# CERAMOGRAPHY ANALYSIS OF MOX FUEL RODS AFTER AN IRRADIATION TEST

HAN SOO KIM*, CHANG YONG JONG, BYUNG HO LEE, JAE YONG OH and YANG HYUN KOO
Korea Atomic Energy Research Institute
305-353, 1045 Daedeokdaero, Yuseong, Daejeon, Korea
*Corresponding author. E-mail : hskim4@kaeri.re.kr

*Received April 02, 2010*
*Accepted for Publication July 27, 2010*

KAERI (Korea Atomic Energy Research Institute) fabricated MOX (Mixed Oxide) fuel pellets as a cooperation project with PSI (Paul Scherrer Institut) for an irradiation test in the Halden reactor. The MOX pellets were fitted into fuel rods that included instrumentation for measurement in IFE (Institutt for Energiteknikk). The fuel rods were assembled into the test rig and irradiated in the Halden reactor up to 50 MWd/kgHM. The irradiated fuel rods were transported to the IFE, where ceramography was carried out. The fuel rods were cut transversely at the relatively higher burn-up locations and then the radial cross sections were observed. Micrographs were analyzed using an image analysis program and grain sizes along the radial direction were measured by the linear intercept method.

Radial cracks in the irradiated MOX were observed that were generally circumferentially closed at the pellet periphery and open in the hot central region. A circumferential crack was formed along the boundary between the dark central and the outer regions. The inner surface of the cladding was covered with an oxide layer. Pu-rich spots were observed in the outer region of the fuel pellets. The spots were surrounded by many small pores and contained some big pores inside. Metallic fission product precipitates were observed mainly in the central region and in the inside of the Pu spots. The average areal fractions of the metallic precipitates at the radial cross section were 0.41% for rod 6 and 0.32% for rod 3. In the periphery, pore density smaller than 2 μm was higher than that of the other regions. The grain growth occurred from 10 μm to 12 μm in the central region of rod 6 during irradiation.

KEYWORDS : MOX Fuel, Irradiation Test, Ceramography, Metallic Fission Product Precipitates, High Burnup Structure

## 1. INTRODUCTION

MOX fuels have been developed and commercially used in power reactors for the last few decades. Recently, MOX fuels have become a subject of interest because of soaring oil and uranium prices and the advent of weapon-derived plutonium from the reduction in strategic nuclear weapons. The usual fabrication process of MOX fuel does not differ in broad outline from that of $UO_2$ fuel. Both $UO_2$ and MOX fuel pellets are usually fabricated by powder processes such as mixing, milling, pressing, sintering and centerless grinding. The pellets are loaded into Zircaloy-4 cladding tubes, which are seal-welded at both ends. The main differences in the fabrication processes between the two fuels are a powder preparation step and a glove box system that requires very special techniques to assure the worker's safety and the efficiency. The homogeneity and the sinterability of a MOX powder mixture are key aspects in MOX fuel fabrication processes in regards to getting higher fuel performance. The first stage of the powder mixture treatment was a direct co-milling method, but the resultant Pu distribution of pellets was found to be heterogeneous. Several powder treatment methods [1-4] have been developed to improve the homogeneity of the MOX fuel including MIMAS (Micronized Master blending), OCOM (Optimized Co-milling), SBR (Short Binderless Route), etc. The sintering process is also important in controlling the density and microstructure of fuel pellets. Many experimental studies are needed to develop and qualify the fabrication process of the MOX fuel.

KAERI has developed the MOX fuel fabrication process using cerium oxides as a surrogate for $PuO_2$ [5]. As part of the framework of the cooperation project between KAERI and PSI, MOX fuel pellets were fabricated in PSI using the KAERI processes for an irradiation test in the Halden reactor. The MOX pellets were transported to IFE, then loaded into Zircaloy-4 claddings and instrumented and welded at both ends of test rods. The test rods were assembled into a test rig and irradiated in the Halden reactor up to 50 MWd/kgHM. The irradiated MOX rods were moved from Halden to Kjeller, where ceramography was carried out.

