

Low-Temperature Oven Method for Spent Fuel Oxidation Testing

- Activity Plan (D-20-45) -

for

YMP WBS Element 1.2.2.3.1.1

LLNL-YMP Spent Fuel Waste Form Testing

Lawrence Livermore National Laboratory

UNCONTROLLED

Revision 0

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CHANGE NOTICE

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Affected Document: Low-Temperature Oven Method for Spent Fuel Oxidation Testing
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Currently Read as Follows:

Paragraph 3.3, 1st sentence, "... Section 2.0 of the test plan ..."

Changed to Read:

Paragraph 3.3, 1st sentence, "... Section 2 of the test plan ..."

NOTE: THIS CHANGE NOTICE IS TO BE FILED AT THE FRONT OF THE AFFECTED DOCUMENT

1.0 INTRODUCTION

The Yucca Mountain Project Office (YMPO) is evaluating a site at Yucca Mountain, Nevada, for the U.S. Department of Energy (DOE) Office of Civilian Radioactive Waste Management (OCRWM) to determine the suitability of this site for a high-level nuclear waste repository. The horizon that is under investigation for repository development is the Topopah Spring Member of the Paintbrush Tuff, a welded, devitrified ash flow tuff. At Yucca Mountain, this unit lies in the unsaturated zone; the water table is hundreds of meters below the reference repository horizon. Lawrence Livermore National Laboratory (LLNL) is developing designs for waste packages and testing the performance of waste forms and metal barriers under expected repository conditions for the YMPO Project.

The Environmental Protection Agency (EPA)⁽¹⁾ and the Nuclear Regulatory Commission (NRC)⁽²⁾ have imposed requirements limiting potential radionuclide release from a high-level nuclear waste repository. The potential change in the oxidation state of spent fuel during its residence in a repository must be known to evaluate its radionuclide retention capabilities. Analyses⁽³⁾ indicate that UO_2 will oxidize to higher states under the temperature and atmospheric conditions expected in a tuff repository. If the oxidation progresses sufficiently, cladding that contained breaches might split open, or significant quantities of higher oxides with potentially higher leach rates might form.

1.1 OBJECTIVE OF DRY BATH TESTING

An integrated technical approach⁽⁴⁾ was developed at Pacific Northwest Laboratory^(a) to study spent fuel oxidation at low temperatures characteristic of the post-container breach period. The objective of the long-term oxidation testing is to verify at low temperatures the predictions based on the thermogravimetric analysis (TGA) results of the influence of important fuel characteristics (i.e., gas release, burnup, fuel type, etc.) and atmospheric variables (i.e., moisture content, radiation field) on oxidation rates and

(a) Operated for U.S. Department of Energy by Battelle Memorial Institute under Contract DE-AC06-76RLO 1830.

strong enhancement of grain boundary attack with a saturated moist atmosphere at 150°C.⁽⁶⁾ The majority of the oxidation work has been conducted on PWR fuel. The few studies on BWR fuel looked at burnup effects and powder formation.⁽⁷⁾ Burnup over the range of 10 to 35 Gwd/MTU had little effect on the oxidation rate of Quad Cities BWR fuel at 230°C. Monticello experimental BWR rodlets showed as much as 2% weight gain, equivalent to that of U₃O₇, in only 6000 h at 170°C; however, the uncertainty was as much as 50%. The efforts of that BWR study and its companion PWR studies⁽⁷⁾ were aimed more at determining powder formation applicable to dry storage than mechanisms of U₃O₇ formation applicable to repository work. Little difference was found between the behavior of BWR and PWR fuel. These BWR and PWR studies were conducted in a strong (5×10^5 R/h) imposed gamma field, which would not be present in the repository but which might affect the laboratory results.

Fifty PWR fuel samples are being oxidized in air with dew points of ~+80°C and -74°C at 175°C, 130°C, and 110°C. Though the tests have run for only 3200 to 5800 h, some preliminary observations can be made.⁽⁸⁾

1. At temperatures above 175°C, the rate of weight gain due to oxidation is independent of the particle size, but at lower temperatures the rate is dependent on the particle size. The largest particles oxidize slowest.
2. Over the dew point range of -74°C to 80°C, the moisture in the air appears to have no effect on the oxidation rate.
3. When multiple identical samples are oxidized, there is scatter in the oxidation data of ~20%. This must be accounted for when making extrapolations or performing temperature change oxidation studies using only a few samples.

