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PERFORMANCE OF MOX FUEL FROM NONPROLIFERATION PROGRAMS

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Abstract: In support of nonproliferation efforts, the U.S. Department of Energy has decided to dispose of a portion of the nation's surplus plutonium by reconstituting it into mixed oxide (MOX) fuel and irradiating it in commercial power reactors. As part of the fuel qualification process, four lead assemblies were manufactured with this plutonium and irradiated to a maximum fuel rod burnup of 47.3 GWd/tonne heavy metal. Five fuel rods with varying burnups and plutonium contents were selected from one of the assemblies and shipped to Oak Ridge National Laboratory for hot cell examination. This is the first hot cell examination of commercially irradiated MOX fuel with a $^{240}Pu/^{239}Pu$ ratio of less than 0.10. The rods have been examined nondestructively with the ADEPT apparatus and are currently being destructively examined. Nondestructive exams included length measurements, visual examination, gamma scanning, profilometry, and eddy-current testing. Destructive exams completed to date include gas measurement and analysis, optical metallography of both fuel pellets and cladding, transmission electron microscopy of the cladding, radiochemical measurements (including burnup determination), gallium analysis of pellets and cladding, and hydrogen analysis of cladding. Representative results of these examinations are reviewed and found to be consistent with predictions and with prior experience. The results will be used to support licensing of MOX for batch use in commercial power reactors.

Keywords: MOX fuel; lead assemblies; hot cell examination

1. INTRODUCTION

In support of nonproliferation efforts, the Russian Federation and the United States agreed to dispose of a portion of each nation's surplus plutonium. In the United States, the U.S. Department of Energy has decided to implement the agreement by reconstituting the plutonium into mixed oxide (MOX) fuel and irradiating it in commercial power reactors. This work is part of the Fissile Materials Disposition Program being conducted by the DOE's National Nuclear Security Administration. MOX fuel licensing and production has been contracted to Shaw AREVA MOX Services.

MOX fuel made with recycled plutonium from power reactor fuel has been successfully used in over 30 European reactors for many years.[1] Japan has likewise irradiated such MOX fuel, and its use is well established. But recycled plutonium from power reactors typically has a $^{240}Pu/^{239}Pu$ ratio of about 0.3. In contrast, the MOX fuel produced under the Fissile Materials Disposition Program will contain plutonium from military stockpiles, with a $^{240}Pu/^{239}Pu$ ratio of no more than 0.10. Commercial use of MOX with a low $^{240}Pu/^{239}Pu$ ratio is new, and the fuel has not yet been licensed for batch use. AREVA has applied its European and U.S. experience to facilitate licensing of this fuel in the U.S.

The licensing strategy is to irradiate and examine lead assemblies to confirm that their performance is similar to that of MOX assemblies that contain recycled plutonium from power reactors. As part of the fuel qualification process, four lead assemblies were manufactured in France and irradiated for two 18-month cycles at the Catawba Nuclear Station, Unit 1, operated by Duke Energy.[2] The irradiations ran from June 2005 to May 2008, and the assemblies achieved a maximum fuel rod burnup of 47.3 GWd/tonne heavy metal. Five irradiated fuel rods, with rod-average burnups of about 40 to 47 GWd/tonne heavy metal, were selected and shipped to Oak Ridge National Laboratory for hot cell examination. Both the fuel pellets and the M5® cladding were examined. This is the first hot cell examination of commercially irradiated MOX with such a low $^{240}Pu/^{239}Pu$ ratio. Fig. 1 shows the rods selected and their nominal plutonium contents.

The MOX fuel rods were examined both nondestructively and destructively to ensure that the fuel performance is consistent with expectations. Nondestructive exams included length measurements, visual examination, gamma scanning, profilometry, and eddy-current testing. Destructive exams completed to date include gas measurement and analysis, optical metallography of both fuel pellets and cladding, transmission electron microscopy of the cladding, radiochemical measurements (including

burnup determination), gallium analysis of pellets and cladding, and hydrogen analysis of the cladding. The gallium and hydrogen concentrations were measured on both irradiated and unirradiated cladding. All five rods were examined nondestructively, and four were selected for destructive examination. The remaining rod, B-14, is being kept as a spare. B-14 and B-04 had the same initial plutonium concentration and have very similar burnups.