The ceramography samples were cut transversely at the relatively higher burn-up locations. The radial cross sections of the rods were observed macroscopically in polished condition to analyze fuel swelling, crack pattern and gap closing. The polished sections were observed microscopically with higher magnification so that pores and metallic precipitates were analyzed using an image analysis program. Grain structures were also observed along the radial direction of the cross section and average grain sizes were compared with that of as-fabricated MOX fuel.

## 2. FUEL FABRICATION AND IRRADIATION TEST

### 2.1 Fuel Fabrication

The MOX fabrication process was simulated in KAERI using $CeO_2$ as a surrogate of $PuO_2$; MOX pellets were fabricated in PSI as a cooperation program between KAERI and PSI. The peculiarity of the KAERI MOX fabrication processes is in the preparation process of the powder mixture, which uses the continuous type attrition mill [6] and the sintering of MOX compacts in a slightly oxidizing atmosphere [5]. The attrition mill consists of a vertical axis with impellers and two jars that are separated by an inconel grid into an upper and a lower part. The inside walls of the milling jars are lined with zirconia tubes; zirconia balls with diameter of 8mm are used in the upper jar, whereas balls with diameter of 5mm are used in the lower jar as milling media. A granulator consisting of crusher and sieve is installed in the attrition mill. Raw powders of $PuO_2$ and IDR (Integrated Dry Route)-$UO_2$ were weighed to meet the final fuel composition, and mixed for 1h. The powder mixture was directly milled by passing it through the attrition mill jars fifteen times. Zinc stearate and Azodicarbonamide were added to the milled powder as a lubricant and a pore former, respectively. The milled powder was granulated through pre-compaction, crushing and sieving steps, and then compacted into green pellets. The green pellets were sintered in $CO_2$ gas at 1723K for 4h, and subsequently in 8%$H_2$+92%$N_2$ at 1473K for 2h. The sintered pellets were ground to final diameters using a centerless grinder. The characteristics of the as-fabricated MOX pellets are shown in Table 1. The plutonium distribution of the as-fabricated MOX pellet was very homogeneous, as shown in Fig. 1. The maximum diameter of the Pu rich spot was 13 μm, with a Pu concentration of less than 18wt%. Average grain size of the pellets was 10 μm, larger than those of MOX fuels produced by other processes [1-4].

The MOX pellets were transported from PSI to IFE and then drilled, loaded into Zircaloy-4 claddings with a nominal inner and outer diameter of 8.36mm and 9.50mm, and instrumented. Test rods were seal-welded and identified as rod 3 and rod 6 in a test rig. Rod 3 was instrumented with an expansion thermometer to monitor the central temperature. Rod 6 was instrumented with a fuel stack elongation sensor as well as a thermocouple at the top of the fuel stack to measure axial elongation and central temperature of the MOX fuel. In addition, both rods were instrumented with a pressure transducer at the bottom end to detect fission gas release.

### 2.2 Irradiation Test

Two KAERI MOX rods, one SBR MOX rod and three IMF (Inert Matrix Fuel) rods were assembled into a test rig and irradiated in the Halden reactor. The irradiation test was completed and revealed good fuel integrity of the MOX fuel. The average burnup for the two KAERI MOX fuel rods reached 50 MWd/kgHM with the irradiation time of 1020 EFPD. The linear heating rate exceeded 300W/cm occasionally, but most of the irradiation was performed between 200 W/cm and 300 W/cm. The peak fuel center temperature at the mid-plane of the fuel stack was estimated to be around 1673 K in rod 6 and 1573 K in rod 3. Since the two MOX rods were irradiated under a high linear heating rate level, significant fission gas release, estimated to be 26% in rod 6 and 15% in rod 3, was observed. This is confirmed by the increment of the rod internal pressure.

