Results are shown for all three temperatures in Figs. 1 (a) and (b), but only for 100K in Fig. 1(c). The 10 and 20 keV points have been slightly displaced along the axis to differentiate the three temperatures.

There does not appear to be a systematic dependence on irradiation temperature in the results shown in Fig. 1; therefore, a decision was made to treat all the "data" as a single database for this analysis. The solid lines shown in Fig. 1 were obtained from a least-squares fit to the data,

Fig. 1 Dependence of the MD-derived primary damage parameters on cascade energy and temperature: (a) total point defect survival, (b) total fraction of surviving interstitials in clusters, and (c) fraction of surviving interstitials in clusters of size 10 or larger. Note change of scale on energy axis in (c).

yielding the following three functions for the cascade survival efficiency (η), the total interstitial clustering fraction (f_{icl}^T), and the interstitial fraction in clusters of 10 or larger (f_{icl}^{10}):

$$\eta = 0.5608 \cdot E_{MD}^{-0.3029} + 3.227 \times 10^{-3} \cdot E_{MD} \quad (1)$$

$$f_{icl}^T = [0.097 \cdot \ln(E_{MD} + 0.9)]^{0.3859} - 7 \times 10^{-6} \cdot E_{MD}^{2.5} \quad (2)$$

$$f_{icl}^{10} = 4.40376 \times 10^{-3} \cdot \ln(E_{MD} - 0.9)^{0.7453} \quad (3)$$

The line is shown dashed above 40 keV in Figs. 1 (a) and (b), because this was the highest energy that had been completed at the time the fitting was done. The value at 40 keV was used for all higher energy damage energies in the analysis discussed below. This was based on the nearly asymptotic behavior seen in Figs. 1 (a) and (b), and the subsequent 50 keV cascades provided limited confirmation for this assumption. As discussed elsewhere,^{11,18} subcascade formation appears to be responsible for this behavior. Because there were no clusters of size 10 or larger below 10 keV, Eqn. (3) was not obtained until recently when the 50 keV cascades were completed. There are relatively few such clusters even at the higher energies, and the standard deviations are greater than the absolute value of the averages on the points shown in Fig. 1(c).

However, the large clusters could be a significant nucleation site for extended defects, so this parameter was chosen in an initial attempt to evaluate the potential impact of the tail in the cluster size distribution that appears at high energies.

The impact of the energy dependence expressed by Eqns. (1) to (3) was evaluated using the SPECOMP and SPECTER codes,^{19,20} as discussed elsewhere.¹⁸ SPECOMP was used to calculate effective cross sections for the production of surviving point defects and clustered interstitials, and these cross sections were added to the SPECTER libraries. SPECTER runs for various neutron spectra thereby produced spectrum-averaged values for the point defect and interstitial clustering fractions. The primary results of these calculations are summarized in Figure 2. The PKA-spectrum-averaged defect survival fraction is shown in Fig. 2(a), the total interstitial clustering fraction in Fig. 2(b), and the fraction of interstitials in clusters of 10 or more Fig. 2(c). Values are shown for various irradiation environments: the ITER first wall (DT fusion), the HFIR peripheral target position (PTP) and removable beryllium reflector (RB*), the FFTF midcore and below-core (BC) positions, the 1/4-thickness location in the pressure vessel of a commercial pressurized water reactor (PWR), and the radiation effects facility in a 450 MeV spallation neutron source (IPNS).

As pointed out previously, there is little dependence on PKA energy spectrum observed in Figs. 2 (a) and (b).¹⁸ This result arises from the fact that the PKA energy spectrum is relatively independent of energy in the region where the total defect survival and clustering fractions vary with energy (i.e. E_{MD} less than ~ 10 keV, see Fig. 1), while the total defect survival and clustering fractions are relatively flat at the higher energies where the PKA spectrum is energy dependent. The dependence of primary damage formation on neutron energy spectrum is quite relevant to the use of fission reactors to obtain data for predicting the performance of materials in fusion and spallation neutron environments. Therefore, the spectrum dependence seen in Fig. 2(c) is

Fig. 2 Spectrum-averaged defect production cross sections (per NRT dpa) for various irradiation environments: (a) total point survival, (b) total interstitial clustering fraction, and (c) interstitial fraction in clusters of size 10 or more.

noteworthy. The significance of the interstitial cluster size distributions need further investigation, but this is the first of the primary damage parameters that has shown a high level of dependence on the neutron (or PKA) energy spectrum.

APPLICATION OF MD-BASED PARAMETERS

Two relatively simple examples can be used to illustrate the application of the MD-based primary damage parameters. The first is relevant to light water reactor pressure vessel (RPV) steels, and the second to predictions of void swelling under fast neutron irradiation.