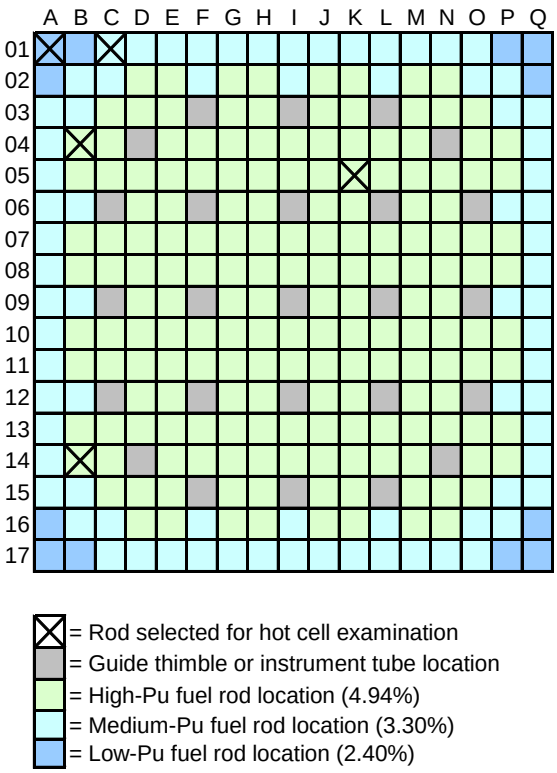

Fig. 1 Fuel rods selected for hot cell examination

Nondestructive examinations were performed with the Advanced Diagnostics and Evaluation Platform (ADEPT), which handles fuel rods horizontally and provides precise, computer-controlled positioning in both the axial and azimuthal directions.[3] ADEPT also handles rod puncturing and sample cutting.

The results of nondestructive exams, plus gas measurement and analysis, have been reported previously[4] and were consistent with experience. The following sections provide representative results from the destructive exams.

2. OPTICAL METALLOGRAPHY

Nine sections of fuel rods were examined by optical metallography. Each sample was examined in three conditions: as-polished, etched to reveal pellet structure, and etched to reveal hydrides in the cladding.

The as-polished samples provided a clear view of the pellet cracking, gross microstructure, and internal oxidation. Fig. 2 shows a typical cross section of rod B-04, taken near the middle of the stack. Cracking of the pellet is typical, and the pellet and cladding are in excellent condition.

The microstructure of the fuel pellet was typical of MOX fuel. Figs. 3, 4, and 5 provide more detailed views of the cross section shown in Fig. 2. In all three figures, the plutonium-rich agglomerates are dark areas within the fuel pellet. In Fig. 3, the cladding is the light area at upper right. Figs. 3 and 4 show the plutonium-rich agglomerates clearly. The agglomerates are evenly distributed, and the agglomerate size is well controlled. The agglomerates are more difficult to see near the center of the fuel rod, where high temperature promotes diffusion and homogenization.

Figs. 6 and 7 show the as-polished microstructure of rod C-01 near the middle of the fuel stack. Because of the higher local burnup in the plutonium-rich agglomerates, the fission gas release is also higher, and the agglomerates become porous. Fig. 6 was taken with the standard bright-field illumination, whereas Fig. 7 shows the same area with dark-field illumination. The dark-field image is of particular interest because it gives a clearer view of the oxide layer on the interior of the cladding. The oxide thickness is estimated to be 6 to 8 µm, with possibly a slightly increased thickness adjacent to an agglomerate. Similar oxide layers have been seen previously for MOX fuels with larger $^{240}Pu/^{239}Pu$ ratios.[5]

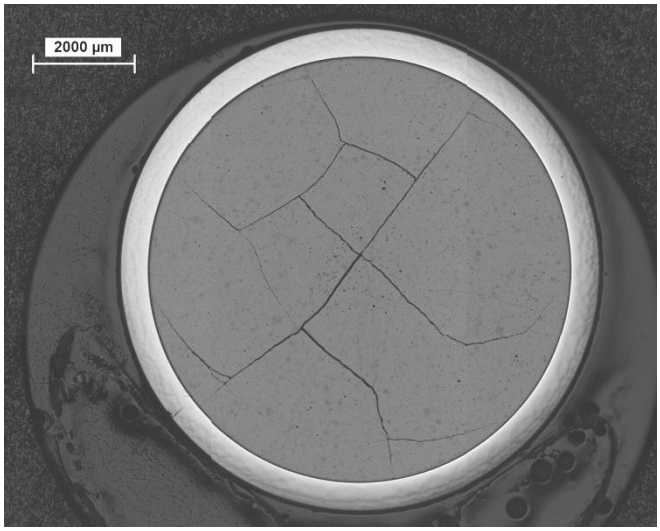

Fig. 2 Cross section of fuel (rod B-04, middle of stack)

