Study of Rock-like Oxide Fuels under Irradiation*

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Abstract
To evaluate the irradiation behavior of the rock-like oxide fuel, irradiation experiments were carried out. Three fuels were prepared; a single phase fuel of yttria-stabilized zirconia containing UO₂ (U-YSZ) and two types of particle-dispersed fuels of U-YSZ particles in spinel or corundum matrix. U-YSZ particle sizes were about 100 - 200 µm. These fuels were irradiated in Japan Research Reactor No.3 for about 280 days. The burnups were about 11% FIMA. The fission gas release rate (FGR) was determined by puncture test and gas analysis. Corundum-based fuel showed extremely high FGR (88%). The irradiation behavior of spinel-based fuels in conditions avoiding the spinel decomposition was superior to corundum-based fuels, in view of their retention of FP gases. The temperature of U-YSZ single-phase fuel pellets was highest among the fuels, because of its low thermal conductivity. Nevertheless the U-YSZ single-phase fuel showed very low FGR (5%). Microstructure analyses of irradiated fuel pellets were carried out by ceramography and electron probe micro-analysis (EPMA). The restructuring of fuel pellet was not observed in the spinel-based fuel irradiated below 1400 K. Significant appearance changes were not also observed for corundum-based fuel, in the range of about 800 K to 1900 K, where the irradiation tests were carried out.

Key words: Rock-Like Oxide Fuel, Yttria Stabilized Zirconia, Spinel, Corundum, Ceramography, FP Gas Release Rate

1. Introduction

The concept of the rock-like oxide (ROX) fuel has been developed for burning excess plutonium in light water reactors (LWRs). Features of the ROX-LWR system are the deep burning of plutonium and the direct disposal of spent ROX fuels without reprocessing (1, 2). The matrix of ROX fuel is uranium-free, and it consists of several phases such as fluorite (yttria-stabilized zirconia; YSZ), MgAl₂O₄ (spinel) and Al₂O₃ (corundum). Plutonium, other actinides and rare earth fission products (FPs) dissolve into the fluorite phase. The spinel or corundum phase immobilizes alkali and alkaline earth FPs, and improves thermal conductivity. The resistance of spinel to neutron irradiation is high (3), but that to fission fragment damage might not be sufficient. For the improvement of swelling behavior, we have also proposed dispersion of coarse particles of actinides-containing phase in spinel or corundum matrix (2, 4).

In previous studies, in-pile irradiation examination of five types of ROX fuels was carried out: a single-phase fuel of a YSZ containing UO₂ (Z fuel), particle-dispersed fuels of...
U-YSZ particles in spinel or corundum matrix (SD, CD fuels), and homogeneously-blended fuels of U-YSZ and spinel or corundum (SH, CH fuels) \(^{(2, 5, 6)}\).

Because of high irradiation temperature which estimated about 2000K at center of the pellets, decomposition of the spinel and subsequent dissociation of MgO was observed for spinel-based fuels. The vaporization of Mg was caused by oxygen dissociation from MgO because of low oxygen potential. The spinel-based fuels showed high fission gas release as compared with corundum-based fuels. The restructuring might be the primary cause for the high fission gas release. From comparison of the estimated temperature distribution and the aspect of the fuel pellet surface, it was expected that the dissociation of MgO could be avoided by lowering the fuel temperature below 1700 K \(^{(5)}\).

On the other hand, under irradiation conditions of sufficiently high irradiation temperature to effect annealing of the amorphous corundum, no significant appearance changes such as swelling and heterogeneity of the fuel structures were observed for the corundum-based fuels.

We have performed a new irradiation examination of the ROX fuel with the condition at lower irradiation temperatures in order to confirm the irradiation behavior of ROX fuel. It was important to confirm the irradiation behavior of spinel-based fuel under the lower irradiation temperature, which is conceivable to avoid the spinel decomposition. It was also essential for the evaluation of the behavior of corundum-based fuel to ascertain the occurrence of amorphization and subsequent swelling by lowering the irradiation temperature. The maximum center temperature of the fuel pellets was designed around 1500 K for spinel and corundum-based fuels.

In this paper, the results of puncture test and microstructure analyses will be described and discussed.

