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A molecular dynamics study of radiation induced diffusion in uranium dioxide

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ABSTRACT

The nuclear oxide fuels are submitted 'in-pile' to strong structural and chemical modifications due to the fissions and temperature. The diffusion of species is notably the result of a thermal activation and of radiation induced diffusion. This study proposes to estimate to what extent the radiation induced diffusion contributes to the diffusion of lattice atoms in UO_2. Irradiations are simulated using molecular dynamics simulation by displacement cascades induced by uranium primary knock-on atoms between 1 and 80 keV. As atoms are easier to displace when their vibration amplitude increases, the temperature range which have been investigated is 300–1400 K. Cascade overlaps were also simulated. The material is shown to melt at the end of cascades, yielding a reduced threshold energy displacement. The nuclear contribution to the radiation induced diffusion is compared to thermally activated diffusion under in-reactor and long-term storage conditions.

1. Introduction

During reactor operation, fission fragments generated within the oxide fuel lose their kinetic energy through two different processes. At high energy, the fission fragment energy loss essentially originates from inelastic interactions such as electronic excitation of atoms in the fuel matrix, which could result in the displacement of atoms located along the ion trajectory. At lower energies, energy loss occurs through ballistic collisions between atoms. This second process of energy loss, which is also relevant under long-term storage conditions, leads to the formation of displacement cascades, liable to induce long range atomic migration. The electronic and nuclear contributions to migration processes associated with the irradiation are usually referred to radiation induced diffusion (RID). Since this phenomenon is a key ingredient in all fuel performance applications, it is essential, if one aims at developing predictive approaches, that atomistic models be used to ascertain what physical processes contribute to it and to what extent.

Basic experimental data demonstrating RID in uranium dioxide is hard to come by. Höh and Matzke [1] estimated the cation RID coefficient through a set of in-pile trace diffusion experiments at roughly 10^{-20} m^2 s^{-1} for fission densities of about 10^{19} m^{-3} s^{-1}. Later RID was shown to be completely a thermal below 1375 K. Turnbull et al. [2] studied the in-pile release of volatile fission products, rare gases in particular. They deduced from their experiments a thermal diffusion coefficients very similar to those obtained by Höh and Matzke (between 1×10^{-21} and 5×10^{-21} m^2 s^{-1} for xenon at similar fission rates). Hocking et al. [3] have more recently attempted to characterise RID of iodine through experiments involving iodine in implanted polycrystalline sintered samples irradiated with energetic ions simulating the effects of fission fragments. Which physical phenomena actually cause the observed mobility of atoms in-pile (displacement cascades, electronic excitations of slowing fission fragments, temperature assisted migration in the presence of enhanced quantities of defects...) still remains unclear. The aim of this paper is to help shed light on the matter using MD models.

Molecular dynamics (MD) tools can indeed be used to estimate irradiation induced phenomena [4]. In this paper classical molecular dynamics simulations are applied using the interatomic potential developed by Morelon et al. [5] in an attempt to estimate ballistic mixing effects and their possible temperature dependence. Collision cascades were simulated at varying temperatures from 300 to 1400 K, a range which covers the temperatures relevant under normal operating conditions and under long-term storage conditions. Because of the computational resources required for such calculations, the energy of the projectile, a uranium primary knock-on atom (PKA), is limited to several tens of keV. Simulations were therefore performed with various incident projectile energies in order to enable the extrapolation of results for more realistic PKA energies.

2. Calculation conditions

A UO_2 infinite matrix with periodic boundary conditions is simulated by molecular dynamics using the empirical interatomic

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potentials described in [5] based on a rigid ion model, with respective charges for oxygen anions and uranium cations of −1.61362 and of +3.22725. The U–U interaction is a pure repulsive Coulomb interaction. The analytical form of the U–O potential is composed of a Born–Mayer–Huggins (BMH) repulsive term, and of an attractive part composed of a Van Der Waals term and a coulombic term. The repulsive O–O potential is unconventional and is defined by intervals: short distance interactions are simulated by a BMH potential, long range interactions by a Van Der Waals term and medium range interactions by successive fifth-degree and third-degree polynomials.

This potential provides results relative to point defects which are in good agreement with experimental data [6]. It is also consistent with other experimental data relative to physical properties such as the thermal expansion coefficient, heat capacity [7] or oxygen diffusion coefficient [8,9]. Molecular dynamics simulations of displacement cascade overlaps have moreover shown the fluorite structure not to be susceptible to amorphisation under irradiation, which corroborates experimental observations.

The BMH like potentials give a good description of the interaction between two ions at equilibrium but interatomic distances can be much less than their equilibrium distance during a displacement cascade event. For interatomic distances typically <0.16 nm, a Ziegler–Biersack–Littmark (ZBL) potential is therefore used, of which the continuity with the BMH potential is ensured by a fifth-degree polynomial. The forces and their first derivative are continuous at the transition point.