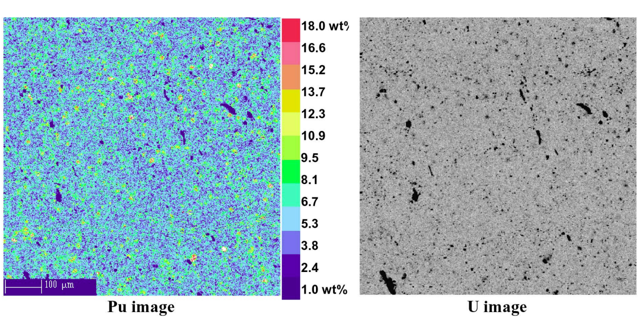



Fig. 1. X-ray Mappings of as-Fabricated MOX Fuel

**Table 1**. Characteristics of as-Fabricated MOX Pellets

| Characteristics | Values |
|---|---|
| Dimensions | D 8.193±0.006 × L 9.82±0.18mm |
| Sintered density, | 10.40~10.44g/cm$^3$ (94.5~94.9%TD) |
| O/(U+Pu) ratio | 1.998±0.001 |
| Pu/MOX, | 7.38±0.29wt%, |
| (U+Pu)/MOX | 90.4± 1.8wt% |
| $Pu_{fissile}$/(U+Pu), | 6.07wt%, |
| $Pu_{fissile}$ content | 0.57g/cm$^3$ |
| Average grain size | 10μm |

## 3. CERAMOGRAPHY AND IMAGE ANALYSIS

The irradiated MOX rods were transported to IFE, where ceramography was carried out. The irradiated MOX rods were transversely cut at the axial position where the burn-up reached a maximum, and a piece of the radial section was sampled from each fuel rod for optical microscope examination. The microscope sample was prepared by mounting, grinding, polishing, washing and drying in a hot cell.

Macrostructures showing entire radial sections of the rods were observed on a polished section. Micrographs of pores and metallic fission product precipitates were taken along the radial direction of the polished sections at high magnification. Characteristics of the pores and the metallic precipitates, such as area fraction and size distribution, were measured by image analysis of the micrographs. The irradiated MOX fuel is fragile and contains cracks. Some artifacts that looked like pores were caused by boundary plucking and grain pull-out during the sample grinding. The image analysis was performed using Image Plus Pro, and the artifacts were mostly excluded from the captured images by a visual discrimination and by an application of filters that limit the size and irregularity of the images. The pores intersecting the edges of the micrographs were excluded from the captured images in measuring pore size.

The polished samples were chemically etched using 50vol%$H_2O_2$+50vol%$H_2SO_4$ solution for about 45seconds. The etchant attacked the fuel periphery faster than it did the central region. Grain size was measured by the linear intercept method at three positions along the radial direction.

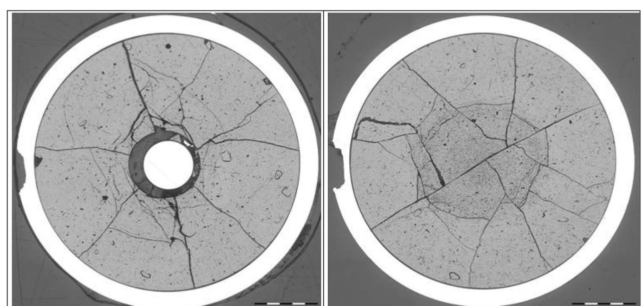
## 4. RESULTS AND DISCUSSION

### 4.1 Macroscopic Observation

Macrographs of the irradiated MOX fuel rods were taken to observe the whole radial cross sections, as shown in Fig. 2. The macrograph of rod 3 shows a central hole drilled for the instrumentation with the expansion thermometer. Fig. 2 shows a solid cross section of rod 6. Only eight pellets were drilled; these were far away from the axial cutting position for the instrumentation with the fuel thermocouple. Both macrographs show some radial cracks that were generally circumferentially closed at the pellet periphery and slightly open in the hot central region. A circumferential crack was formed along the boundary between the dark central and outer regions, as has also been observed in macrographs of other irradiated fuel rods [7]. Diametral swelling of the irradiated MOX pellets was around 1.41% (rod 6) and 1.65% (rod 3). It is due to a compensation of the swelling by some more densification of the pellets for rod 6 than that for rod 3 during the beginning of irradiation. The inner surface of the cladding was covered with an oxide layer that is composed of the main cladding elements, oxygen, fuel elements and fission products [8]. The fuel pellets were not unloaded from cladding by a tilting or tapping of the rod since the fuel swelling and the oxide layer made the gap closed.