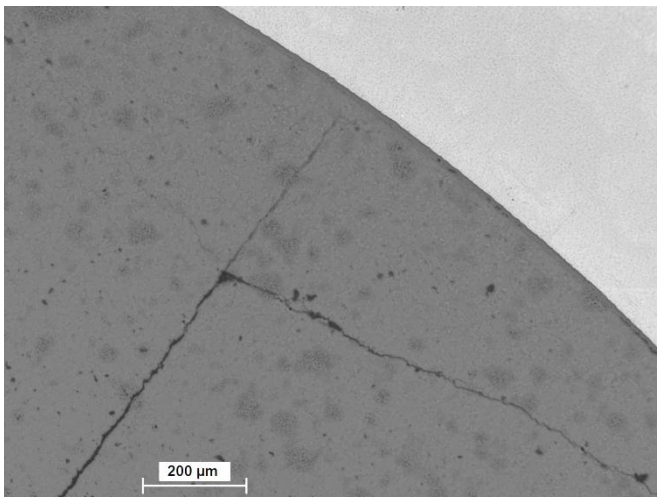

Fig. 3 Microstructure near surface of pellet (rod B-04, middle of stack)

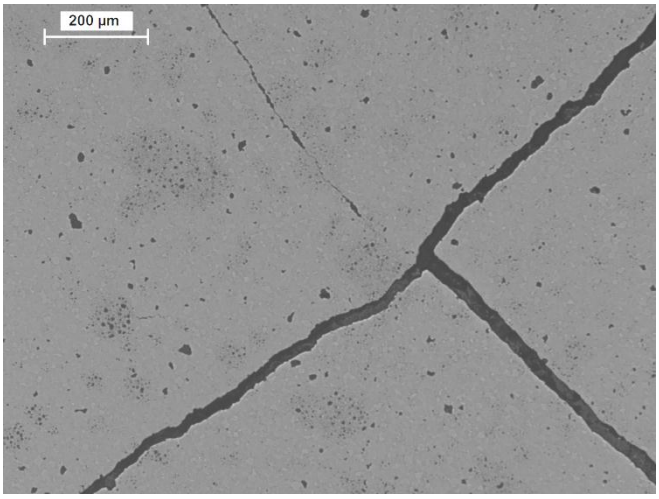

Fig. 4 Microstructure at mid-radius of pellet (rod B-04, middle of stack)

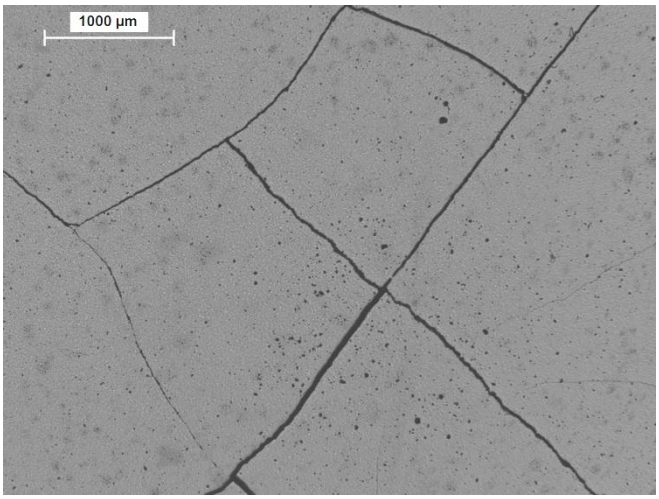

Fig. 5 Microstructure near center of pellet (rod B-04, middle of stack)

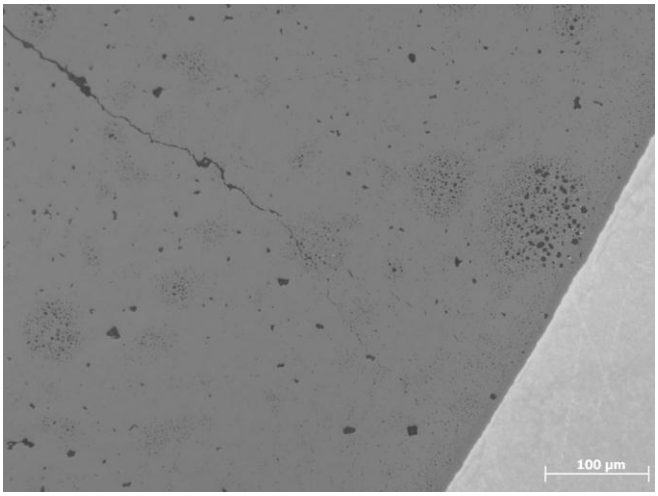

Fig. 6 Microstructure near surface of pellet, bright field (rod C-01, middle of stack)

