LA-UR-09-06761

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Intended for: Scripta Materiala

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Stress-induced Phase Transformation in Nanocrystalline UO_2

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Abstract

We report a stress-induced phase transformation in stoichiometric UO_2 from fluorite to $\alpha\text{-PbO}_2$ 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 $\alpha\text{-PbO}_2$ 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 $\alpha\text{-PbO}_2$ structure, showing that it is energetically favored under tensile loading conditions.

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 $\alpha\text{-PbO}_2$ 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 $\alpha\text{-PbO}_2$ 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 $\alpha\text{-PbO}_2$ 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 -PbO₂ 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 [100] columnar samples containing 6 grains within the 3-D 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 (100) atomic planes in the periodically repeated columnar direction, giving a total number of ions of 611,010. UO₂ 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 the ions are obtained by numerically integrating Newton’s equation using a 5th 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 step-wise 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, ν , $(\Delta V/V_o) = (1 - 2\nu)\sigma/E$, 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 sub-lattice 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 $\alpha\text{-PbO}_2$ structure. That is, a new phase – $\alpha\text{-PbO}_2$ – 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.

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/UO₂ 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 $t = 53$ ps and 59 ps (Fig. 2b and 2c, respectively). At $t = 66$ ps, the fluorite phase is completely transformed to α -PbO₂ throughout the entire system, and microcrack formation has begun (Fig. 2d).

In Fig. 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 such an analysis, the data is averaged over 0.27 ps. Only those ions with a tensile stress lower than 60 GPa are shown. Comparing with Fig. 2a, it is seen that, under tension, the uranium ions in the α -PbO₂ phase exhibit a lower stress state than those in the fluorite phase. It is this reduction in the stress state that drives the phase transformation. In these MD simulations, this

stress-induced phase transformation is completely reversible. As the external stress is released, the α -PbO₂ structure completely reverts to the fluorite structure. However, when an external stress is applied on single-crystal UO₂ under similar conditions, no phase transformation is observed. Thus, in our study on asymmetric GBs, only GBs with high-energy act as nucleation sites for the phase transformation to relieve the applied stress. This result suggests that low-energy, symmetric GBs are less likely to act as nucleation sites and a higher stress might be required to initiate a phase transformation, stresses that might lead to microcracking first. Further study needs to be done to confirm this analysis.

To verify that the phase transformation seen in the MD simulations is not an artifact of the potential used, we have calculated the phase stability of UO₂ as a function of volume under tensile conditions using DFT. In these calculations we employ the VASP code [12] with the PW91 functional and the projector augmented wave method [13] on supercells containing 12 lattice ions (4U and 8O) and a plane wave basis with an energy cutoff of 500 eV. We use a k-space sampling of 2×2×2 of the Monkhorst-Pack type [14]. This sampling is likely to be inadequate to completely converge the absolute energy of a given structure, but we expect that the trends revealed from these calculations are physically meaningful. Using a 24 ion cell, the formation energies of point defects changes by less than 0.05 eV as the k-point sampling is increased from 2×2×2 to 4×4×4. [15]

In Fig. 4a we compare the energy vs. volume curves for the regular fluorite structure of UO₂ and the *newly found* α -PbO₂ structure with both DFT and the empirical Basak potential. In the DFT calculations, the α -PbO₂ structure is unstable at 0K and zero

pressure. Since we are unable to constrain the structure to a given symmetry in the DFT calculations, we impose constraints on the cell in order to maintain the α -PbO₂ structure. This is done by keeping the relative position of the ions as well as the volume of the cell constant, but allowing the cell shape to change. These constraints yield an approximate energy vs. volume curve for UO₂ in the α -PbO₂ structure. Surprisingly, in the single-crystal simulations with the Basak potential, the α -PbO₂ structure is stable at 0.1K and zero pressure. The structure becomes unstable when compressed beyond a hydrostatic volume strain of 0.98. To aid the comparison of the DFT results to those of the empirical potential, the energy of the fluorite structure is taken as 0 eV for both calculations.

