

UO₂ Oxidative Corrosion by Nonclassical Diffusion

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Using x-ray scattering, spectroscopy, and density-functional theory, we determine the structure of the oxidation front when a UO₂ (111) surface is exposed to oxygen at ambient conditions. In contrast to classical diffusion and previously reported bulk UO_{2+x} structures, we find oxygen interstitials order into a nanoscale superlattice with three-layer periodicity and uranium in three oxidation states: IV, V, and VI. This oscillatory diffusion profile is driven by the nature of the electron transfer process, and has implications for understanding the initial stages of oxidative corrosion in materials at the atomistic level.

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Oxidative corrosion is a key cause of material failure. This is especially true of uranium dioxide, which is the most economically important uranium mineral [1], the primary constituent of most nuclear fuels [2], and the desired product of many bioremediation strategies for uranium contamination [3]. UO₂ is an end-member in a complex metal-oxide system that is fundamentally important to experimental and computational actinide science (e.g., Refs. [4–7]). Despite more than 60 years of UO₂ oxidation research [8], moving beyond a macroscopic or empirical description to an understanding of the underlying atomistic processes has been difficult due to experimental challenges and the complex oxidation behavior of uranium oxides.

Uranium dioxide exhibits a broad range of structural transformations due to oxidation. The UO₂ lattice readily incorporates interstitial oxygen atoms up to a stoichiometry near UO_{2.25} (U₄O₉) with minimal unit cell distortion [9]. Further oxidation to U₃O₈ leads to structural rearrangement, volume expansion, and material failure [10,11]. When U(IV) in UO₂ is oxidized to U(VI) under water, dissolution occurs since U(VI) readily forms soluble uranyl (UO₂²⁺) that can be released into the environment, although surfaces can be passivated [12]. Single-crystal surface structures and oxidation have been studied under vacuum [10,11,13–21], and by computational methods [22,23], but little is known about atomic-level oxidation mechanisms under atmospheric conditions, especially in the earliest stages of oxidation.

We have combined crystal truncation rod (CTR) x-ray diffraction—an *in situ* method that is sensitive to surface atomic structure [24,25]—with density-functional theory (DFT) and x-ray photoelectron spectroscopy (XPS) to detail the initial stages of UO₂ oxidation via the (111) surface. This surface is the natural cleavage plane and

predicted to be the most stable when dry [26–28]. We show that the oxidation front does not follow classical diffusion, but instead exhibits complex self-organization behavior, with interstitial oxygen atoms preferentially occupying every third layer below the surface.

A freshly polished surface was measured with CTR (time 0), exposed to ~1 atm dry oxygen gas, and remeasured several times up to 21 days (504 hours) of exposure [29]. As the surface oxidizes, broad, bulk-forbidden peaks develop at L values slightly greater than integers (see Fig. 1 and Fig. S1 in the Supplemental Material [29]), consistent with a contracted three-slab (see Fig. S2 [29]) superlattice in the surface-normal direction. Minor asymmetries (with shifts to higher L) about the Bragg peaks and valleys become more pronounced with increased O₂ exposure, indicating surface-normal contraction of the near-surface layers. The appearance of oscillations indicates development of a coherent thin layer with a different electron density extending a well-defined distance into the bulk. Oscillations appear on both off-specular and specular rods, demonstrating that the thin-layer region shares the bulk in-plane order. These observations indicate an orderly advancing oxidation front that is distinct from classical exponential diffusion fronts.