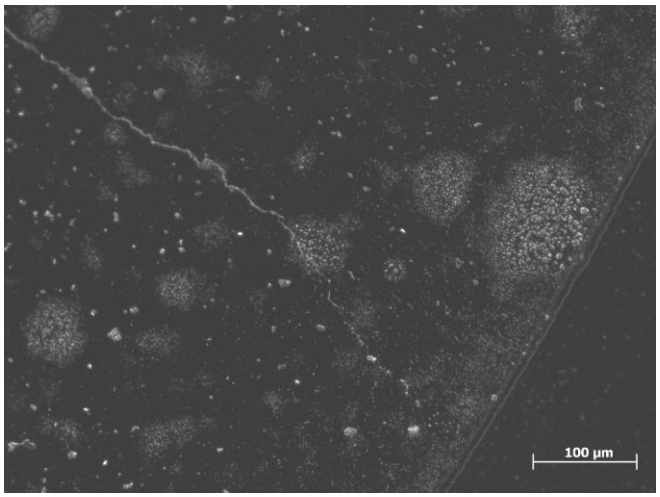

Fig. 7 Microstructure near surface of pellet, dark field (rod C-01, middle of stack)

Figs. 8 through 10 show the structure of the fuel pellet after etching. The sample was taken from the upper part of the fuel stack of rod B-04. The agglomerates are visible as porous regions without visible grain boundaries. In contrast, the UO_2 matrix has clearly visible grain boundaries and little or no porosity. The dark polygonal areas are pull-out.

The structure of the agglomerates is similar to that seen in MOX fuel with a larger $^{240}Pu/^{239}Pu$ ratio: the porosity becomes progressively coarser from the surface to the center of the pellet.[6]

Fig. 11 provides a typical example of hydride density and orientation. The sample was taken from the upper portion of the fuel stack of Rod A-01. The hydriding is light, and the hydrides are predominantly circumferential, as is common for M5® cladding. Staining near the surfaces of the cladding is an artifact of sample preparation rather than an indication of cladding oxidation.

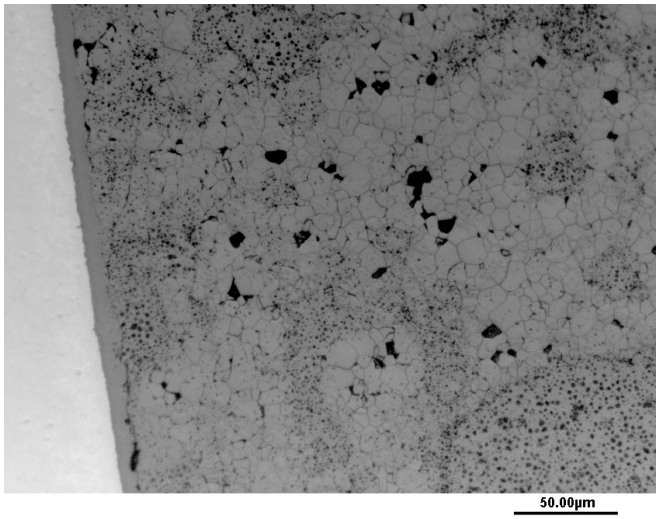

Fig. 8 Agglomerate microstructure near surface of pellet (rod B-04, upper part of stack)

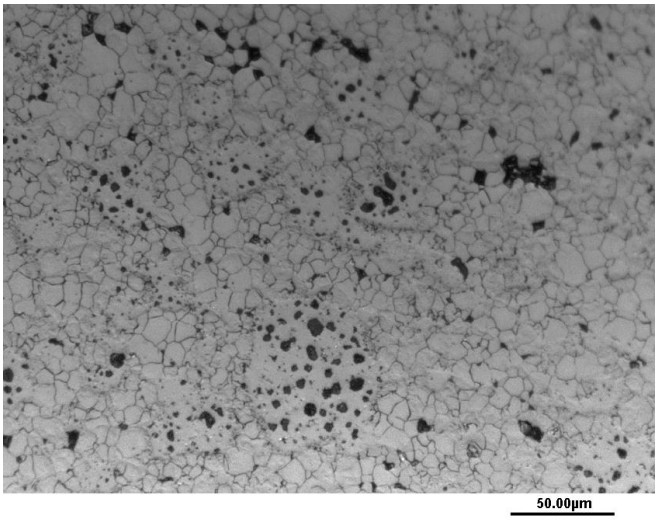

Fig. 9 Agglomerate microstructure at mid-radius of pellet (rod B-04, upper part of stack)