2. Experimental

2.1 Preparation of Fuels

Three types of fuels were prepared using 20 % enriched U a surrogate of Pu for the irradiation tests; single phase fuels of YSZ containing UO\(_2\); U-YSZ (Z2 fuel), particle dispersed fuels of U-YSZ particles in spinel or corundum matrix (SM, CM fuels). The compositions of these fuels are listed in Table 1. The fuels were designed to make the number density of fissile equal in all fuels in order to compare the irradiation behavior, and the amount of fissile element was determined on the basis of linear powers presumed from average neutron flux on normal operating condition of Japan Research Reactor No.3 (JRR-3) to control the irradiation temperature.

The Z2 fuel was fabricated by mixing oxide powder of each component. The U-YSZ particles for particle-dispersed fuels in previous study were fabricated by external sol-gel process \(^{(4)}\), we attempted to adopt more simplified method in this experiment.

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Fuel type</th>
<th>U-YSZ inclusion size</th>
<th>Composition / mol%</th>
<th>(^{235})U / cm(^3)</th>
<th>Density g·cm(^{-3})</th>
<th>%TD**</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z2</td>
<td>Solid solution</td>
<td>Solid solution</td>
<td>78.00</td>
<td>22.00</td>
<td>-</td>
<td>1.158x10(^{21})</td>
</tr>
<tr>
<td>SM</td>
<td>Particle dispersed</td>
<td>100-200 µm</td>
<td>33.35</td>
<td>29.65</td>
<td>37.00</td>
<td>1.159x10(^{21})</td>
</tr>
<tr>
<td>CM</td>
<td>Particle dispersed</td>
<td>100-200 µm</td>
<td>27.70</td>
<td>24.63</td>
<td>-</td>
<td>47.67</td>
</tr>
</tbody>
</table>

*YSZ: 78.6mol% ZrO\(_2\) + 21.4 mol% YO\(_{1.5}\) ** TD: theoretical density
The U-YSZ particles for SM and CM fuels were prepared by crashing presintered U-YSZ pellets whose density was 65% of theoretical density and then by sieving them. The particles of size 125 - 250 µm were sifted out. Those U-YSZ particles were blended with fine powder of spinel or corundum and pressed to pellets.

The green pellets of SM, CM, and Z2 were sintered at 1820 K for 24 h in a stream of 4% H₂/He mixed gas. The size of each pellet was 5.2 - 5.4 mm in diameter and 5.5 - 5.7 mm in height. After sintering, the homogeneous distribution of the U-YSZ particles in the matrix was confirmed by ceramography for the particle-dispersed fuels. The size of U-YSZ particle was about 100 – 200 µm. Figure 1 shows the appearance and the aspects of the fabricated ROX fuel pellets.

2.2 Irradiation

Ten pellets of each fuel were loaded in a stainless steel cladding tube and He gas at ambient pressure was sealed off. SUS316 stainless steel tube with outer diameter 6.5 mm and wall thickness of 0.5 mm was used for the cladding. The length of fuel pins was 125 mm. The irradiation capsule for the targets was designed to remove the heat of the fuels efficiently by cooling water to lower the irradiation temperature. The three targets of Z2, SM, and CM were irradiated in JRR-3 for 280 days. Irradiation conditions are summarized in Table 2.

The burnups were determined by analyzing ¹⁴³Nd inventory. The segments of ~ 100mg were cut from the midsections of the fuel rods, taken off the cladding, heated in Aqua regia with hydrogen fluoride until completely dissolved. The added amount of hydrogen fluoride was determined from the estimated Zr content. The determined burnups were 10.8, 10.7 and 12.0 FIMA% for SM, CM and Z2 fuel, respectively. Those corresponded to about 25.7, 25.3 and 28.4 GWD·t⁻¹ of LWR UO₂ fuel.

The linear power was estimated from the activity measurement of fluence monitors placed close to each fuel pin. The ratio of burnup calculated by SRAC95 code (7) to that measured by analytical method was over 0.99 for Z fuel. The liner power of CM fuel was determined from analytically measured burnups, because the activity measurement was failed. Temperature of each fuel target was measured by a thermocouple placed close to the cladding. The surface and center temperatures of the fuel pellets were estimated from the obtained linear powers, the measured surface temperatures of cladding, and the thermal conductivities of the components before irradiation.