Atomic-level models yielding excellent fits to the CTR data (see the Supplemental Material [29], Fig. S1) required inclusion of oxygen adatoms above the vacuum-terminated surface and refinement of the thicknesses and interstitial O atom occupancies for increasing numbers of structural slabs as oxidation proceeded. The refined slab contractions and interstitial oxygen occupancies are plotted vs depth in Fig. 2. The extent of subsurface slab contractions and interstitial oxygen occupancies all increased with O₂ exposure. After 21 days of dry O₂ exposure, the oxidation

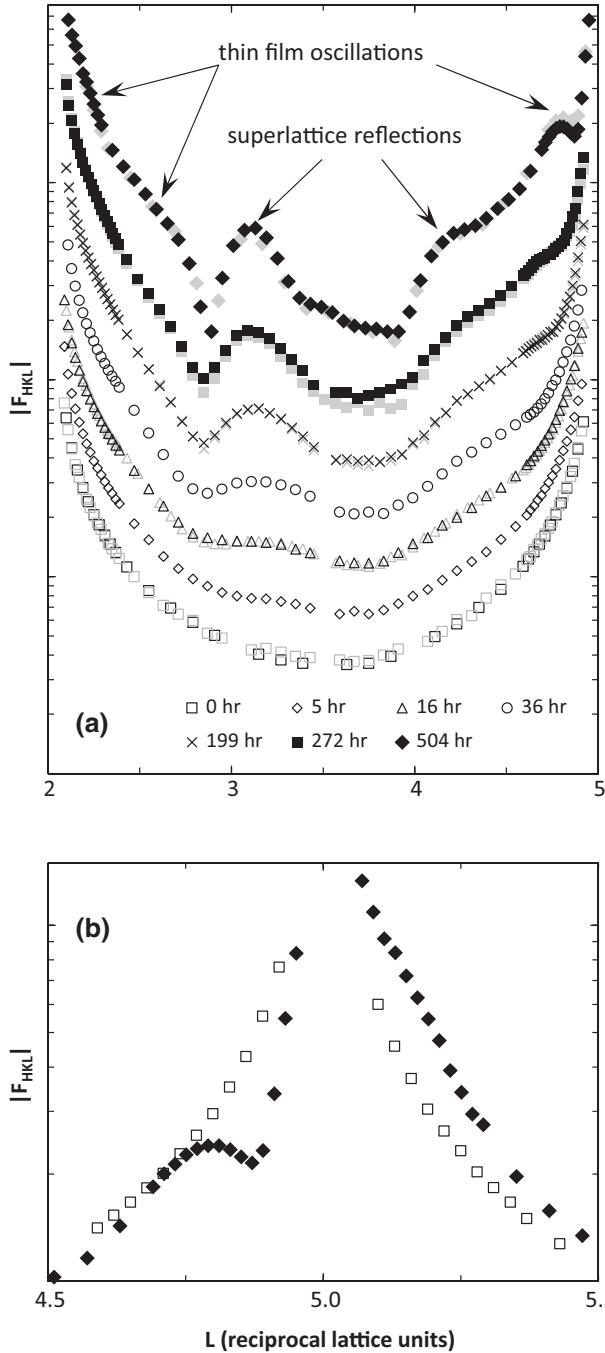


FIG. 1. $10L$ rod segments collected during oxidation. (a) Oxidation is accompanied by development of superlattice reflections and thin-film oscillations. Statistical error bars are smaller than symbols. Data collected at the start (black symbols) and end (gray symbols) of long data sets show surfaces were stable during measurement. (b) Region around 105 Bragg peak shows development of asymmetry and oscillations upon oxidation.

front penetrated 11 slabs, or 35 \AA into the crystal. Figure 2 reveals oscillatory profiles with three-layer periodicity in both slab contraction and interstitial O occupancy, with the longest exposures showing peaks in slab contraction in slabs 0, 3, 6, and 9, and peaks in interstitial occupancy in