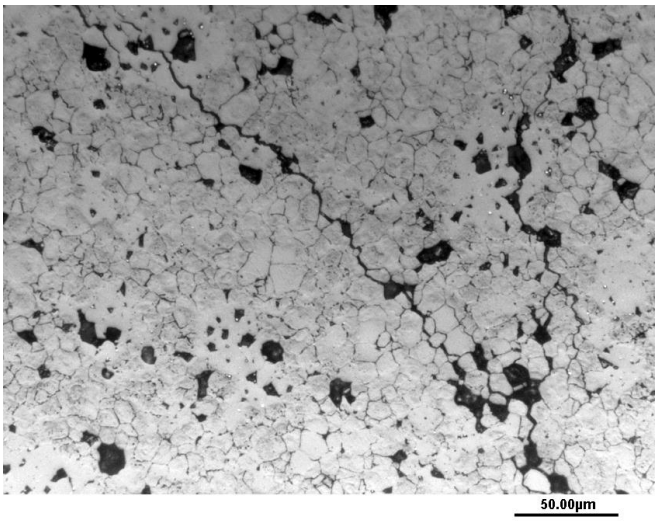

Fig. 10 Agglomerate microstructure near center of pellet (rod B-04, upper part of stack)

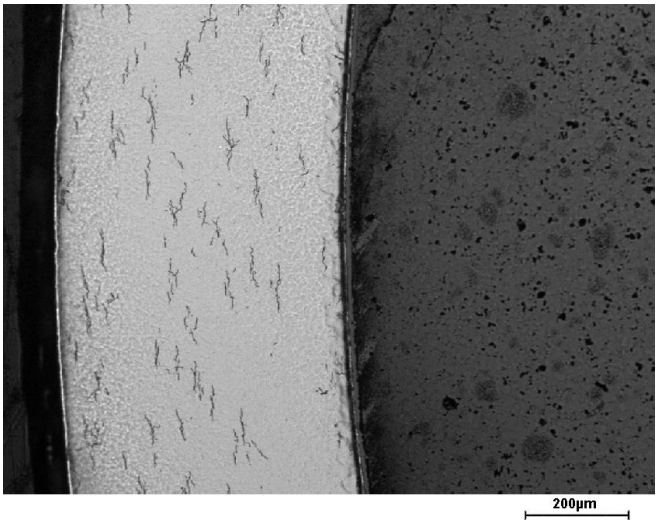

Fig. 11 Hydrides in fuel cladding (rod A-01, upper part of stack)

3. TRANSMISSION ELECTRON MICROSCOPY

Samples of fuel cladding were examined by transmission electron microscopy to ensure that the behavior of the cladding was similar to that for other fuel types. The samples included four samples taken from within the fuel stacks of rods A-01 and B-04, one sample taken from the plenum of rod B-04, and one piece of archival cladding from the lot used for rod B-04. The specimens for examination were selected at widely spaced elevations along the fuel rod. The specimens from within the fuel stacks of rods A-01 and B-04 had fast fluences of about 1.0×10^{22} n/cm^2 (E > 1 MeV). The cladding specimen examined from the plenum location of rod B-04 was irradiated to 0.08×10^{22} n/cm^2 (E > 1 MeV). The features examined included the grain size of the α-Zr matrix, the particle size and density changes with irradiation of β-Nb and radiation enhanced precipitates (REPs), hydrides, and irradiation-induced dislocations. The types of dislocations examined included *a*-component and *c*-component dislocation loops.