It is expected that the testing of BWR fuel proposed in this test plan will yield similar results.

2.0 TEST DESCRIPTION

The tests described in this plan will be conducted in a bank of six covered dry baths that provide the proper atmosphere. The fuel samples will come from Cooper BWR fuel rods. After the test, samples may be examined by x-ray diffraction (XRD), ceramography, transmission electron microscopy (TEM)/electron diffraction, or other means before being made available for leaching experiments. The data will be compared with predictions based on the TGA testing of⁽⁹⁾ BWR fuel and dry bath oxidation of PWR fuel⁽⁸⁾ to confirm the oxidation mechanisms and compare behavior. These tests, which will run for up to two years, will be used to confirm the effects of atmospheric moisture and temperature.

2.1 TEST MATRIX

The initial test matrix for the Series 2 tests, consisting of 30 samples, is given in Table 2.1. The justification for the choice of variables that follows is based primarily on the PWR fuel testing series.⁽⁸⁾ The matrix may be adjusted to reflect the latest data from the TGA testing program⁽⁹⁾ and data obtained as the test progresses.

2.1.1. Test Temperature

Tests will be conducted at 175°C, 130°C, and 110°C. A major function of the testing is to define the rate constant (k') versus $1/T$ curve. Since the intermediate temperature data are being gathered on the TGA apparatus⁽⁹⁾ and the low-temperature data in the present dry bath tests, one set of the dry bath tests will be run at 175°C to provide temperature range overlap between the two sets of tests.

Test temperatures of 130°C and 110°C were chosen for the PWR Series 1 tests to extend the rate constant curve to the lowest possible experimental temperature that is expected to produce measurable oxidation in a 2-year test. The Series 1 Test⁽¹⁰⁾ plan describing the dry bath testing of PWR fuel provides the rationale for temperature selection. The selection of these temperatures was dictated by 1) an expected weight gain of the crucible of ~2 mg

fuel in the repository. Earlier testing⁽¹¹⁾ indicated that oxidation may be a two-step process consisting of oxygen diffusion down the grain boundary, followed by diffusion of oxygen into the grains; the second step is the rate-controlling mechanism. If the grain boundary diffusion is rapid with respect to the test duration, such as in the tests at 200°C and 225°C, then samples consisting of fragments are suitable as test specimens.

If diffusion down the grain boundaries takes longer than the test duration, then measuring weight gain of fuel fragments will not reflect the rate-limiting diffusion into the grains.⁽¹²⁾ The grain boundary diffusion step can be significantly enhanced if the fragments are pulverized into smaller particles.

Thermogravimetric analysis testing of PWR fuel⁽¹³⁾ indicated that pulverization does little to enhance oxidation above 175°C. At 140°C there appeared to be some enhancement of the oxidation. This observation was supported by the results of the dry bath oxidation tests on PWR fuel,⁽⁸⁾ which showed no enhancement at 175°C but a distinct spread of over a factor of 2 in the rate of weight gain due to oxidation for the different particle sizes at 130°C and 110°C. A lengthy argument based on the onset of bulk diffusion was made in the Series 1 test plan⁽¹⁰⁾ to justify the selection of particle size. The reasoning presented there still holds. The particle sizing for the pulverized fuel used in the Series 1 PWR fuel oxidation tests will again be used in the BWR fuel oxidation tests.

Fuel can easily be sieved or pulverized so that each size fraction has the same chemical composition and radiation spectrum. In the 175°C experiment, as-irradiated fragments will be used primarily. Pulverized samples, primarily in the -10/+24 Tyler mesh range, will be used in the 130°C test, and pulverized samples, primarily in the -24/+60 Tyler mesh range, will be used in the 110°C test. The maximum diameter of particles passing through the number 10, 24, and 60 Tyler meshes are 1.7 mm, 0.71 mm, and 0.25 mm, respectively. The complete matrix is in Table 2.1.

conducted while some of the baths remain at temperature without affecting either the accuracy of the balance or the temperature stability of those baths still operating, interim examinations may be conducted more frequently.