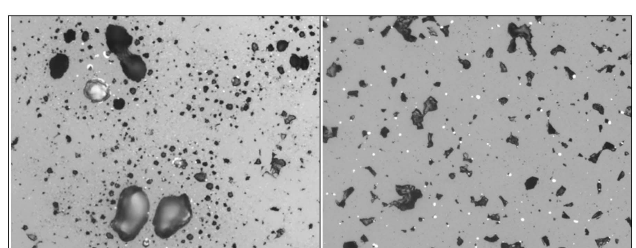
### 4.2 Microscopic Observation

As microscope magnification increased, pores, Pu-rich spots and metallic fission product precipitates became clearly visible on the polished sections of the rods. The Pu spots were observed in the middle and peripheral regions, but not in the central region, as shown in Fig. 3. Pu in the spots diffuses out to the $UO_2$ matrix in the hot central region [9, 10]. Most of the fission reactions occur within the Pu spots where the metallic precipitates and the fission gas bubbles exist as a consequence of high burn-up. As fission products accumulate within the spot, a portion of them migrate to the surrounding matrix by athermal processes such as recoil and knockout [10-12]. The high density of the small pores forms a ring around the spot that becomes visible in the polished fuel cross section [12]. Fig. 3(a) shows that the Pu spot is surrounded by a ring of many small pores. The ring is called a halo [13]; some larger pores and metallic fission product precipitates exist in it.



Rod 3 at axial position of 337.5mm from lower end | Rod 6 at axial position of 319.5mm from lower end

Fig. 2. Macrographs of MOX Fuel Rods after Irradiation



(a) Pu rich spots in the periphery | (b) Metallic precipitates in the central region

Fig. 3. Micrographs of MOX Fuels at Polished Section

The halos with a diameter of less than 15 μm were mainly observed in the periphery region on the radial cross sections. The halo thickness is on the order of a few fission fragment recoil distances [12]. The halos serve as gas storage sites but most of the fission gases and the solid fission products stay within the spot throughout the fuel life [13]. Fig. 3(b) shows the metallic precipitates, which appear as white spots. The precipitates mainly consist of Pd, Ru, Mo, Rh, and Tc, but the compositions differ with the radial position in the fuel [10].