Highlights of the results are as follows:

- The average α-Zr grain size was 2.5 µm. The grain size was the same for archival and irradiated samples, as expected.
- The β-Nb particles were homogeneously distributed through the material. Irradiation produced a slight increase in the average particle size. In the high-fluence (fuel stack) samples, the particle size was about 7 nm greater than that in the archival material. The number of particles per unit volume did not change significantly between the irradiated and archival materials.
- As expected, REPs were not observed in the archival cladding. The number of REPs per unit volume was about the same for the low-fluence (plenum) and high-fluence (fuel stack) samples, but the particles were larger in the high-fluence samples. The particle size and density were in good agreement with published values. Typical REPs in a high-fluence sample are shown in Fig. 12.
- No *c*-component dislocation loops were seen in the archival or low-fluence samples. The density of *c*-component dislocation loops in the high-fluence samples was consistent with previous measurements for M5® cladding, as is shown in Fig. 13.
- Hydrides were identified by electron diffraction as δ-ZrH_{2-x} and were found either to be contained within one α-Zr grain or to be composed of multiple sections that branched intergranularly along high angle grain boundaries. Not all of the samples contained hydrides; that was not surprising in light of the rather sparse hydriding that is seen in Fig. 11. The branching structure of the hydrides was consistent with observations from optical metallography.

All results were consistent with expectations.

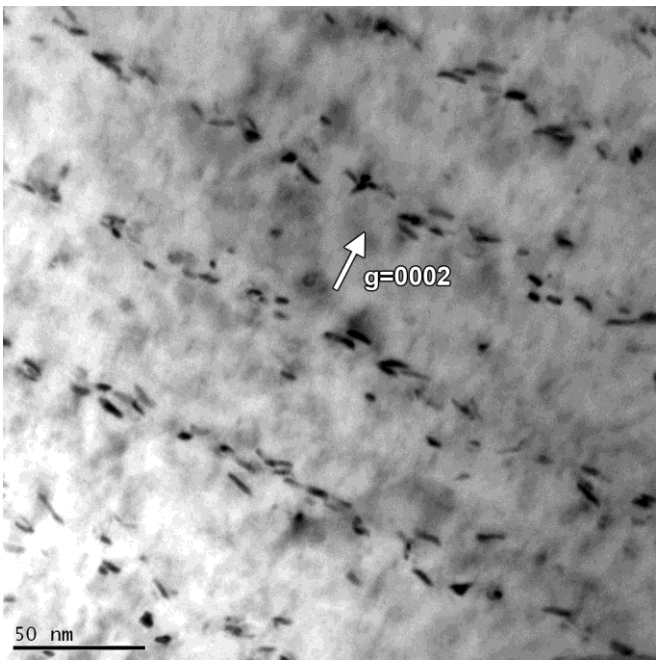

Fig. 12 Typical REPs in high-fluence cladding

4. RADIOCHEMICAL MEASUREMENTS

The fuel pellets from eleven samples of the fuel rods were dissolved and analyzed. The analysis included several rare earth elements (cerium, neodymium, samarium, europium, and gadolinium) as well as cesium, uranium, and plutonium. Mass fractions and isotopics were measured for each element by high precision isotope dilution mass spectrometry. Burnups were determined from the Nd-148 concentration in accordance with ASTM E 321.