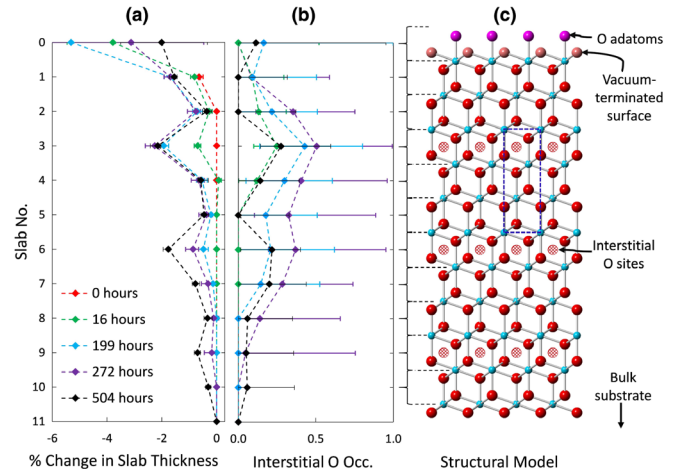


FIG. 2 (color online). Refined slab contractions (a) and interstitial occupancies (b) are plotted vs depth and show three-layer periodicity. (c) Proposed model for oxidized UO_2 (111) surface. U is cyan, structural O is red, surface O adatoms are magenta, and interstitial O is hatched red. Surface is oxygen terminated. YZ projection of surface unit cell is indicated by blue dashed lines.

slabs 3 and 6. This three-slab periodicity is the source of the superlattice reflections and the increased electron density resulting from slab contraction and interstitial oxygen incorporation gives rise to the thickness oscillations. Additional CTR measurements (see the Supplemental Material [29], Fig. S3) of surfaces oxidized under more complex, aqueous conditions show a similar front develops, but at an accelerated rate, demonstrating that this oxidation mechanism applies over a broad range of conditions.

The source of the three-slab periodicity can be understood by considering the nature of uranium oxidation from a quantum mechanical perspective using partial densities of states (PDOS). Chaka *et al.* [23] used PDOS calculations to show that uranium oxidation can be quantified by the extent of electron transfer from localized U $5f$ bands to O $2p$ orbitals. Using a 1×1 seven-slab model with a fully oxygen-coordinated surface uranium, Chaka *et al.* found that interstitial oxygen occupation of either slab 1, 2, or 3 resulted in the partial oxidation of three subsurface uranium atoms. Our present calculations on 1×1 systems (with an interstitial occupancy of either 0 or 1 in a given slab) show that if the surface uranium is oxidized by an oxygen adatom, it is thermodynamically most favorable to incorporate a layer of interstitial O into slab 3 rather than slab 1 or 2 due to greater availability of U $5f$ electrons. Deeper below the surface, the U $5f$ electron density is uniform and there is no thermodynamic driver for the initial interstitial oxygen atom to go below slab 3 [Fig. 3(a)]. Once slab 3 is occupied, the availability of unoxidized U thermodynamically favors occupation of an additional interstitial layer in slab 6 over slabs 1, 2, 4, and 5 [Fig. 3(a)]. The interstitial energy in slab 7 is comparable to slab 6; hence, there is no thermodynamic driver to go deeper until slab 6 is occupied.

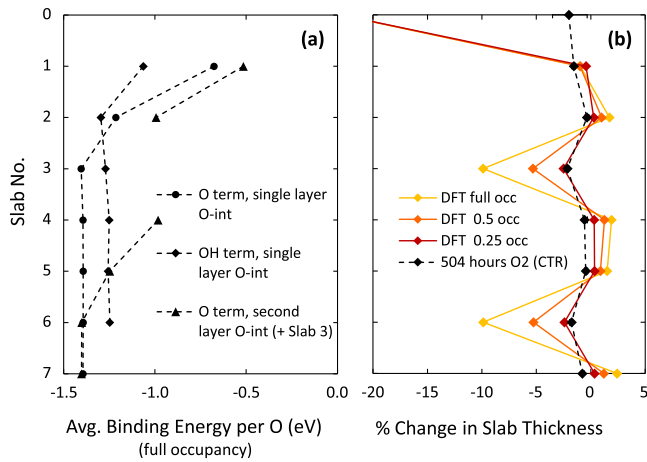


FIG. 3 (color online). DFT results. (a) Binding energies for one layer of interstitial oxygen atoms below hemiuranlyl (oxygen) and hydroxyl-terminated 1×1 surfaces, and for a second layer below the hemiuranlyl terminated 1×1 surface when the slab 3 interstitial position is occupied. (b) Predicted slab thickness changes for fully-, half-, and quarter-occupied interstitial positions in slabs 3 and 6 overlain on thickness changes derived from 504-hour CTR data.

