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Stress-induced phase transformation in nanocrystalline UO_2

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We report a stress-induced phase transformation in stoichiometric UO_2 from fluorite to α-PbO_2 structure using molecular dynamics (MD) simulations and density functional theory (DFT) calculations. MD simulations, performed on nanocrystalline microstructure under constant-stress tensile loading conditions, reveal a heterogeneous nucleation of α-PbO_2 phase at the grain boundaries followed by the growth of this phase towards the interior of the grain. The DFT calculations confirm the existence of the α-PbO_2 structure, showing that it is energetically favored under tensile loading conditions.

Keywords: Heterogeneous nucleation of phase transformations; Nanocrystalline microstructure; Simulation; Fluorite

Uranium dioxide (UO_2) is one of the most widely used materials for nuclear fuel because it is easy to fabricate and is highly stable under intense heat and radiation conditions in the reactor core. It has a high melting temperature (~3100 K) [1,2] but poor thermal conductivity. In the reactor, as the heat is removed from the exterior regions of the UO_2 pellet via a coolant fluid, the temperature in the interior remains comparatively high, leading to large thermal gradients and a complex stress state across the fuel pellet. In addition, at high burnups and in presence of fission products, voids and gas bubbles, the UO_2 matrix is likely to be under high stress. However, little is known about any stress-induced structural transformations in UO_2. Experiments and simulations have confirmed that UO_2, which is primarily found in the fluorite structure, transforms to the cotunnite structure under compression at 69 GPa [3]. However, to the best of our knowledge, there has been no examination of structural transformations under tension. In this work, we use two different computational techniques – molecular dynamics (MD) and density functional theory (DFT) – to study the structural changes of UO_2 under high-stress tensile loading conditions. We find that UO_2 shows a stress-induced phase transformation from fluorite (space group 225) to the α-PbO_2 structure (space group 60). The MD simulations were performed on idealized, nanocrystalline model structures of stoichiometric UO_2. Under constant-stress tensile loading conditions of 4.5 GPa and at a temperature $T = 800$ K, we observe the heterogeneous nucleation of UO_2 in the α-PbO_2 structure at the grain boundaries (GBs) with the subsequent growth of this phase towards the grain interior. Our simulations indicate that the GBs are crucial in the nucleation of the new phase. Once the transformation to the α-PbO_2 structure is complete, microcracks form along the GBs, ultimately leading to intergranular fracture. In order to validate the findings from the MD simulations, which are based upon an empirical potential, DFT calculations are performed. The DFT calculations qualitatively agree with the MD simulations, showing that the α-PbO_2 structure is energetically favored over the fluorite structure under tensile conditions.

The MD simulation model – a columnar microstructure with grains of identical hexagonal shape and diameter ($d = 20$ nm), but different orientations – follows that used in Ref. [4]. The Voronoi tessellation method [5] is used to construct [1 0 0] columnar samples containing six grains within the three-dimensional periodic simulation cell. The grain orientations are chosen such that they generate only high-energy, asymmetric GBs, each with a misorientation angle of 30°. The simulation cell contains 20 (1 0 0) atomic planes in the periodically repeated columnar direction, giving a total number of ions of 611,010. UO_2 is modeled using the potential by Basak et al. [6]. We use the Wolf method for the evaluation of the Coulomb energy with a cutoff radius $R_c = 10.8$ Å and a damping parameter of 1.5 [7]. The trajectories of

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the ions are obtained by numerically integrating Newton's equation using a fifth-order predictor–corrector algorithm with a time step of $\Delta t = 0.5 \times 10^{-15}$ s. In order to obtain thermally equilibrated GBs at the temperature of interest, the unrelaxed zero-temperature structure is gradually heated up to 3000 K, slowly cooled down in a stepwise fashion, and finally annealed at $T = 800$ K for 7 ns. The temperature is maintained using a velocity-rescaling thermostat.

In order to induce a tensile loading condition, a constant stress of 4.5 GPa is applied in the z-direction (see Fig. 2), which is normal to the columnar axis, by using the Parrinello–Rahman constant-stress technique [8]. Figure 1 illustrates the observed tensile strain in the loading direction as a function of time. During the early stages of the loading ($t < 5$ ps), the material deforms elastically. About 27 ps after the initial loading is applied, an increase in strain in the loading direction is seen. After 65 ps, a total strain of approximately 17% is observed, at which point microcracks begin to form at the GBs. The strain in volume of the simulation cell follows the same qualitative behavior as the tensile strain. From the definition of Poisson's ratio, $\upsilon, (\Delta V/V_o) = (1-2\upsilon)\sigma/E$, where $(\Delta V/V_o)$ is the volume strain, σ is the applied stress and E is the Young's modulus, the change in volume due to elastic strain $(\Delta V/V_o)$ can be estimated from the elastic constants [9] as 0.85%. However, the observed volume strain of 10% (before microcrack formation, not shown) suggests that, in addition to the elastic contribution, there are other factors involved.

