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Proton irradiation-induced blistering in UO₂

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Abstract

Proton (H⁺) irradiation effects in polycrystalline UO₂ have been studied. The irradiation was carried out using three ion energies and two different ion fluxes at 600 °C. Scanning electron microscopy (SEM) investigations showed that significant surface flaking took place. Focused ion beam (FIB) milling in SEM was successfully applied for extracting lamellas from uneven blistered surfaces for transmission electron microscopy (TEM) investigations allowing detailed investigations for the degradation mechanisms. High-resolution TEM for the flaked UO₂ surfaces revealed that the implanted H⁺ formed sharp two-dimensional cavities at the peak ion-stopping region instead of diffusing to the matrix. The resulting lateral stress likely caused UO₂ surface deterioration in good agreement with previous blistering and flaking studies on crystalline materials.

Introduction

The behavior of fission products and evolution of irradiation damage in nuclear fuels are of great interest in fuel operation [1]. The atomic percentage of volatile fission products may reach up to 10% and the damage up to thousands of displacements per atom (dpa) at the end of nuclear fuel operation cycle [2]. Some of the fission products are chemically stable, such as noble gases Kr and Xe [3], while others, such as Ba and Zr [4], tend to change the local fuel chemistry and produce complicated microstructures.

Ion irradiation of UO_2 has been performed for decades to simulate the microstructure changes in nuclear fuels and

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to examine irradiation damage evolution without significant activation. The advantage of deep penetration depth and fairly homogenous irradiation damage at the plateau region motivates the use of light ions (such as H and He) to irradiate UO_2 and other ceramic materials especially for studying bulk-like irradiation effects [5–7]. In contrast, heavy ion irradiations, in general, produce micron-scale layers at maximum with substantial gradients in displacement dose and concentration of implanted ions [8–10]. However, one of the main challenges with light ion irradiation of bulk ceramics is to prevent surface flaking, which takes place due to pileup of implanted ions in the narrow peak ion-stopping range [6].

Blistering following surface flaking in H⁺-irradiated single and polycrystalline UO₂ has been shown to take place at a relatively small fluence [5]. Surface flaking in UO₂ results in a rough surface and makes the determination of displacement damage difficult in the remaining sample because, in general, the exact flaking depth and the time for surface flaking are not known. When the new surface is exposed to the ion beam after the flaking event, the integrated total fluence does not hold for the freshly exposed surface and the depth cannot be related to the amount of irradiation damage either. Flaking also limits opportunities to perform additional characterization of the implanted surface using methods that require very low surface roughness. Furthermore, flaking of UO₂ may cause a contamination risk for the irradiation facility.

In this work, we studied proton irradiation effects in UO_2 to elucidate irradiation response of this fluorite crystal under



irradiation at 600 °C. The irradiation conditions were chosen to understand the impact of higher temperatures and multiple fluxes compared to those previously reported in the literature [5]. The main objective for these modifications was to increase H migration from the peak damage region in an attempt to limit blistering. Despite these modifications, blistering took place in each of the irradiated samples. To examine the crystal failures in detail, the blistered surfaces were examined using high-precision focused ion beam (FIB) in scanning electron microscopy (SEM) system and highresolution transmission electron microscopy (HR-TEM) techniques. Sharp crack-like features were found at the vicinity of the blistered surface further supporting the hypothesis of H pileup at the peak ion-stopping region.

Materials and methods

The polycrystalline samples of depleted UO₂ were sintered at Los Alamos National Laboratory following the procedure outlined previously [5]. A toroidal volume ion source (Torvis) and Pelletron® tandem accelerator (University of Wisconsin-Madison [11]) were used for the ion irradiations. The irradiation chamber pressure was in the range 10^{-6} – 10^{-7} mbar during irradiations. The sample temperature was monitored with thermocouples attached to the sample stage right next to the sample disks. The target irradiation temperature was 600 °C. Two irradiation runs were made with high and low ion fluxes. For the high flux irradiation, only beam heating contributed to the sample temperature. For the low flux irradiation, the sample holder was resistively heated to 300 °C from its backside and beam heating contributed the remaining 300 °C. With this instrumentation, the measured ion currents at the irradiation stage were about 15 μ A and 5 μ A, resulting in fluxes of 4.2×10^{13} and 1.4×10^{13} H⁺/cm²s, respectively. With the low and high ion fluxes, ion energies of 1.5, 2.0, and 2.5 MeV were applied. The change for the ion energy required only a minor realignment for the ion beam optics, and the samples were not subjected to the ion beam during the alignment. It is unlikely that the quick alignment step induced blistering, as the samples were not actively cooled during this step and the temperature gradients were smaller than they were during the irradiation startup. It is also noted that somewhat similar irradiation startup conditions using mono-energetic beam did not induce blistering in [5]. The fluence for each energy was set to about the UO₂ blistering limit reported previously for 300 °C irradiations [5]; 5×10^{17} , 7.5×10^{17} , and 1×10^{18} ion/cm² for 1.5, 2.0, and 2.5 MeV, respectively. With the separated ion-stopping ranges, the peak region could be examined by preparing TEM samples from the flaked surfaces using FIB, in which the practically examined depth is only about 10 µm. However, this applies only if flaking

occurs near the end of irradiation and the flaked surface is parallel to the original sample surface.

The Stopping and Range of Ions in Matter (SRIM) code was used to simulate the profiles of atomic displacements in UO_2 [12]. Procedure outlined in [13] was utilized in calculating the displacement damage in Kinchin–Pease (KP) mode. O and U displacement energy was set as 20 and 40 eV, respectively [14]. The resulting displacement damage and ion concentration profiles are presented in the Supplementary material.