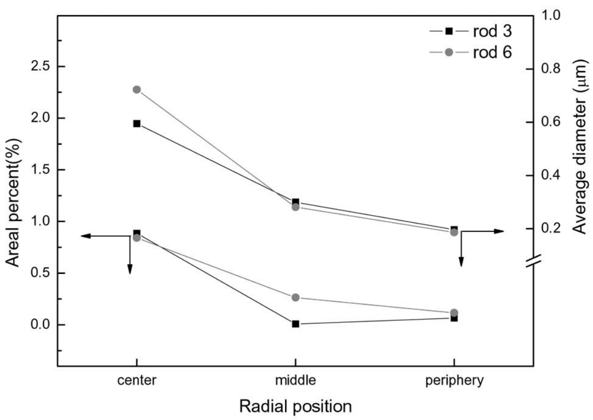



Fig. 4. ImAge Analysis of Metallic Fission Product Precipitates

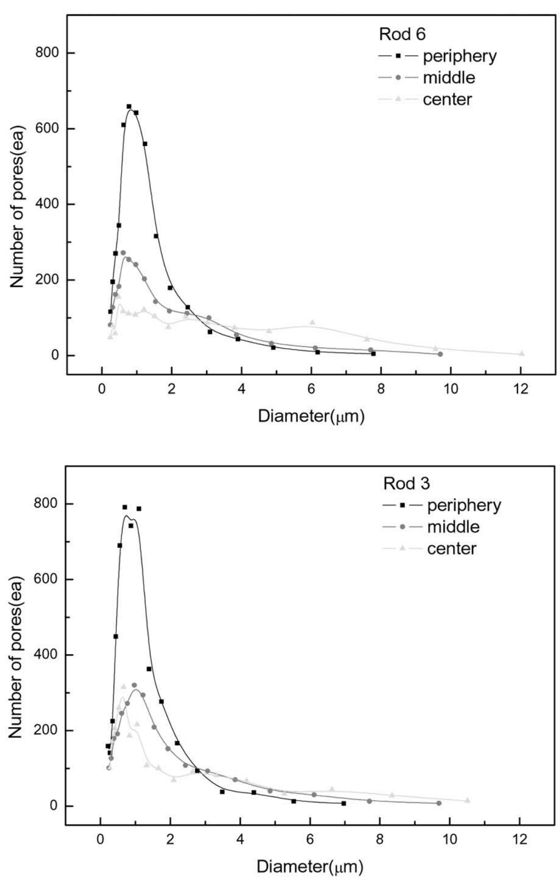



Fig. 5. Pore Distributions of the Irradiated MOX Fuels

## 4.3 Image Analysis of Micrographs

Fig. 4 shows the image analysis results of the metallic fission product precipitates. Most of the precipitates are distributed in the central region where their size is also larger than it is in other regions. In the periphery, the precipitates were very small and were observed at the Pu rich spots. In the case of rod 3, the area percentage of the precipitates in the intermediate region was less than that in the periphery and much less than that in the same position of rod 6. The size of precipitates for rod 3 was smaller than for rod 6 in the central region but was similar in the other regions. The MOX fuel pellets of both rods were the same but local burn-up and temperature were different from each other because of the central hole for the insertion of the expansion thermometer in rod 3. This may explain the differences between the measurements for the two rods. Cross-section average area fractions of the precipitates were 0.41% for rod 6 and 0.32% for rod 3.

Fig. 5 shows the pore distributions of the irradiated MOX fuels in the three radial regions. The distribution density of the small pores, less than 2 μm, showed the highest value in the periphery and the next highest in the intermediate region, and then in the central region, as would be expected considering the temperature dependence of the fuel densification. Pores larger than 4 μm were distributed at the fuel center of rod 6. According to the review of post irradiation results for OCOM and MIMAS MOX fuel [11], the fission gas bubble size within the Pu spots varies with radial position; the bubbles at the Pu spot in the cooler peripheral region are generally smaller than in the central region where a few large pores with several micron-sized are often observed. In a peripheral Pu spot of MIMAS MOX fuel with an average burnup of 63MWd/kgHM, the bubble sizes ranged between 1μm and 8μm in diameter [12]. In the case of rod 6, some large pores are related to the gas bubbles in the central region. Fine pores with a diameter of around 1 μm were found in greater numbers for rod 3 than for rod 6, as shown in Fig. 5; this can be explained by the higher fuel temperatures in rod 6, which lead to increased densification.

## 4.4 Grain Structures

Fig. 6 shows the grain structures of the irradiated MOX pellet from rod 6, compared with the as-fabricated fuel structure. The grain size of the fresh KAERI MOX pellet was 10 μm, which was larger than that of the other MOX pellets [1-4]. The grain structure of the irradiated fuel in the periphery region was very similar to that of the as-fabricated fuel. The grain size of the irradiated fuel was different from the central region to the periphery, as shown in Fig. 6. In the central region, the grains are more round in shape and larger in size than in other regions. Many fine pores are mainly distributed within grains and large pores are observed at the intersections of grains. Metallic precipitates were observed as white spots at the grain boundaries of the central region. There are many fine pores and features with needle shape in the periphery. Halos were observed in the middle and periphery but not in the central region. The microstructure of the inside of the halo was invisible since the etchant did not attack there. It is known that the insides of the halos have transformed into a HBS (High Burnup Structure) [12, 13]. The HBS is formed at the cooler outer region of the fuel cross section when a local burnup is higher than about 60 MWd/kgHM and the temperature is below about 1273 K [12]. This structure is formed by a recrystallization process that produces small (<1 μm) grains with many accompanying pores for fission gas storage. Gas storage within the pores of the HBS adds to the effect of the fission product insertions into the fuel lattice, thereby inducing additional local swelling [12, 13].