To understand the microstructural processes involved leading to this volume strain of 10%, we perform common neighbor analysis (CNA) [10] on the uranium ions which form a face-centered cubic (fcc) sublattice within the UO_2 fluorite lattice. CNA performed on the initial structure identifies only those uranium ions residing in the GBs as being in a non-fcc arrangement. Figure 2 shows results from CNA performed on the nanocrystalline microstructure as a function of loading time. For visualization purposes, only those uranium ions not in an fcc environment are shown. At $t = 33$ ps (Fig. 2a), significant amounts of the crystalline structure near three of the GBs contain uranium ions in a non-fcc environment. Upon detailed analysis of the structure in these regions, we find that the crystal structure is no longer fluorite but rather is in the α-PbO_2 structure. That is, a new phase, α-PbO_2, is nucleated at the GBs. Normally, the driving force for the homogeneous nucleation of a new phase is attributed to a decrease in the Gibb's free energy per unit volume of the system during the phase transformation [11]. However, the homogeneous nucleation of a new phase within an existing phase requires energy as it creates an interface between the two phases. In contrast, heterogeneous nucleation at microstructural features – such as GBs, cracks or other interfaces – requires less energy as the amount of interface created between the two phases is reduced. Hence, these features act as a perfect source for heterogeneous nucleation.

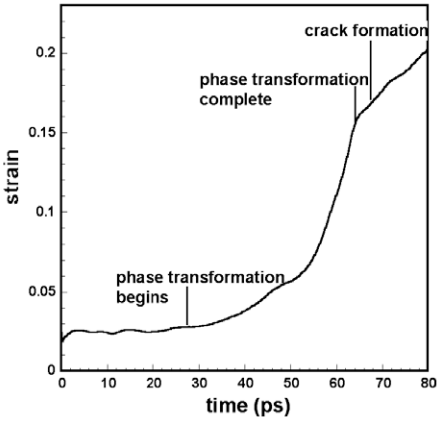

Figure 1. Strain in the loading direction, plotted as function of time. The increase in strain reflects the phase transformation from the fluorite to α-PbO_2 structure. A strain of approximately 17% is seen before microcrack formation at the GBs.

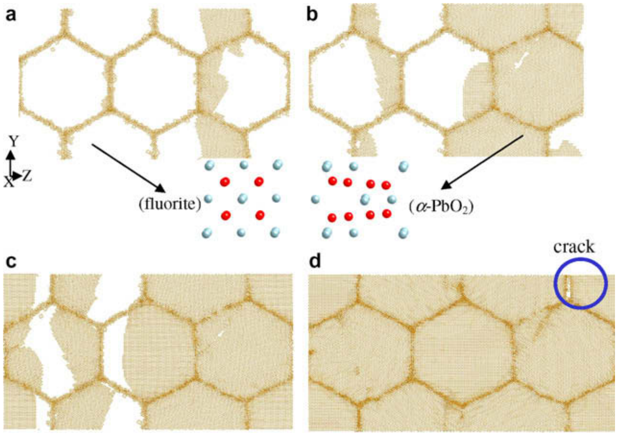

Figure 2. CNA analysis performed on snapshots of stress-induced phase transformation from fluorite to α-PbO_2 structure. Only those uranium ions which do not lie in a fcc arrangement are shown. (a) $t = 33$ ps, the nucleation of the new phase (α-PbO_2) occurs at the GBs. (b) $t = 53$ ps; (c) $t = 59$ ps, the new phase then grows toward the interior of the grain. (d) $t = 66$ ps. After the phase transformation is completed, microcracks are formed at the GBs.

In our MD simulations, GBs are the only source of heterogeneous nucleation and we thus observe that the nucleation of this new phase occurs on the GBs. On analysis of the energies of the GBs that lie normal to the loading direction, we find that the new phase is first nucleated at the GB that has the highest GB energy of -42.34 ± 0.01 eV/UO_2 formula unit (fu). The new phase was never nucleated at the GB with the lowest energy (-42.41 ± 0.01 eV/fu) throughout the entire duration of the simulation. Apart from this dependence of nucleation on GB energy, other factors involved, such as dynamic shear stress along the GBs, may also play a role in initiating the nucleation of the new phase. The nucleation and growth process of the new phase in subsequent grains can be clearly seen in the structure at $t = 53$ and 59 ps (Fig. 2b and c, respectively). At $t = 66$ ps, the fluorite phase is completely transformed to α-PbO_2 throughout the entire system, and microcrack formation has begun (Fig. 2d).

In Figure 3, the atomic virial stress on the uranium ions in the loading direction is shown for the structure at $t = 33$ ps. To reduce the thermal noise inherent in