According to the test matrix (Table 2.1), either one, three, or five samples of any particular type (i.e., fragments, -10/+24 mesh, or -24/+60 mesh) will be run in a test. If five samples are used, two samples will be removed between 6,000 and 12,000 h. The three remaining samples will be tested for the duration, currently estimated to be 2 years. If three samples are used, one will be removed at ~1 year and two will remain for the duration of the test. If a single sample is used, it will remain for the full test duration. Additional samples may be placed under test, replacing those removed, if such action is indicated to be necessary by fuel examinations. The intervals for fuel sample removal may change as a result of the ceramographic, electro-optical, and leaching examinations.

2.1.5. Radiation Fields

No external radiation fields will be applied to the samples because the fields expected at the time of container breach are nearly the same or less than the self fields generated by samples of ten-year-old fuel used in these tests. Therefore, the results should establish a conservative upper bound with respect to radiation enhancement of oxidation at repository conditions.

The alpha field resulting from the decay of the actinides, which can cause localized ionization of the oxygen, will be predominant after 1,000 years. Since the actinides responsible for the alpha activity do not readily migrate, and the actinides have very long half-lives, the alpha fields at 1,000 years and at emplacement will not differ significantly. Since the alpha is a short-range particle, the radiation field resulting from alpha decay is independent of sample size when the sample is over ~30 μm in diameter.

The neutron field present in the reactor is far greater than that ever experienced by the fuel in the repository. All the atomic displacement damage that might significantly affect the oxidation rate of the fuel will have occurred in the reactor. No further neutron radiation damage is expected in the repository.

TABLE 2.2. Characteristics of ATM-105 Cooper BWR Fuel from General Electric

<u>Fuel Type</u>	<u>BWR 7 x 7</u>
Assembly Identification	CZ-346
Discharge Date	(a)
Nominal Burnup	~26 MWd/kgHM
Fission Gas Release	(b)
Initial Enrichment	2.93%
Initial Pellet Density	(a)
Initial Rod Diameter	(a)
Cladding Material	Zircaloy-2
Cladding Thickness	(a)
Rod Identification	ADD-2974

- (a) Information to be provided in a characterization report to be released at a later date by MCC.
 (b) To be measured by MCC.

The MCC¹ will characterize the rods. Prior to cutting, the rods will be punctured for both chemical and isotopic fission gas sampling. Gross and spectral gamma scanning will be used to determine the burnup profile. Burnup analyses will be conducted at three locations in the bottom half of the rod. Transverse and longitudinal ceramography examinations will be performed adjacent to the burnup samples to determine grain size and to look for unusual features.

These tests are not concerned with burnup effects, so 18 in. of fuel with nearly equal burnup as indicated by the gamma scans will be used for testing. At ~10 g per sample and 31 g of fuel per in., there is sufficient fuel for ~55 samples. The fuel segments will be cut dry into 4- to 6-in.-long pieces for handling purposes. The cladding will be split with a carbide end mill and then pried open for removal of the fuel fragments. Six fragments will be set aside for possible characterization, ~25 fragments will be used in TGA testing, and the remainder of fuel will be used for dry bath test samples.

mesh, and N is the sample number. For subsequent sample divisions, a suffix (a, b, etc.) will be attached to the sample identification. Bu refers to the burnup of the sample relative to the rod maximum; it will range from zero to one. BWR1 identifies the source of the fuel, which may change in future tests; it corresponds in this case to Cooper fuel.

Methods of physically attaching identification to the sample and crucibles and performing the indicated fuel preparation and characterization will be detailed in approved test procedures.

2.3 EQUIPMENT DESCRIPTION

The test apparatus is essentially identical to that used for the PWR dry bath oxidation tests.⁽⁸⁾ It consists of a dry bath, air delivery system, temperature measurement system and sample crucible. There are nine such systems installed in the 327 Building "I" air cell. Adjacent to the cell is a Mettler balance with a sensitivity of ± 0.1 mg that will be used to weigh the samples.