Identifying the positions and quantifying the occupancies of oxygen interstitials in UO_2 is complicated by the large atomic-number contrast between U ($Z = 92$) and O ($Z = 8$), but the CTR-derived occupancies are always $\ll 1$. DFT calculations are invaluable in interpreting the shifts in U atom positions that result from the interstitial oxygen atoms. The extent of measured slab 3 contraction saturates at $\sim 2.2\%$ [Fig. 2(a)], and likely represents the maximum interstitial site occupation. DFT calculations of full, half, and quarter slab occupancy for slabs 3 and 6 result in slab 3 contractions of 9.9%, 5.4%, and 2.4%, respectively, the latter consistent with the CTR measurements [Fig. 3(b)]. Therefore, the maximum interstitial occupancy is likely about 25%. In this configuration, each interstitial O obtains a total of 0.71 electrons from its nearest, 0.84 electrons from its next-nearest, and 0.46 electrons from its next-next-nearest U neighbors (see the Supplemental Material [29], Fig. S4), creating a sphere of 38 oxidized U atoms around it that makes the occupation of adjacent interstitial sites less favorable. This charge delocalization results in subsurface U oxidation states distributed between IV and V while that of the topmost U is VI. Penetration of oxygen interstitials below the surface depends on availability of higher energy U $5f$ electrons at the Fermi level in multiple U atoms.

The CTR fit results [29] indicate that even under nominally anoxic conditions, the topmost U atoms are fully coordinated by O, OH^- , or H_2O adatoms in positions that continue the bulk O lattice. The surface U atoms are relaxed into the bulk, broadly consistent with theoretical predictions of surface behavior under oxygen [22,23]. These findings differ from those of ultrahigh vacuum (UHV) experiments, which indicate incomplete U coordination and outward relaxation

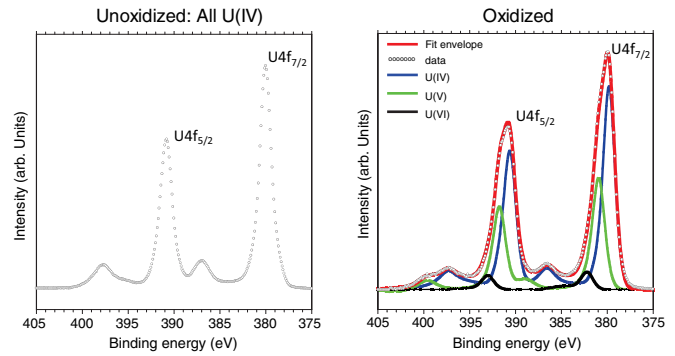


FIG. 4 (color online). X-ray photoelectron spectra collected at normal emission. The nominally unoxidized surface shows strictly U(IV), whereas the oxidized surface shows significant U(V) and minor U(VI).