2.3 Post-irradiation Examination

Post-irradiation examinations were carried out at the Reactor Fuel Examination Facility in JAEA. The irradiation capsule was disassembled and three fuel pins were taken out. The
non-destructive post-irradiation examinations (profilometry, X-ray radiography and γ scanning) were carried out earlier. The results were described and discussed elsewhere (8).

After the non-destructive examinations such as visual inspection, X-ray radiography and γ scanning were carried out, the gases in the fuel pin were collected and analyzed through the puncture test. The isotopic abundance of Kr and Xe were measured using mass spectrometry. The fuel pins were cut off and some pellets were taken out from fuel pins. The appearance of the fuel pellets was observed. Epoxy resin was injected into the remaining pellets within cladding tube. After polishing the cross section of the pellets, X-ray diffraction analysis (XRD), metallography, scanning electron microanalysis (SEM) and electron probe microanalysis (EPMA) were carried out.

3. Results and Discussions

3.1 Fission Gas Release

Gases in the fuel targets were collected and analyzed by means of a puncture test. Total yield and isotopic abundance of Kr and Xe were obtained from the burnup calculation using the SRAC95 code.

The measured Xe and Kr values and calculated ones are listed in Table 3. The released Xe / Kr gas ratios were measured to be about 7.4, which agreed well with the calculated results. The FGR is the ratio of the measured Xe and Kr volume and the calculated one. Obtained FGR for each fuel is also listed in Table 3. The FGR of CM fuel was extremely high. That was about twice higher than spinel-based fuel. Since the U-YSZ particles for the SM and CM fuels were similar, and the irradiation conditions were almost the same, the difference in behavior was caused by the difference in the properties of the matrices. The FGR of previous studies (5) are also shown in the table for comparison. FGR of corundum-based fuel of previous studies (CD, CH) are not so high as that of this works.

In case of composite fuels, the generation of hair cracks is a primary factor of the high FGR. Such hair cracks occur by the stress caused from a thermal expansion difference between the U-YSZ and matrices. The thermal stresses would become larger by increasing the temperature. And furthermore, FP gases have higher diffusion rates in higher temperature condition. However, the irradiation temperature of the CM fuel was much lower than those of the CD and CH fuels as shown in table 3. The irradiation temperature of CM fuel was close to the recovery temperature of Al₂O₃ amorphous, about 1173 K (9). However, the upper limit of observable temperature of Al₂O₃ amorphization has not clarified.

Table 3 Measured and calculated FP gas volume, FP gas release rate and swelling of the ROX fuels Z2, SM and CM. This work; Z, SD, CD, SH and CH, previous study (5).