One difference between commercial pressurized water reactors (PWR) and boiling water reactors (BWR), is that the distance between the outer fuel elements and the RPV is greater in the BWR than in the PWR. This space is filled with water, leading to both a lower neutron flux and a softer neutron spectrum impinging on the BWR RPV. In light of the energy dependence of defect survival illustrated by Fig. 1(a), concerns have been raised about the impact of the softer neutron spectrum on radiation-induced embrittlement in BWRs. Specifically, the concern is whether or not the PKA spectra are sufficiently different between the two types of reactors that the embrittlement per unit fluence might be higher for the BWR. In addition, the neutron energy spectrum shifts as a result of attenuation, and this could produce different responses in material irradiated in surveillance capsules than in the RPV at the 1/4 or 3/4 thickness locations.

The NRT-normalized, spectrum-averaged defect production cross sections for typical BWR and PWR neutron spectra are shown in Fig. 3 for four locations: the last transport node in the water before entering the RPV, the 1/4-T and 3/4-T RPV positions, and the first transport node in the cavity beyond the RPV. Note that the values for interstitials in large clusters are referenced to the right-hand scale in the figure. It is clear that for both total defect survival and total interstitial clustering, there is essentially no difference between the PWR and BWR parameters, nor is there any significant effect of the spectrum shift that arises from attenuation. The total interstitial clustering values for the two reactors are indistinguishable at each location. However, as might be expected from Fig. 2, a much more significant effect is observed for the fraction of interstitials in clusters of 10 or more. Since only a small fraction of the interstitials produced are in such clusters, more analysis is required to assess the significance of this spectrum effect.

Fig. 3 Comparison of primary damage parameters as a function of location through pressurized (PWR) and boiling (BWR) water reactor pressure vessels.

Void swelling has been the subject of extensive theoretical and experimental investigation. Models which simulate the kinetics of point defect processes using the reaction rate theory provide generally good agreement with the data.³ However, even the most detailed models do not

Fig. 4 Evaluation of dislocation bias based on spectrum-averaged defect production cross section and swelling data from FFTF: (a) varying both bias and point defect survival, and (b) varying bias with calculated point defect survival.

include a complete description of the relevant physics, and all models rely on material and irradiation parameters that are not always well known. Because of the uncertainty about input parameters, data are used both to help calibrate the models and to evaluate their predictive capability. One limitation in this process is that multiparameter models may yield nearly equivalent predictions with different parameter sets. This limitation can easily be demonstrated by a simple calculation of the void swelling rate under steady state conditions.

If the point defect kinetics are controlled by absorption at dislocations with sink strength S_d , the swelling rate is proportional to the product of the cascade survival efficiency η and the net dislocation-interstitial bias ($Z_i^d - 1$):

$$\frac{dV}{dt} = \frac{\eta G_{dpa}}{S_d} (Z_i^d - 1) \quad (4)$$

In this case, data fitting can not be used to obtain a unique value for either η or Z_i^d . This is shown in Fig. 4(a), where the predictions of a more complex microstructural model³ are compared with swelling data for AISI 316 stainless steel irradiated in the FFTF. Calculations using either of the parameter sets shown in the figure fit the data equally well. However, if the spectrum-averaged FFTF value of $\eta=0.35$ obtained from the MD results is assumed to be valid, then the model can be used to discriminate between possible values for the bias as shown in Fig. 4(b). It should be clear that this example does not provide a definitive estimate of the dislocation-interstitial bias in stainless steels. Rather, it simply illustrates how parameters derived in modeling on one scale can be used to help improve models on another scale.

SUMMARY

The results obtained from MD cascade simulations up to 50 keV have been parameterized and neutron-energy-spectrum-averaged, damage production cross sections have been calculated for several neutron irradiation environments. The MD-based cross sections can be used to make direct comparisons of the various irradiation environments, and to provide an improved estimate for the primary radiation damage source term in kinetic models. Very little dependence on the neutron energy spectrum is seen in two of the three parameters that have been analyzed. A third parameter, the fraction of surviving interstitials in clusters of 10 or larger exhibits a much higher degree of spectrum dependence. More work is required to determine the significance of this

parameter in radiation-induced microstructural evolution or mechanical property changes.

Multiscale modeling can be conducted in several ways. The development of hybrid models that bridge different time and length scales is one approach. An alternate approach that involves passing selected information between different models is illustrated by the example of using MD-based parameters in a kinetic microstructural model. These two approaches could be referred to as handshaking and handing-off, respectively.

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