The temperature measurement and control system is the same as described in the PWR dry bath oxidation test plan⁽¹⁰⁾ with the following change. Originally, the three thermocouples, one in each of the aluminum blocks of the dry bath, were averaged to determine the operating temperature versus time history for that dry bath. Since the temperature variation between the three thermocouples is 1°C or less in Dry Baths 8 and 3, an average temperature is used for these baths. On the other hand, Thermocouples 6C, 4A, 7C and 2A, in Baths 6, 4, 7, and 2, respectively, indicate temperatures that are $\sim 3^{\circ}\text{C}$ lower than their counterparts. Due to the configuration in the hot cell, it was not possible to determine if the low temperature reading was due to a slight misalignment of the thermocouple in a block where the actual temperature was the same as the other blocks in the bath, or if the block itself was at a slightly lower temperature due to misalignment on the heating element. Analysis⁽⁸⁾ of the temperature data from the PWR fuel oxidation tests Series 1 supports the position that the temperature readings of the thermocouples are real. For these four baths, both an average and block-specific temperatures will be determined. It is expected that an individual sample will be at a uniform temperature known to at least $\pm 3^{\circ}\text{C}$, but in reality much nearer $\pm 1^{\circ}\text{C}$.

2.4.3 Final Examination

At designated intervals, selected samples will be removed from the tests for interim examinations, for further examination, and for use as leaching samples. After weighing, the fuel will be poured into a labeled metal can for transfer out of the cell. The empty crucible will be ultrasonically rinsed with ethyl alcohol and reweighed.