<table>
<thead>
<tr>
<th>Fuels</th>
<th>Z2</th>
<th>SM</th>
<th>CM</th>
<th>Z</th>
<th>SD</th>
<th>CD</th>
<th>SH</th>
<th>CH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Measured volume of released FP gas / cm³</td>
<td>Kr</td>
<td>0.06</td>
<td>0.41</td>
<td>0.87</td>
<td>0.004</td>
<td>0.08</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>Xe</td>
<td>0.42</td>
<td>3.04</td>
<td>6.46</td>
<td>0.021</td>
<td>0.60</td>
<td>0.36</td>
<td>0.36</td>
<td>0.11</td>
</tr>
<tr>
<td>Xe/Kr ratio</td>
<td>7.0</td>
<td>7.4</td>
<td>7.4</td>
<td>5.4</td>
<td>7.5</td>
<td>7.2</td>
<td>7.2</td>
<td>7.0</td>
</tr>
<tr>
<td>Calculated volume of produced FP gas / cm³</td>
<td>Kr</td>
<td>1.14</td>
<td>1.01</td>
<td>1.00</td>
<td>0.131</td>
<td>0.219</td>
<td>0.234</td>
<td>0.229</td>
</tr>
<tr>
<td>Xe</td>
<td>8.38</td>
<td>7.38</td>
<td>7.35</td>
<td>0.946</td>
<td>1.57</td>
<td>1.68</td>
<td>1.65</td>
<td>1.42</td>
</tr>
<tr>
<td>Xe/Kr ratio</td>
<td>7.4</td>
<td>7.3</td>
<td>7.3</td>
<td>7.1</td>
<td>7.2</td>
<td>7.1</td>
<td>7.2</td>
<td>7.2</td>
</tr>
<tr>
<td>FP gas release rate / %</td>
<td>5</td>
<td>41</td>
<td>88</td>
<td>2.4</td>
<td>38</td>
<td>22</td>
<td>22</td>
<td>8</td>
</tr>
<tr>
<td>Volume increase of pellet / %</td>
<td>5.6</td>
<td>7.2</td>
<td>4.7</td>
<td>&lt;4.0</td>
<td>5.5</td>
<td>4.3</td>
<td>10.2</td>
<td>5.7</td>
</tr>
<tr>
<td>Average T center of pellet / K</td>
<td>1490</td>
<td>1060</td>
<td>1020</td>
<td>1490</td>
<td>1740</td>
<td>1820</td>
<td>1940</td>
<td>1730</td>
</tr>
<tr>
<td>Maximum T center of pellet / K</td>
<td>1960</td>
<td>1360</td>
<td>1350</td>
<td>1580</td>
<td>1850</td>
<td>1930</td>
<td>2080</td>
<td>1830</td>
</tr>
<tr>
<td>Burnup / FIMA%</td>
<td>12.0</td>
<td>10.8</td>
<td>10.7</td>
<td>3.7</td>
<td>4.1</td>
<td>4.2</td>
<td>4.2</td>
<td>3.6</td>
</tr>
</tbody>
</table>
X-ray diffraction analysis was carried out at two points; the center region of fuel pellet, and the periphery region. A collimator with 1mm diameter and a receiving slit with 0.6 mm were used for the measurements. The estimated irradiation temperature was about 1000 K and 800 K, for the center and periphery region of CM fuel, respectively. The XRD patterns of the center and the surface region of CM fuel pellet are shown on Fig. 2, with the XRD pattern of CM fuel as fabricated. The peaks of fluorite phase broadened by irradiation, both XRD patterns of the irradiated CM fuel clearly showed the existence of crystalline corundum phase, and no peaks resulted from amorphization were observed. It is confirmed that the overall amorphization did not occur in the temperature range. The cause of the high FGR of CM fuel that irradiated at lower temperature is not explicable from the structure analysis.

It is known that the neutron resistance of corundum is inferior to that of spinel, and corundum becomes amorphous by fission damage. Berman et al. (10) reported that the fuel specimen irradiated at low temperature (about 560 K) showed a large swelling (about 30 %) due to amorphization of the corundum phase. The confirmation of swelling behavior of corundum under the irradiation condition of around 1000 K was an important objective of this irradiation test. The volumetric swellings of the fuels are also summarized in table 3. In this work, the swelling of the CM fuel fuels was substantial but not very large, about 4.7%.

In the previous study (5) the spinel-based fuels (SD, SH) showed higher FGR than corundum-based fuels (CD, CH), presumably due to the spinel decomposition and subsequent restructuring. The restructuring was not recognized for SM fuel from cross sectional appearance observation (8). The FGR of SM fuel was higher than SD and SH fuels. However, in view of the increase of burnup, total gas yields and the duration of irradiation, the increment of the FGR of SM fuel was rather small.

The U-YSZ single-phase fuel showed very low FGR. The FGR of the Z2 fuel is only about 5%, in spite of a central hole formation (8), high irradiation temperature, and high burnup. YSZ had a great retention capability of FP gases. The open paths of micro crack for the single-phase fuel is harder to form than that for particle-dispersed fuels, the FP gases were confined in grain boundaries. Besides, the composition of U-YSZ phase for Z2 fuel was different from those for SM and CM fuels. The mole fraction of U in U-YSZ phase was 47.1 mol% for SM and CM fuel, and 22.0 mol% for Z2 fuel. The difference of composition may cause the difference of the density of produced FP gases and the ease of gas bubble formation. Those factors were considered to have resulted in the lower FGR for the Z2 fuel.

3.2 Microstructure

The microstructure analyses of irradiated fuel pellets were carried out by ceramography and electron probe microanalysis.

The SEM image of the Z2 fuel is shown in fig. 3. Several radial cracks and a central hole within 0.8 mm diameter can be observed, as is Fig. 3 The SEM image of Z2 fuel.
similarly observed in high burnup LWR UO$_2$ fuel. Probably, the central hole was caused by
densification and migration of pores at the high temperature. The Z2 fuel pellet was porous
in the middle region and some columnar grains were grown from middle towered center
region.

