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68

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# IN-PILE IRRADIATION OF ROCK-LIKE OXIDE FUELS

N. Nitani, K. Kuramoto, T. Yamashita, Y. Nakano, H. Akie
Japan Atomic Energy Research Institute, Tokai, Ibaraki, 319-1195, Japan.

## ABSTRACT

Five kinds of ROX fuels were prepared and irradiated using 20% enriched U instead of Pu. Non-destructive and destructive post-irradiation examinations were carried out. FP gas release rates of the particle-dispersed type fuels and homogeneously-blended type fuels were larger than that of the yttria-stabilized zirconia containing $UO_2$ single phase fuel. From results of SEM and EPMA, decomposition of the spinel was observed. The decomposition of the spinel is probably avoided by lowering the irradiation temperature, less than 1700K. The regions suffering the irradiation damage of the particle dispersed type fuels were less than those of the homogeneously-blended type fuels.

*Keywords: Rock-like oxide fuel, Yttria-stabilized zirconia, Spinel, Corundum, Post-irradiation examination,*

## 1- INTRODUCTION

The concept of the rock-like oxide (ROX) fuel has been developed for the annihilation of excess plutonium in light water reactors (LWRs). Features of the ROX-LWR system are almost complete burning of plutonium and the direct disposal of spent ROX fuels without reprocessing [1]. The ROX fuel consists of such phases as fluorite (yttria-stabilized zirconia; YSZ), $MgAl_2O_4$ (spinel) and $Al_2O_3$ (corundum). Plutonium, other actinides and lanthanide fission products (FPs) are to be solidified into the fluorite phase. The roles of spinel or corundum are to immobilize alkali and alkaline earth nuclides and to improve thermal conductivity. In previous study, in-pile irradiation examination for plutonium ROX fuel disks with ternary system of YSZ, corundum and spinel was carried out. The existence of excess corundum caused unfavorable behaviors, such as large swelling and high FP gas release [2].

For the improvement of swelling behavior, a particle-dispersed type fuel was proposed [3]. In the case that appropriate size of YSZ particles are dispersed homogeneously in the spinel or corundum matrix, damaged area of the matrix is limited to thin layers surrounding the particles.

In this study, we have performed the irradiation examination in order to confirm the effect of the particle-dispersed type fuels on irradiation resistance. The ROX fuel of YSZ and spinel system, which was the most hopeful composition was used to the experiment. The fuel of YSZ and corundum system was also irradiated, because it was expected that the swelling of corundum is reduced on particle dispersed type fuel. Moreover, the homogeneously-blended type fuels were irradiated to compare the irradiation behavior. Fuel pellets of 5.3 mm in diameter and 5.5 mm in height were used in the experiment. Because, it was considered the high FP gas release in previous study was concerned with the fuel shape, disk of 1 mm in thickness.

The results for the non-destructive examinations of ROX fuels; profilometry, X-ray photograph and $\gamma$ scanning, and for destructive examinations; puncture test, fission gas analysis, SEM and EPMA will be described and discussed.

## 2-EXPERIMENTAL

Five kinds of fuels were prepared using 20% enriched U instead of Pu; a single phase fuel of U-YSZ (Z), two particle-dispersed type fuels of U-YSZ particles in spinel or corundum matrix (SD or CD), two homogeneously-blended type fuels of U-YSZ and spinel or corundum (SH or CH). The compositions of these fuels are shown in Table 1. Number density of $^{235}U$ is designed as $10^{27}$ $m^{-3}$ in all fuels. The U-YSZ particles in particle-dispersed fuel pellets were fabricated by an external sol-gel process [4]. The size of U-YSZ particles was about 250 $\mu m$ in diameter. The homogeneously-blended type fuels and the U-YSZ single phase fuel were fabricated by mixing oxide powder of each component. All fuel pellets were sintered at 2020K for 4h in a stream of $75\%H_2/25\%N_2$ mixed gas. The characterization tests showed that the pellets fabricated had small void volume fraction (<9%). The homogeneous distribution of the particles and grains of U-YSZ in the matrix was confirmed by the ceramography. The X-ray diffraction analysis showed the formation of homogeneous U-YSZ solid solutions and no appreciable interactions between the U-YSZ phase and the matrix materials (spinel or corundum).

Ten pellets of each fuel were loaded in a stainless steel cladding tube and He gas at ambient pressure was sealed off. These fuels were irradiated in Japan Research Reactor No.3 (JRR-3) for about 100 days. Nominal reactor power was 20 MW and maximum neutron fluence was estimated to be about 7 x $10^{24}$ $m^{-2}$. The linear

33/30

power was estimated from the activity measurement of fluence monitors placed close to each fuel pin. The surface and center temperatures of fuel pellets were estimated from obtained linear power. Estimated linear power and temperature of each fuel are listed in Table 2. In Table 2, the "Average" indicates the burnup averaged values, and the "Maximum" indicates the maximum values throughout the irradiation period. It must be mentioned that the temperature of each fuel is remarkably higher than that of irradiation condition in LWRs.