2.5 POST-TEST SAMPLE EVALUATION

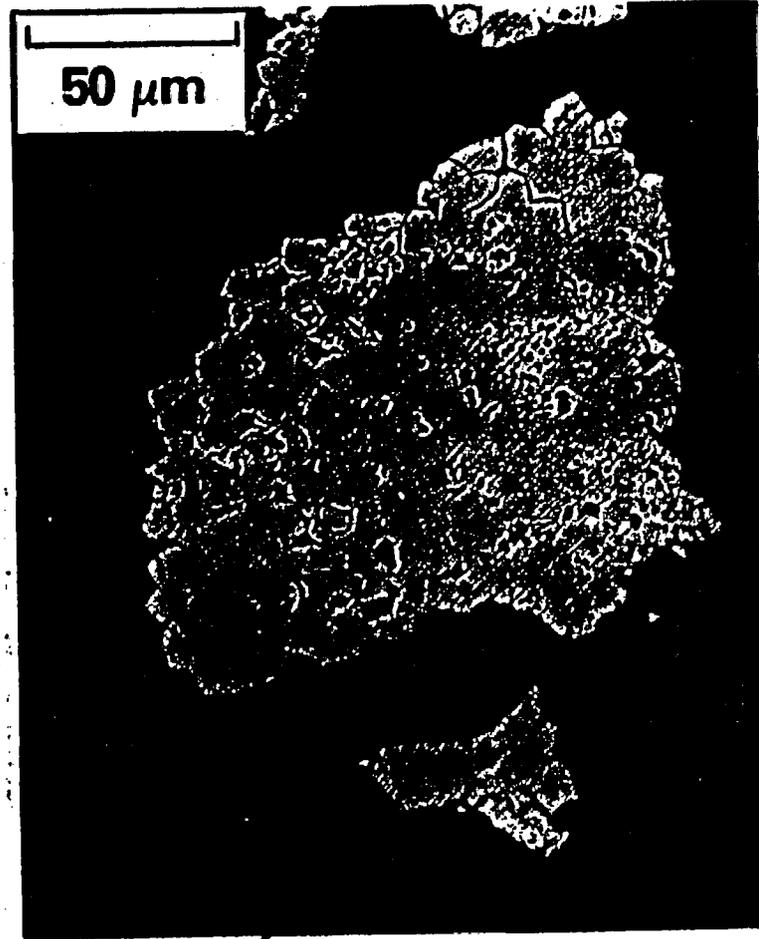
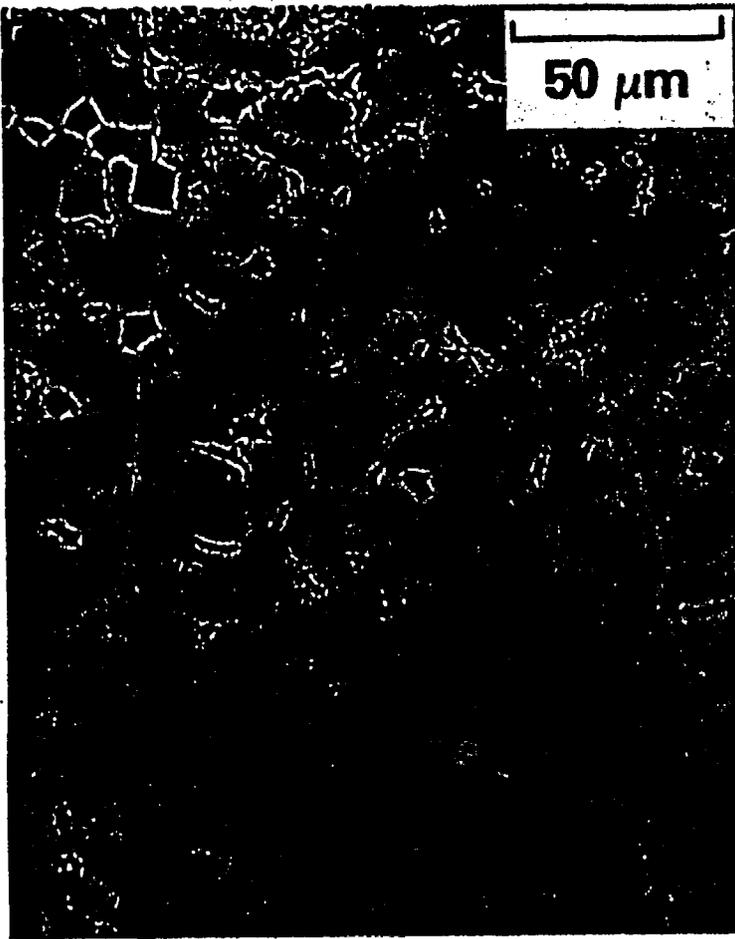
The weight change of the samples will be checked at intervals during the test, but weight measurements cannot determine the uniformity of oxidation or the location of the oxidation process in the sample. Only limited information can be determined about the oxide phases. For instance, complete conversion of UO_2 to U_3O_7 yields a weight gain of 1.98%, and complete conversion to U_3O_8 yields a weight gain of 3.96%. If the sample weight gain is found to be greater than 1.98%, it might be expected that at least some U_3O_8 has formed. However, the sample could be almost uniformly U_3O_7 with a minor amount of U_3O_8 , or it could be partly UO_2 and partly U_3O_8 . In all likelihood, a combination of the phases will occur. Following the test, selected samples will be examined ceramographically by SEM, XRD and TEM/electron diffraction to obtain additional phase information. All samples consisting of fragments will be visually examined to see if there is any spallation.

The goal of the waste form testing program is to determine the radionuclide release characteristics of the spent fuel waste form. Part of this task is to determine the change in leaching characteristics with oxidation state. After post-test evaluations, the test material will be stored in sealed containers and labeled with the sample identification. These samples will be available for leach testing.

2.5.1. Ceramography

Ceramography will be used to visually determine the gross grain boundary degradation and to evaluate the extent of the oxidation into the fragment from the external surfaces. In addition, it will serve as a sampling guide for taking TEM specimens.

2.13



WHC 8709-078.5

OXIDIZED GRAIN BOUNDARY RIM

FIGURE 2.1. As-Polished Ceramography of Oxidized Fuel Showing Widened Grain Boundaries and Oxidized Fuel Rims