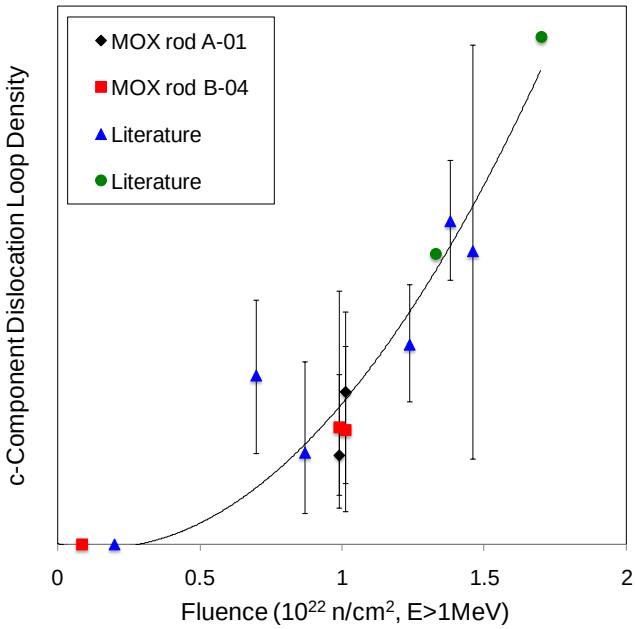

Fig. 13 *c*-component dislocation loop density as a function of fluence

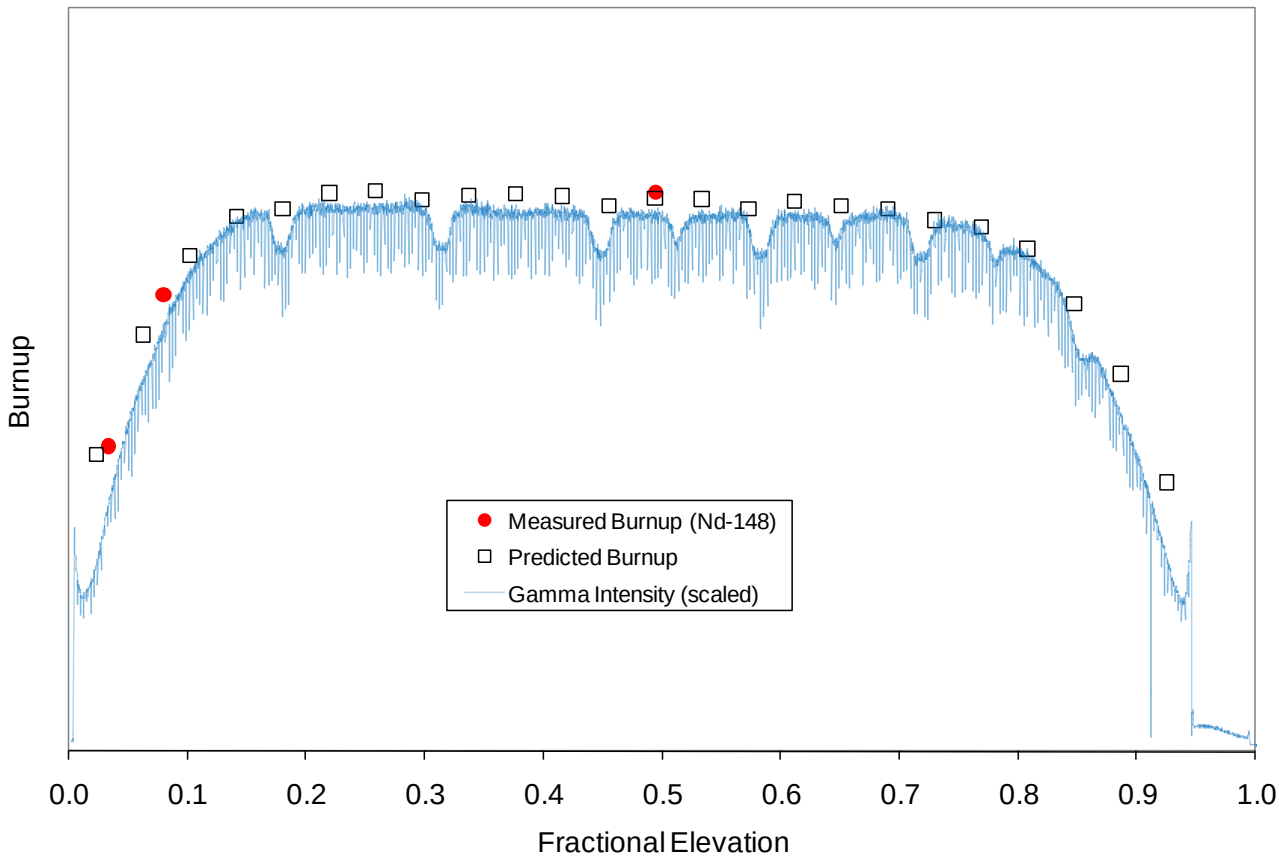

Fig. 14 Comparison of measured burnup, predicted burnup, and gamma intensity

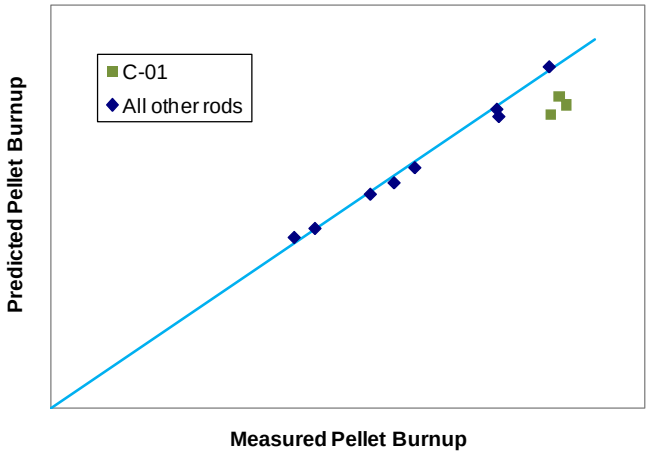

Fig. 15 Comparison of measured and predicted pellet burnups

One of the primary goals of the radiochemical measurements was to confirm that fuel burnups are accurately predicted. Fig. 14 shows a burnup comparison for rod K-05. Measured burnups were determined from the Nd-148 concentrations. Predicted burnups are derived from CASMO-4 / SIMULATE-3 MOX calculations performed by Duke Energy. The gamma intensity is the gross activity for an energy range of 400 to 950 keV. Rather than making a quantitative correlation with burnup, the gamma intensity has simply been scaled to allow a visual comparison.