Cross sections perpendicular to the sample surfaces were prepared in a Quanta 3D FIB system. A protective platinum layer was first deposited onto the surface. A lamella was then created by coarse trenching $15 \,\mu\text{m} \times 10 \,\mu\text{m} \times 1 \,\mu\text{m}$ sample. The lamella was then lifted out and welded to a copper TEM grid. A final thickness of 100 nm was prepared using 30 keV Ga ions. Final cleaning of the sample was conducted first using 5 keV and subsequently 2 keV ion energy. A Tecnai TF-30 field-emission gun TEM was used for microstructural analysis. Both the FIB sample preparation and TEM characterization were performed at the Center for Advanced Energy Studies (CAES) in Idaho Falls, ID.

Results

Large-scale SEM images for all the irradiated samples are shown in Fig. 1. As is clearly seen, surface flaking was evident for both UO_2 samples, Fig. 1a and b. The flaking in UO_2 samples proceeded via laminar removal of material from the surface. The sample irradiated with the low flux clearly showed three terraces, while the amount was larger for the high flux sample. FIB was applied to fabricate crosssectional TEM samples from the UO_2 fracture surfaces, Fig. 2. Even though the surface was uneven, Fig. 2a and b, the lamellas were successfully lifted out, and microstructures just beneath the fracture surface were examined. Characteristic for all the FIB lamellas was that they contained a significant number of pores, seen as round holes, and local inhomogeneity, large cavities, originating most likely from the sample sintering process, Fig. 2 (c) and (d).

In one particular location, a several micrometers' long sub-surface crack was located below the UO₂ fracture surface, Fig. 3. The UO₂ grain which contained the crack was tilted to [110] zone axis and imaged by using HR-TEM, Fig. 4. Albeit the crack was several microns long, it was laterally confined in a thickness of few nanometers, Fig. 4a. HR-TEM also showed that the crystal orientation on both sides of the crack was identical, Fig. 4b to d, which is a clear evidence of transgranular crack propagation rather than intergranular. Interestingly, faceted fracture surfaces, resembling intergranular cracking, were found in polycrystalline







Fig. 2 a Pt stripe was first deposited at the specific location on the sample, and subsequently b trenched and lifted out for further thinning. FIB lamellas showed that the polycrystal samples contained small pores (c) and inhomogeneity (d) originating from the sintering process of the samples

UO₂ samples in [5] but the current TEM-observation clearly indicates that the cracking mode was transgranular.

Discussion

Both irradiated UO_2 samples with high and low ion fluxes had experienced a complete surface deterioration during proton ion irradiation. The reasons leading to the surface flaking are discussed below. First, we rule out oxidation and associated pulverization as a mechanism for flaking. UO₂ can readily oxidize at the temperatures of this investigation [15]. Oxygen-rich phases, such as U₃O₈, are known to cause surface flaking due to a significant volume expansion as compared to UO₂ [16]. Irradiation under vacuum and with H ions (reducing local environment) is not capable of inducing bulk oxidation and associated spallation. Reduction of UO₂ during irradiation to





Fig.3 Cross section of the UO_2 surface showed a region which was almost flaked off from the surface. The sub-surface crack travels between the white arrows

induce substoichiometry (UO_{2-x}) is not considered probable, as hypostoichiometry of the fluorite UO_2 phase is not thermodynamically possible at the temperatures of this study [17]. Deviations from stoichiometry may have an impact on UO_2 fracture under H irradiation, but the possible off-stoichiometry effects would have to be local. Some supporting theoretical models have been presented on the defect-induced suppression of H-diffusion in UO_2 [18], but further work is needed to clarify this aspect.

SEM investigations showed that the magnitude of ion flux influenced flaking, but both UO_2 samples irradiated with low and high fluxes suffered from severe flaking. The number of terraces on the sample surface was three at the minimum, which indicates that the blistering took place at all the applied ion energies. At the low flux, the surface flaking was not as complete as in the case of high flux, which may indicate a slight improvement via enhanced diffusion. However, FIB revealed that all the UO_2 samples contained pores and inhomogeneity, which apparently did not contribute to the out-diffusion of the implanted H ions from the peak implantation region. Comparing these results to the observations in [5] indicates that increasing the temperature from 300 to 600 °C or changing the ion flux did not have a major impact on surface flaking.

HR-TEM provided direct evidence for blistering mechanism, in agreement with previous works on surface blistering and flaking [5, 6] that the most likely cause for UO₂ flaking was the high concentration of implanted ions at the peak damage regions and subsequent crystal stress. Extremely narrow cracks were found propagating parallel to the fracture surfaces. These few nanometers wide and several microns long cracks showed highly localized crystal deterioration within the UO₂ lattice. The cracks were of intragranular type and did not have a major impact on the lattice below or above of the cracking site. In connection to the phase stability issues discussed above, no indication of other phases was found in the vicinity of the cracks. Also, no clear indication of H bubbles was found at the vicinity of the cracks, which indicates that the H atoms remain in the matrix, form bubbles smaller than the TEM resolution, or rapidly migrate to the crack after its initiation.

Conclusions

Polycrystalline UO_2 samples were irradiated with protons at 600° C at two flux levels and three energy values. The samples showed significant flaking at the same fluence. HR-TEM indicated that cracks of few nanometer wide



Fig. 4 a–d HR-TEM showed that the narrow crack propagated through the grain



formed at the peak implantation region of the irradiated UO_2 samples, further indicating that the H build-up in that region was the most probable reason for flaking.

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1557/s43580-021-00149-3.

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