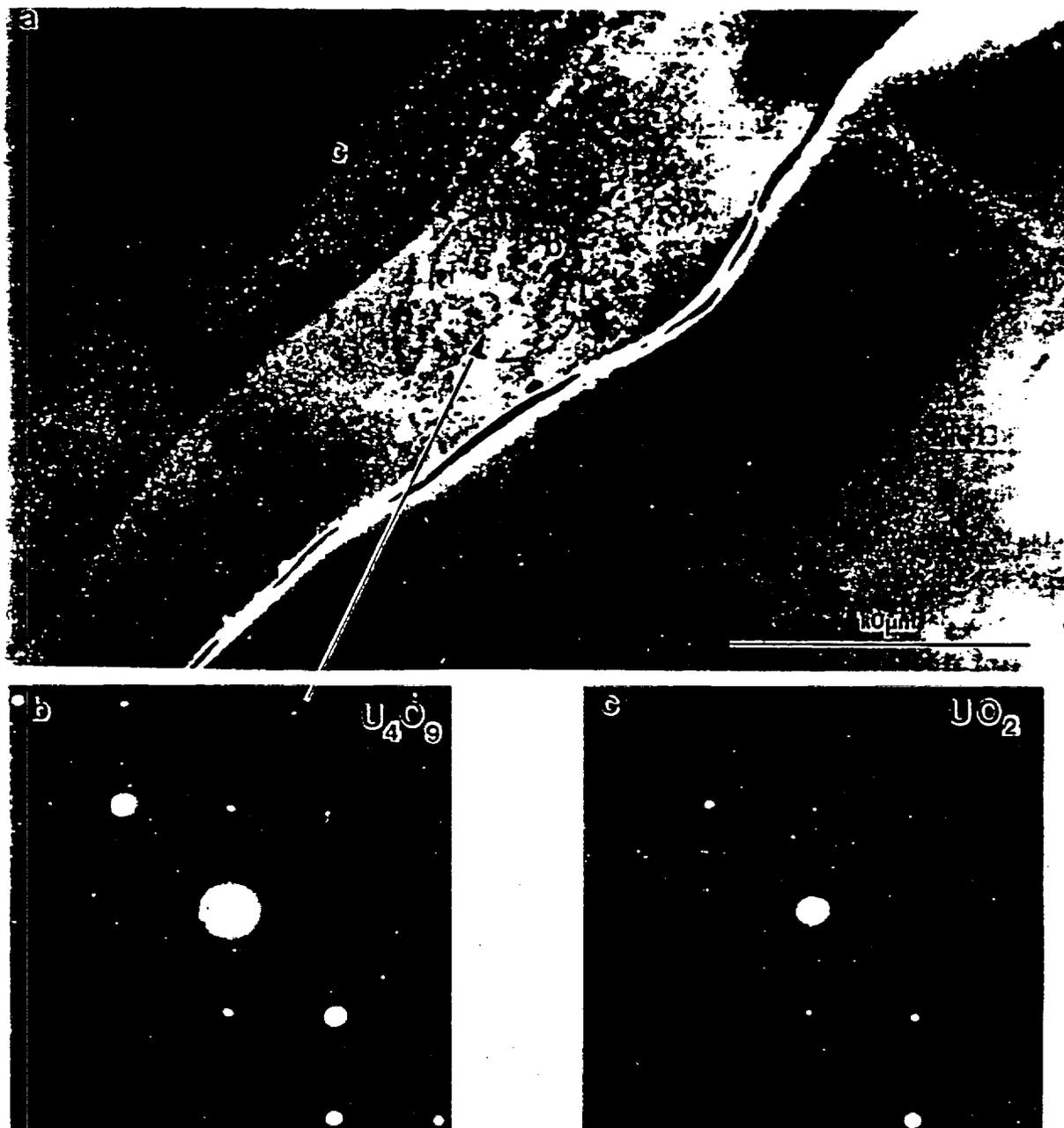


FIGURE 2.2. Grain Boundary Region in Oxidized Fuel. Sample G7-14-3-#8 (155°C test, O/M = 2.05). (a) Darkfield TEM taken with diffuse-scattered intensity from U_4O_9 , showing enhanced intensity from U_4O_9 on one side of grain boundary. (b) Selected-area diffraction pattern from U_4O_9 region in (a), showing diffuse scattering from short-range ordered oxygen interstitials. Near (001) orientation. Arrow indicates aperture position used to form darkfield image (a). (c) SAD pattern for UO_2 region in (a). Same crystal orientation as (b).

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