The initial cubic box that contains 25^3–68^3 perfect UO_2 unit cells is first relaxed under constant number of atoms, pressure and temperature (NPT conditions), the temperature of the box being regulated by a Nosé chain [10]. The second step consists in accelerating a single uranium ion at constant volume and a conservative energy (NV″E″ conditions) inside the core of the simulation box which has reached equilibrium after the first run to simulate a primary knock-on atom (PKA). A thermostat is applied at the box sides by rescaling the velocities of some atoms within the first atomic cell (over 0.3 nm). Cascades were performed with uranium PKA from 1 to 80 keV at temperatures ranging between 300 and 1400 K. Each MD simulation lasts ~25 ps divided into 50 000 time steps. The used variable-step algorithm, which enables the reduction of the computational time, is described in [11]. The cascade initiated at 80 keV has been presented previously [12]. Ten initial PKA directions were chosen to cover as different directions as possible: the angle between the normalised initial velocities and all equivalents towards the UO_2 crystal of any two PKA is at least 9°. Several calculations were performed for each set of conditions to provide a statistical approach to the modelling results, changing only the initial direction and location of the uranium PKA. Cascade overlaps were also simulated by starting cascade simulations from the final configuration of previous runs. Table 1 gathers the conditions of all simulations sets for different initial PKA energies and at different temperatures, each temperature corresponding to a specific equilibrium lattice parameter.

Table 1
Overview of the temperatures and uranium PKA energies which were used to simulate each simulation set of MD cascades in NV″E″ conditions.

Uranium PKA energy (keV)	Temperature (K)	Cascade overlaps	Number of cascades	Lattice parameter (nm)
80	300	–	1	0.5468
10	1400	2–6	15 (5 × 3)	0.56382
10	1400	–	9	0.56382
10	1100	–	9	0.5608
10	700	2–14	39 (13 × 3)	0.55635
10	700	–	9	0.55635
5	700	–	9	0.55635
2	700	–	9	0.55635
1	700	–	9	0.55635

3. Description of displacement cascades

3.1. Successive stages which describe a cascade

As described in [12], different successive phases occur during a displacement cascade. Fig. 1(a), which shows all atoms of the initial perfect UO_2 lattice in a plane perpendicular to the <1 1 0> direction at 700 K, reveals the empty octahedral interstitial sites which are aligned along this direction. Atoms which have been displaced by more than 0.15 nm appear in Fig. 1(b), (c) and (d) at different stages of a 10 keV cascade. First, within a few tenths of ps, a ballistic phase is created during which long range migration of atoms can occur. This phase leads to the formation of sub-cascade branches. During a second stage, the energy of the cascade is thermally dissipated and a molten volume appears which lasts a few ps. During this stage, an elastic wave similar to that described in [12] for an 80 keV PKA can be observed (see Fig. 1(c)) but not as clearly as in [12] because of the relatively low amplitude of the grouped displacement of atoms. Finally the temperature inside the box decreases progressively under the influence of the thermostat applied to atoms externally placed at the box boundaries since the system is completely relaxed after a few tens of ps.

Both first stages of the cascades, the ballistic one and the thermal one are shown in Fig. 1(b) and (c). In Fig. 1(d), the stable configuration is given after cooling and relaxation of the simulation box. In this latter figure, it appears that some octahedral interstitial sites along the <1 1 0> direction have been filled.

Fig. 2 shows the distance distributions of U (a) and O (b) atoms displaced over distances smaller than 1.6 nm after relaxation at 700 K, averaged on nine simulations. These distributions extend up to 9 nm but only 10 atoms have been displaced over 1.6 nm in average. The distributions of atoms after the displacement cascade (continuous lines) and the distribution of atoms due to thermal vibrations at 700 K only (dashed lines) are indicated in Fig. 2. This figure reveals several interesting features. Firstly, if atoms have covered distances inferior to ~0.15 nm, then they have not been moved out of their original lattice site. Secondly, it is clear from Fig. 2 that a vast majority of atoms (in fact more than 70% of all displaced atoms) cover distances less than one cell parameter (see also [13]). Finally, following the cascade event, displaced atoms occupy one of two possible crystallographic sites: an original lattice site or for a smaller proportion of displaced atoms interstitial octahedral sites. This is quite obvious from the U atom distribution, but less so regarding the O atom distribution. It was however checked by averaging atoms position upon time to remove the thermal spreading from the O displacement distribution.

3.2. Kinchin–Pease type modelling

A model based on a very simplified Kinchin–Pease (KP) [14] approach was developed in order to evaluate the energy density and distribution functions of the displaced atoms in the case of a diatomic material (here, U and O) and when the displacement thresholds are not necessarily small compared to the energy of the moving atoms. The strong assumption of this model is that the energy distribution of both moving particles generated by a collision is a couple of Dirac delta functions at the average energy of the particles after the collision (instead of being uniform between 0 and the energy of the incident particle as in the classical KP model). The energy ratio between the energy E_1 of the incident particle and that (E_2) of one of the particles after the collision is thus given by Eq. (1):