The energy vs. volume trends for the Basak potential and the DFT calculations shown in Fig. 4a are very similar. Clearly, fluorite is the stable phase at zero temperature and pressure. The volume of the fluorite structure as found from the Basak potential and DFT are slightly different. However, under tensile conditions both indicate that the energetically favored structure is α -PbO₂. The difference in energy between the fluorite and the α -PbO₂ structures is different for the two methods: +0.0145 eV/ion from MD simulations and +0.186 eV/ion from DFT calculations. However, the volume at which the α -PbO₂ becomes more stable is quite similar in both descriptions (178 Å³ with the Basak potential and 187 Å³ with DFT). This, in addition to the small energy difference from DFT, suggests that the transformation would also occur within a DFT description of the material, though there may be a larger activation energy for the transformation to occur. The MD simulations based upon the empirical potential are clearly not perfect, but neither is the DFT itself. It is known that, in the calculation of defect properties in UO₂, DFT tends to agree with DFT+U in reproducing trends, but the quantitative details differ

[16]. Similarly here, the difference in energy between the two phases might change if calculated with DFT+U. However, as both DFT and the Basak potential predict qualitatively similar behavior, we are confident that the observed existence of the α -PbO₂ phase is not an artifact of our methodology. Finally, to verify that the imposed constraints are not adversely affecting our calculations, we also perform DFT calculations for the largest volume considered in this work, with the α -PbO₂ structure of UO₂ used as a starting structure, allowing both the cell shape and the ionic positions to relax while keeping the volume constant. The α -PbO₂ structure is found to be stable, confirming that there is definite transition away from the fluorite structure at larger volumes.

In conclusion, from two different simulation techniques we establish a phase transformation from fluorite to α -PbO₂ structure in UO₂ under tensile loading conditions. In the MD simulations, the nucleation of the α -PbO₂ structure is seen at the GBs. This role of GBs as one of the most favorable nucleation sites is well known in martensitic transformations in ferrous alloys [17,18]. However, Kajiwara also pointed out that the transformation depends on the character of the boundaries [19]. In our MD simulations, we find that high-energy GBs play a major role in nucleation of the new phase. In addition, we do not see any dislocation nucleation from the GBs. In order to ensure unimpeded dislocation glide in the grain, the columnar direction of the microstructure should match the dislocation slip direction [20]. Since the primary slip system in UO₂ is $\{100\}\langle 110\rangle$, MD simulations were also performed on a columnar microstructure with the columnar direction as $\langle 110\rangle$. Even in this case, instead of any dislocation activity, we also observed the nucleation of the new phase, confirming that the phase transformation is not an artifact of the microstructure. The absence of dislocation nucleation is likely

due to the small grain sizes (20 nm). Experimentally, it has been shown that the dislocation activity is greatly reduced in nanocrystalline oxides [21]. Hence instead of the nucleation of dislocations that normally relieves stress, here the stress is relieved by phase transformation. Thus, we conclude that this phase transformation is crucial for relieving stress in nanocrystalline UO_2 .

Acknowledgements:

T. G. Desai was sponsored through the INL Laboratory Directed Research and Development program under DOE Idaho Operations Office Contract No. DE-AC07-051D14517V, as well as the DOE/BES funded Computational Materials Science Network (CMSN) project on “Multi-scale simulation of thermo-mechanical processes in irradiated fission-reactor materials”. B. P. Uberuaga acknowledges support from the U.S. Department of Energy (DOE), Global Nuclear Energy Partnership and the Office of Basic Energy Sciences. Los Alamos National Laboratory is operated by Los Alamos National Security, LLC, for the National Nuclear Security Administration of the U.S. DOE under contract DE-AC52-06NA25396. We are also grateful for discussions with Dieter Wolf (INL), Paul Millett (INL), Richard Hoagland (LANL), and Kurt Sickafus (LANL).

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Figure Captions:

FIG. 1: Strain in the loading direction, plotted as function of time. The increase in strain reflects the phase transformation from the fluorite to α -PbO₂ structure. A strain of approximately 17% is seen before microcrack formation at the GBs.

FIG. 2: CNA analysis performed on snapshots of stress-induced phase transformation from fluorite to α -PbO₂ structure. Only those uranium ions which do not lie in fcc arrangement are shown. (a) $t = 33$ ps, the nucleation of the new phase (α -PbO₂) 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.

FIG. 3: Atomic virial stress in the loading direction, calculated at $t = 33$ ps. Only those uranium ions with tensile stress smaller than 60 GPa are shown. The uranium ions in the phase transformed state exhibit a lower stress state (compare with Fig. 2a).

FIG. 4: Comparison of normalized energy/ion [eV] as a function of volume [$\text{\AA}^3$] for the fluorite and α -PbO₂ phase by the Basak potential and DFT simulations. In the DFT simulations the relative positions of the ions were held constant. The trends are very similar for the Basak potential and DFT simulations.

Fig. 1

Fig. 2

Fig. 2 (color – online version)

Fig. 3

Fig. 4