The measured and predicted burnups are in good agreement, with the predictions reproducing both the burnup of the high-power section of the rod and the fall-off at low elevations. The measurements are also in agreement with the gamma intensity.

Further comparison of measured and predicted burnups is provided in Fig. 15. Good agreement is seen for all rods except C-01. For that rod, the predictions were slightly low, probably because the strong neutron flux gradient at the periphery of the assembly results in increased uncertainty in rod power reconstructions. Future burnup reconstructions may use more advanced neutronic methods, such as AREVA's ARCADIA code, to improve the agreement.

5. GALLIUM ANALYSIS

The raw plutonium used for this work contained gallium at concentrations of up to 1.2%.[7] There were concerns that the gallium might migrate from the fuel pellets to the cladding and thus embrittle the cladding. Migration would be particularly important if the gallium migrated axially to the cold parts of the fuel rod, such as the plenum. Two approaches were taken to control the effects of gallium. First, the plutonium dioxide was "polished" or purified before it was combined with uranium dioxide. The allowable gallium concentration in the plutonium dioxide powder was 300 ng Ga / g oxide.[7] After dilution with uranium dioxide, this was expected to result in an insignificant contribution to the concentration of gallium in the fuel. Second, the irradiated fuel pellets and cladding were analyzed for gallium to confirm that the quantities of gallium in the cladding were acceptable.

Three pellet samples taken near the middle of the fuel stacks were analyzed. Two of the samples had concentrations of 72 and 77 ng Ga /g oxide, while the third had a concentration of 248 ng Ga / g oxide.

Unirradiated samples of archival cladding were found to have gallium concentrations of less than the detection limit of 50 ng Ga / g metal. The cladding surrounding the three irradiated pellet samples mentioned above was analyzed and found to have a slightly greater gallium concentration, 147 to 168 ng Ga / metal, than that of the archival samples. It therefore appears that some radial migration of the gallium did occur. However, there was no apparent correlation between the concentration of gallium in the pellet and that in the adjacent cladding. It is noted that a typical gallium concentration for unirradiated Zircaloy-4 cladding is 275 ng Ga / g metal,[7] so it is clear that the observed gallium concentration does not threaten the integrity of the cladding.

Two irradiated cladding samples taken from the plenums were also analyzed; they had concentrations of only 68 to 70 ng Ga / g metal. Therefore, axial migration of gallium to the plenum was even smaller than the radial migration.

6. HYDROGEN ANALYSIS

Seven irradiated cladding samples from rods A-01 and B-04 were analyzed for hydrogen concentration. The samples were taken at a wide variety of elevations, with six of the samples being taken from the fuel stack and one from the plenum. The hydrogen concentrations varied from 30 to 55 µg H / g metal. As expected, the concentrations were somewhat greater for the hotter portions of the fuel rod than for the cooler portions (plenum and bottom of the fuel stack). The results were consistent with experience with low-enriched uranium fuel of similar burnup.

Archival samples from two lots of cladding were also analyzed. The concentration in the archival samples was within specification limits.

7. CONCLUSIONS

MOX fuel rods with plutonium from a nonproliferation program and with rod-average burnups of about 40 to 47 GWd/tonne heavy metal have been examined in a hot cell. The fuel had a $^{240}Pu/^{239}Pu$ ratio of less than 0.1, in contrast to typical MOX fuel with recycled plutonium from power reactors, which has a $^{240}Pu/^{239}Pu$ ratio of roughly 0.3. The hot cell examinations indicate that the new fuel behaved normally, that is, in a way that can be predicted on the basis of experience with uranium dioxide fuel and MOX fuel with recycled plutonium. The results therefore support licensing of MOX fuel with a low $^{240}Pu/^{239}Pu$ ratio for batch use in commercial power reactors.

ACKNOWLEDGMENTS

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The following Oak Ridge staff contributed to this work:

- Joe Giaquinto: radiochemistry, hydrogen and gallium analysis
- Keith Leonard: transmission electron microscopy
- Building 3525 staff: sample preparation.

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