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Correlation between crystallographic orientation and surface faceting in UO_2

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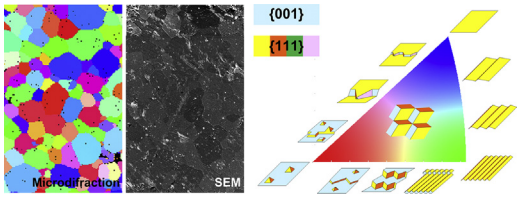
HIGHLIGHTS

- Crystallographic orientation -surface faceting correlation is established for UO_2.
- Equilibrium UO_2 surface is dominated by triple-plane structures.
- Surface morphology may also be influenced by local fluctuation of hydroxidation.
- A method to measure crystallographic orientation using SE images is proposed.

GRAPHICAL ABSTRACT



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ABSTRACT

Here coordinated experimental efforts to quantitatively correlate crystallographic orientation and surface faceting features in UO_2 are reported upon. A sintered polycrystalline UO_2 sample was thermally etched to induce the formation of surface faceting features. Synchrotron Laue microdiffraction was used to obtain a precise crystallographic orientation map for the UO_2 surface grains. Scanning electron microscopy (SEM) was utilized to collect the detailed information on the surface morphology of the sample. The surface faceting features were found to be highly dependent on the crystallographic orientation. In most cases, Triple-plane structures containing one {100} plane and two {111} planes were found to dominate the surface of UO_2. The orientation-faceting relationship established in this study revealed a practical and efficient method of determining crystallographic orientation based on the surface features captured by SEM images.

1. Introduction

Surface properties of UO_2 play an important role throughout the lifetime of this widely-used commercial nuclear fuel material, from manufacturing to storage. The surface features and corresponding thermodynamic characteristics influence the morphology, size, and distribution of fission gas bubbles as well as the initiation and propagation of micro-fractures within the nuclear fuel pellets. Hence, a better understanding of the surface behavior of UO_2 will help interpret the in-pile behavior of UO_2, thereby advancing the capability of precisely predicting fuel performance [1–3]. Like many other materials, the surface energy of UO_2 varies substantially with crystallographic orientation. This energy variation creates anisotropy in surface energy, which leads to the formation of surface faceting features during annealing. Detailed understanding

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of these orientation-dependent surface faceting features can not only expand the fundamental knowledge of the surface characteristics of UO_2, but can also shine a light on the mechanisms involved in gas swelling and micro-fracture of UO_2 fuel [4,5]. Additionally, by establishing a deterministic correlation between the crystallographic orientation and surface morphology, it is possible to develop a method to deduce the lattice orientation of surface grains of a UO_2 sample based on its surface faceting features.

As a consequence of anisotropic surface energy, the surface faceting phenomenon occurs in a great number of crystalline materials. The surface faceting features can also be correlated with the Wulff shape of the crystal [6]. The formation mechanism for surface faceting has been investigated by both experimental and computational approaches [7–10]. Previously, the surface faceting of UO_2 was investigated by low energy electron diffraction (LEED). However, as LEED is limited to the characterization of single crystal specimens, only those planes with low Miller indices; namely, {100}, {110}, and {111} planes; have been examined [11–14]. As the closest packed layer, the {111} surface of UO_2 has the lowest surface energy [15,16] and is, therefore, not subject to surface coarsening or faceting [17]. On the contrary, the {110} surface forms a wavy structure consisting of two {111} planes sharing a <110> edge with the angle of 109.47° as a result of annealing. In addition, although the majority of the {100} surface remains smooth during annealing, hemi-octahedra (square pyramids) that contain four {111} planes, form on the {100} surface. These pyramid features are believed to be due to the deposition of UO_2 vapor, which is generated during annealing. Only {111} and {100} planes are present at equilibrium, while the {110} and higher-index planes are absent. All the edges present on equilibrium UO_2 surfaces are <110> type, as reported by previous studies [14]. The dominance of the {111} and {100} planes and the <110> edge is also comparable to previous studies of the morphology of UO_2 single crystal. Theoretical prediction gives a simple {111} faceted octahedron [15]. Meanwhile, the experimental examination is limited to some SEM observation of voids on UO_2 surfaces, which shows a {111} faceted octahedron truncated by {100} planes [18,19]. The appearance of {100} planes might be explained by non-equilibrium kinetics model [15] or the modification of surface energy due to hydroxidation [20,21]. Hence, further studies are necessary to clarify the morphology of UO_2 crystal. Recently, the {100} and {111} surfaces were characterized by scanning tunneling microscopy (STM), revealing the atomic level structure of these low-index crystallographic planes [22,23].