The needle-shaped features exist in the middle and periphery, as shown more clearly in Fig. 7. It is known that these features are planar defects that could form the boundaries of the polyhedral sub-grains [12]. The planar defects were mostly observed in the periphery regions of the irradiated fuel but not observed within the Pu rich spots or in the central region. The defects can be observed on SEM (Scanning Electron Microscope) fractographs; the defects appear as structural discontinuities with steps about 1 μm long on the fractured surface [12].

Fig. 8 shows the microstructures of the etched sections from the fuel surface to the center with the average grain sizes. The grains grew from 10 μm to 12 μm only in the central region of rod 6 after irradiation. Grain growth did not occur during irradiation for rod 3 since the central temperature of rod 3 was lower than that of rod 6 because of the central hole.

## 5. CONCLUSIONS

MOX fuel was fabricated by an attrition-milling method to obtain a homogeneous Pu distribution and was irradiated in the Halden reactor. Ceramography was performed on the MOX fuel of 50MWd/kgHM burnup.

Radial cracks were observed in the irradiated MOX; these cracks were generally circumferentially closed at the pellet periphery and slightly open in the hot central region. A circumferential crack was formed along the boundary between the dark central and outer regions. The inner

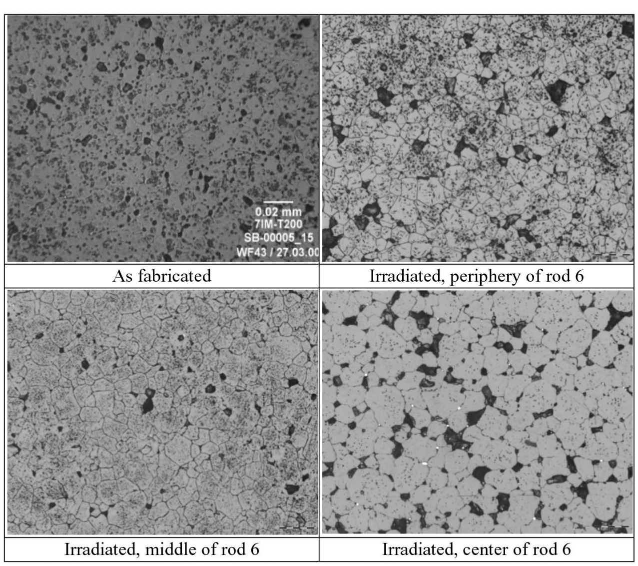



Fig. 6. Grain Structures of MOX Fuel Pellets

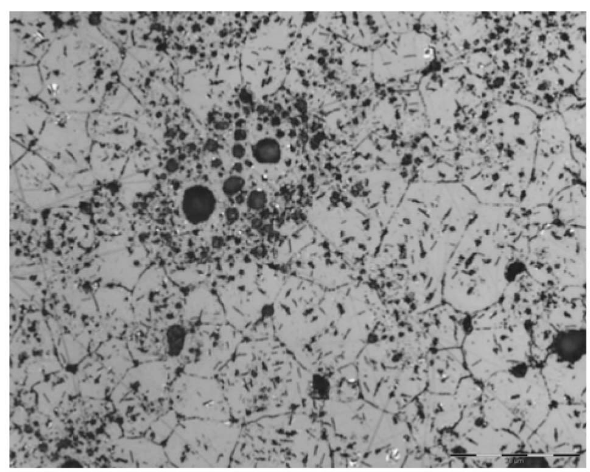


Fig. 7. Planar Defects at Periphery of Rod 6

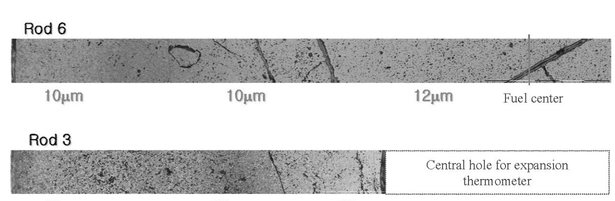



Fig. 8. Micrographs and Average Grain Sizes of the Irradiated MOX Fuels Through Pellet Edge to Center of Radial Section

surface of the cladding was covered with an oxide layer that made the gap closed.