The line profiles of U, Zr, Al, and Mg for the SM fuel and those of U, Zr, and Al on the
CM fuel are shown in Fig. 4 with the SEM images. The line profiles for SD and CD fuels
are also shown in Fig 4 for comparison. The SD fuel irradiated at about 1900 K showed
MgO dissociation and restructuring. The irradiated SD fuel pellet comprised roughly three
regions; the center region consisted only of U-YSZ; the middle region consisted of U-YSZ
and corundum; the outer region consisted of the original U-YSZ and spinel. MgO was
detected on the inner surface of cladding tube. By comparing the aspect of pellet surface
and the temperature distribution, it is expected that the dissociation of MgO occurred in the
area where average irradiation temperature was over about 1700 K (5).

The distributions of the matrix elements for the SM fuel that irradiated blow 1400 K
were homogeneous from the center to the outer region, and the decomposition of spinel and
restructuring are not observed. It was confirmed that the MgO dissociation and the
subsequent restructuring were avoidable by lowering the irradiation temperature form this
irradiation test.

![Line profiles of U, Zr, Al, and Mg](image)

Fig. 4 The line profiles of U, Zr, Al, and Mg and SEM image corresponds to the
position measurement for SM, SD, CM and CD fuels. White line shows the analyzed
position.
The distributions of the matrix elements for the CM and CD fuels were homogeneous from the center to the outer region. The significant structural changes were not observed from the SEM images. Regardless of the irradiation temperature, corundum-based fuels did not show appreciable microstructure change, in the range of about 800 K to 1900 K, where the irradiation tests were carried out.

The microstructures around the boundary between U-YSZ particles and matrix were examined in further detail. The elemental mapping was carried out using EPMA for matrix.

The SEM image of the outer region of SM fuel pellet is shown in Fig. 5. A gray layer of about 10 µm thickness can be observed at the surface of the particle. The maps of chief elements obtained by EPMA at the region surrounded with a square in the SEM image are also shown in Fig. 5. Element maps show that U-YSZ and spinel mixed in this layer. The layer consists of fine grains of spinel and U-YSZ. The thickness of the layer is comparable to the mean range of fission fragments. The formation of this layer might be the direct consequence of the reaction between U-YSZ and damaged spinel matrix by fission fragment irradiation. It is considered that the radiation damage area was related to the swelling behavior. In the previous study, the swelling behavior of homogeneously-blended fuels (U-YSZ inclusion size 10 - 50 µm) was larger than that of particle-dispersed fuels (U-YSZ inclusion size 250 µm). Since the surface area of U-YSZ contacted with matrix was larger in the small inclusion fuel, the radiation damage area was made larger. A typical SEM image of the outer region of the CM fuel is shown in Fig. 6. Difference from the SM fuel was that no layer was observed at the surface of the U-YSZ particles, neither in the SEM image nor in the EPMA distributions of matrices and U, as shown in Fig. 6.

The complex oxides such as spinel decompose to fine grains more easily by fission...
fragment damage, than corundum which is a single oxide. And the difference may be related to the formation of the reaction layer.

4. Summary

The ROX fuels were irradiated and post-irradiation examinations were carried out. The FGR was determined by puncture test and gas analysis. The corundum-based fuel irradiated around the temperature of annealing corundum amorphous showed extremely high FGR. On the other hand, the swelling of the CM fuel fuels was substantial but not very large. The spinel-based fuel that irradiated under the avoidable condition of spinel decomposition was superior to corundum-based fuel, for their retention FP gases. The U-YSZ single-phase fuels showed very low FGR.

The microstructures of fuels were analyzed by ceramography and EPMA. Several radial cracks and a central hole within 0.8 mm diameter were observed for Z2 fuel due to densification and migration of pores at the high temperature. The restructuring of fuel pellet was not observed in the spinel-based fuel irradiated below 1400 K. It is confirmed that the decomposition of spinel and vaporization of MgO is avoidable by lowering the irradiation temperature. For corundum-based fuels, significant appearance change such heterogeneity of fuel structures were not observed in the range of about 800 K to 1900 K, where the irradiation tests were carried out.

Damaged area of spinel matrix due to fission fragment irradiation seemed to be confined to thin layers around the surface of U-YSZ particles. On the other hand, no damaged layer was observed in the corundum-based fuel.

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References