All previous investigations on the surface faceting features of UO_2 are limited to three low Miller index planes present within single crystal specimens. There is a scarcity of comprehensive studies on the faceting features of surfaces with general indices. In order to develop a comprehensive understanding of the faceting behavior of polycrystalline UO_2, two key properties need to be determined: the crystallographic orientation of the grains, and a quantitative description of their corresponding surface faceting features. The coarse surface of UO_2 with faceting features limits the utilization of conventional techniques. For instance, although electron backscattering diffraction (EBSD) is capable of working with coarse surfaces, the faceting features may create shadows on investigated surfaces, preventing the collection of grain to grain matching maps of crystallographic orientation, especially when grains are small. However, synchrotron X-ray diffraction is barely influenced by surface roughness due to the deep penetration ability originating from its high energy and intensity, making it an ideal technique for this study. This synchrotron technique has been adopted to examine a variety of bulk materials, including advanced Fe-based alloys [24–29] and metallic nuclear fuel materials [30,31]. When the X-ray beam is focused to a submicron size, mapping of a micrograined specimen can be easily achieved [32]. Thus, synchrotron Laue microdiffraction [33] has the unique non-destructive capability of measuring the crystallographic orientation of grains with coarse surfaces. The surface features can be characterized by secondary electron (SE) imaging with a scanning electron microscope (SEM). Synchrotron microdiffraction and SE SEM techniques were coordinated in this study to establish the precise correlation between crystallographic orientation and the surface faceting features of multiple grains within a polycrystalline UO_2 specimen.

2. Experiments

2.1. Specimen preparation

The polycrystalline UO_2 specimen investigated in this study was fabricated utilizing spark plasma sintering (SPS) [34]. UO_2 powder was procured from International Bio-analytical Industries Inc. To reduce the particle size, the powders were ball milled for 30 min utilizing tungsten carbide container and milling balls. To produce bulk UO_2 samples, an SPS within an industrial argon atmosphere (<5 ppm oxygen) was used. The temperature was increased to 1600 °C with a 100 °C/min ramp rate, while the pressure was increased from a 10 MPa pre-load to 40 MPa. The sample was sintered for 5 min under these conditions, and then the temperature was decreased to 1500 °C at 20 °C/min as the pressure was decreased to 10 MPa. The sample was annealed for 30 min under these conditions in order to relieve residual stresses induced during sintering. The power was turned off, and the sample was allowed to cool to room temperature. Further details about the ball milling and SPS procedures can be found in Ref. [34]. The sintered UO_2 sample was mechanically polished down to 0.5 μm roughness using diamond lapping films to produce a uniformly smooth surface finish. The sample was then thermally etched by annealing at 1500 °C for 1 h in a He gas environment to activate the formation of surface faceting by enhancing surface diffusion. By measuring the lattice parameter using an PANalytical X-ray diffractometer, the stoichiometry of the sample was determined according to the following equation: $a = 5.4705 - 0.132x$ [35,36], where a is the derived lattice parameter, and x is the stoichiometry parameter as in the formula UO_{2+x}. The stoichiometry of the sample investigated in this study was found to be $UO_{2.00047\pm0.00608}$. No distinguishable oxygen pickup was detected during the thermal etching procedure based on the lattice parameter measurement.

2.2. Synchrotron microdiffraction

Synchrotron Laue microdiffraction measurements were performed at Sector 34-ID-E at the Advanced Photon Source (APS), Argonne National Laboratory (ANL). The synchrotron experiment setup is illustrated in Fig. 1(a). The UO_2 specimen was kept in a sealed container with a Kapton film window. The synchrotron white X-ray beam was focused by a Kirkpatrick-Baez (K-B) mirror system to provide a 0.6 μm × 0.8 μm beam size for 2D scanning. The sample was oriented such that the sample surface was at a 45° angle to the beam direction. Laue diffraction patterns were collected by a 2048 × 2048 2D area detector at an array of points across the sample. The Laue patterns were then processed to determine the reciprocal lattice vectors so that the crystal orientation of all the scanned positions could be derived. The scanning step length in both directions was 2 μm. Because the grain size of the UO_2 sample was 18.93 ± 1.28 μm according to the SEM images, approximately 70 data points were collected for each grain.