The Pu-rich spots were observed in the outer region of the MOX fuel pellets. Each spot was surrounded by a halo composed of small pores with high density. Some big pores and metallic fission product precipitates exist inside the halo.

The metallic fission product precipitates were observed mainly in the central region of the radial cross section, and their area fractions were 0.41% for rod 6 and 0.32% for rod 3.

The pores larger than 4 μm were distributed in the fuel center, whereas the fine pores smaller than 2 μm were mainly in the periphery region.

The grain growth from 10 μm to 12 μm occurred only in the central region of rod 6 after irradiation.

## ACKNOWLEDGMENTS

The authors would like to thank the Nuclear Materials Technology Department of IFE for the ceramography of irradiated MOX fuels. This work was supported by the Ministry of Education, Science and Technology of the Republic of Korea under the Nuclear R&D Project.

## REFERENCES

[ 1 ] R.J. White, S.B. Fisher, P.M.A. Cook, R. Stratton, C.T. Walker, I.D. Palmer, "Measurement and analysis of fission gas release from BNFL's SBR MOX fuel," J. Nucl. Mater., 288, 43 (2001).

[ 2 ] C.T. Walker, W. Goll, T. Matsumura, "Effect of inhomogeneity on the level of fission gas and caesium release from OCOM MOX fuel during irradiation," J. Nucl. Mater., 228, 8 (1996).

[ 3 ] R. Guldner, H. Schmidt, "Optimization of process parameters for the sintering of MOX fuel," J. Nucl. Mater., 178, 152 (1991).

[ 4 ] M.A. Barker, K. Stephenson, R. Weston, "The manufacture and performance of homogeneous microstructure SBR MOX fuel," Proceedings of the 2007 International LWR Fuel Performance Meeting, San Francisco, California, September 30-October 3, 2007, Paper 1025.

[ 5 ] H.S. Kim, C.Y. Joung, B.H. Lee, J.Y. Oh, Y.H. Koo, P. Heimgartner, "Applicability of $CeO_2$ as a surrogate for $PuO_2$ in a MOX fuel development," J. Nucl. Mater., 378, 98 (2008).

[ 6 ] Y.W. Lee, H.S. Kim, S.H. Kim. C.Y. Joung, S.H. Na, G. Ledergerber, P. Heimgartner, M. Pouchon, M. Burghartz, "Preparation of simulated inert matrix fuel with different powders by dry milling method," J. Nucl. Mater., 274, 7 (1999).

[ 7 ] L. Mertens, "FIGARO International Programme Final Report," BN.REF.9904082/221 Rev.A, Issued April 2000.

[ 8 ] K. Tanaka, K. Maeda, S. Sasaki, Y. Ikusawa, T. Abe, "Fuel-cladding chemical interaction in MOX fuel rods irradiated to high burnup in an advanced thermal reactor,"J. Nucl. Mater., 357,58 (2006).

[ 9 ] M.A. Barker, C.P. Chatwin, "Fuel Performance activities at Sellafield Ltd and the United Kingdom National Nuclear Laboratory," WRFPM 2008, October 19-23, 2008, Seoul, Korea.

[10] H. Kleykamp, "Post-irradiation studies on LWR-MOX fuel fabricated by the optimized co-milling process,"J. Nucl. Mater., 324, 198 (2004).

[11] S.B. Fisher, R.J. White, P.M.A. Cook, S.Bremier, R.C. Corcoran, R. Stratton, C.T. Walker, P.K. Ivison, I.D. Palmer, "Microstructure of irradiated SBR MOX fuel and its relationship to fission gas release," J. Nucl. Mater., 306, 153 (2002).

[12] J. Noirot, L. Desgranges, J. Lamontagne, "Detailed characterizations of high burn-up structures in oxide fuels," J. Nucl. Mater., 372, 318 (2008).

[13] J. Spino, D. Baron, M. Coquerelle, A.D. Stalios, "High burn-up rim structure: evidences that xenon-depletion, pore formation and grain subdivision start at different local burn-ups," J. Nucl. Mater., 256, 189 (1998).