of U atoms [15]. DFT calculations indicate that an O-terminated surface should have a $\text{U-O}_{\text{adatom}}$ bond length of $\sim 1.8 \text{ \AA}$ regardless of whether subsurface interstitials are present, and the surface U should be fully oxidized to U(VI), producing a surface species that resembles half of the uranyl cation [22,23]. Our calculations indicate this hemiuranlyl termination energetically favors incorporation of the first oxygen interstitial layer into slab 3, as observed with CTR, whereas hydroxyl termination slightly favors slab 2 [Fig. 3(a)]. XPS analysis of a surface oxidized for 20 days under O_2 gas showed the presence of U(IV), U(V), and U(VI) (Fig. 4), broadly consistent with the DFT results and previous spectroscopic measurements, e.g., Refs. [70,71]. Although U(VI) is the thermodynamically stable form of U under our measurement conditions, the oxidized U speciation is dominated by U(V) as a result of kinetic limitations to oxidation. We detected neither U(V) nor U(VI) on an unoxidized control sample. Given the presence of U(VI) on the oxidized sample and the first interstitial layer occupation of slab 3, the surfaces are likely at least partially hemiuranlyl terminated. The CTR measurements show longer average adatom bond lengths ($2.2\text{--}2.4 \text{ \AA}$) than those predicted by DFT. Furthermore, the fraction of the XPS signal arising from U(VI) is too small for the surface to be fully hemiuranlyl terminated [29]. The surface was prepared using deoxygenated aqueous solutions, and no effort was made to remove bound hydroxyl or water [29], which would require heating in UHV. Previous theoretical studies predict surface U-OH and U-OH₂ bond lengths of 2.2 and 2.6 \AA , respectively [22,28], consistent with the CTR results. Given that the binding energy difference between slab 2 and slab 3 interstitials for a hydroxylated surface is very small [Fig. 3(a)], a mixed termination with some hemiuranlyl component could readily drive the first layer of interstitials into slab 3. We therefore infer a mixed termination with hemiuranlyl, hydroxyl, and/or molecular water at the surface.

The models determined from our CTR and DFT analyses are distinct from previously proposed bulk interstitial cluster models (e.g., Refs. [5,7,9,11,30,34,40,45,47,48]),

few of which are periodic structures with long-range order. The superlattice peaks can only arise from a structure with three-layer periodicity in the $\langle 111 \rangle$ direction. They cannot be explained by a surface layer of β - U_4O_9 with the structure determined by Cooper *et al.* [30]. Allen *et al.* [11] proposed that interstitial clusters might “plate out” between (111) planes in UO_{2+x} , however, their model is inconsistent with enhanced contraction of every third layer. The ordered, oscillatory oxidation front discovered here is driven by the surface and the energetics of the U 5*f* orbitals. Since corrosion is inherently surface mediated, it is ultimately the surface-imposed structure that is most relevant to low-temperature UO_2 corrosion. Using surface scattering and spectroscopy, combined with theory, we have demonstrated nonclassical diffusion of oxygen interstitials into this redox-active material. Each interstitial has a sphere of influence extending over several shells of neighboring cations, influencing the positions and energetics of subsequent interstitials. This provides a conceptual framework to understand the initial stages of oxidation in UO_2 , and may be relevant to a wide class of redox-active materials and minerals that can incorporate interstitial oxygen, including isostructural PuO_2 .

CTR data were collected at GeoSoilEnviroCARS, using resources of the Advanced Photon Source, a US DOE Office of Science User Facility operated for the DOE Office of Science by Argonne National Laboratory (Contract No. DE-AC02-06H11357). GeoSoilEnviroCARS is supported by NSF-Earth Sciences (Grant No. EAR-1128799) and DOE-BES-GeoSciences (Grant No. DE-FG02-94ER14466). A. M. C. and E. S. I. were supported by the Geosciences Research Program at PNNL, US DOE Office of Science, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences and Biosciences. Support was provided by DOE-BER, Subsurface Biogeochemical Research, through the SLAC SFA program (DOE Contract No. DE-AC02-76SF00515). XPS data were collected in the Radiochemistry Annex at EMSL, and a portion of the DFT study was performed using the computational resources of EMSL, a national scientific user facility sponsored by DOE-BER and located at Pacific Northwest National Laboratory. Early sample preparation benefitted from access to the Berkeley Nanogeoscience Center. We thank R. Caciuffo (Institute for Transuranium Elements) and M. Paffett (Los Alamos National Laboratory) for providing UO_2 crystals.

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