The results of burnup calculation by SRAC95 [5] code system are also shown in Table 2. The estimated burnups are about 0.1 $MWD \cdot cm^{-3}$, which is corresponding to about $10GWD \cdot t^{-1}$ of LWR $UO_2$ fuel.

Table 1. Fuel compositions /mol%

| | Single phase fuel | Particle-dispersed type fuel | | Homogeneously-blended type fuel | |
|---|---|---|---|---|---|
| | U-YSZ (Z) | U-YSZ + $MgAl_2O_4$ (SD) | U-YSZ + $Al_2O_3$(CD) | U-YSZ + $MgAl_2O_4$ (SH) | U-YSZ + $Al_2O_3$ (CH) |
| YSZ | 81.75 | 11.90 | 11.93 | 11.90 | 11.93 |
| $UO_2$ | 18.25 | 19.71 | 19.76 | 19.71 | 19.76 |
| $AlO_{1.5}$ | ------ | 45.60 | 68.31 | 45.60 | 68.31 |
| MgO | ------ | 22.79 | ------ | 22.79 | ------ |

YSZ : 78.57 mol% $ZrO_2$ + 21.43 mol% $YO_{1.5}$

Table 2. Estimated irradiation condition and burnup of the fuels

| Fuels | Z | SD | CD | SH | CH |
|---|---|---|---|---|---|
| | Average / Maximum | | | | |
| Linear power / $kW \cdot m^{-1}$ | 13.9 / 15.2 | 23.0 / 25.4 | 24.9 / 27.6 | 23.4 / 26.0 | 20.7 / 22.7 |
| Temperature at | | | | | |
| Surface of pellet / K | 990 / 1030 | 1250 / 1310 | 1300 / 1360 | 1440 / 1510 | 1290 / 1350 |
| Center of pellet / K | 1490 / 1580 | 1740 / 1850 | 1820 / 1930 | 1940 / 2080 | 1730 / 1830 |
| Burnup | | | | | |
| $^{235}U$ / % | 21.01 | 23.28 | 23.89 | 24.15 | 20.87 |
| / $MWD \cdot cm^{-3}$ | 0.059 | 0.100 | 0.105 | 0.103 | 0.088 |

## 3-RESULTS AND DISCUSSION

Non-destructive and destructive post-irradiation examinations were carried out at Reactor Fuel Examination Facility in JAERI. The irradiation capsule was disassembled and five fuel pins were taken out. The stainless steel cladding surface where fuel pellets were loaded was partially discolored by oxidation. Any change in axial pellet stack length was not recognized from the comparison of X-ray photographs taken before and after irradiation.

The precise diameters were measured from four directions of 45 degrees intervals. The measured values from any direction were almost same. No significant diameter change was observed except for the SH fuel, whose irradiation temperature was the highest. The average diameter increase of the SH fuel was about 30 μm at the fuel stack region. It is considered that the diameter increase of the pin was caused by the swelling of the pellet, since the quantity of diameter change was larger than that estimated from thermal expansion. Nevertheless the diameter change of the SH fuel pin was below 0.5 % of the diameter. The other fuels did not cause the shape change of the fuel pin, which suggest that the swelling of the fuels were less than the initial gap of about 100 μm.

Distribution of typical FPs was analyzed by the γ scanning from plenum to bottom of fuel pin. Gamma rays from FPs such as $^{95}Zr$, $^{106}Ru(^{106}Rh)$, $^{134}Cs$, $^{137}Cs$ and $^{144}Ce(^{144}Pr)$ were detected through a thin slit placed in front of germanium detector. From observed nuclides, the distribution of nonvolatile nuclide, $^{95}Zr$ and volatile nuclide $^{137}Cs$ are shown in Figure 1. The dents of the distributions coincide well with pellet-pellet gaps in Z and SH as shown in Figure 1 (a) and (c). In Figure 1 (b), the dark lines seen in the X-ray photograph are not cracks but lack of the particles and the gaps between pellets. The dark lines coincide with the sharp dents of $^{95}Zr$ distribution. A similar tendency can be seen in the CD fuel. In the Z fuel, the volatile $^{137}Cs$ was observed only in the fuel pellets region as shown in Figure 1 (a). On the other hand, a small amount of $^{137}Cs$ moved to the bottom of the insulator in the SD fuel (Figure 1 (b)). It is estimated that about 10 % of $^{137}Cs$ produced in fuel pellets was released not only to the edge of the fuel pellet and the bottom of the insulator but also to the plenum in the SH fuel, by comparison of distribution areas (Figure 1 (c)). The pellet surface temperatures of fuels were estimated to be greatly higher than Cs boiling temperature, 941.5 K, which may cause the Cs release.

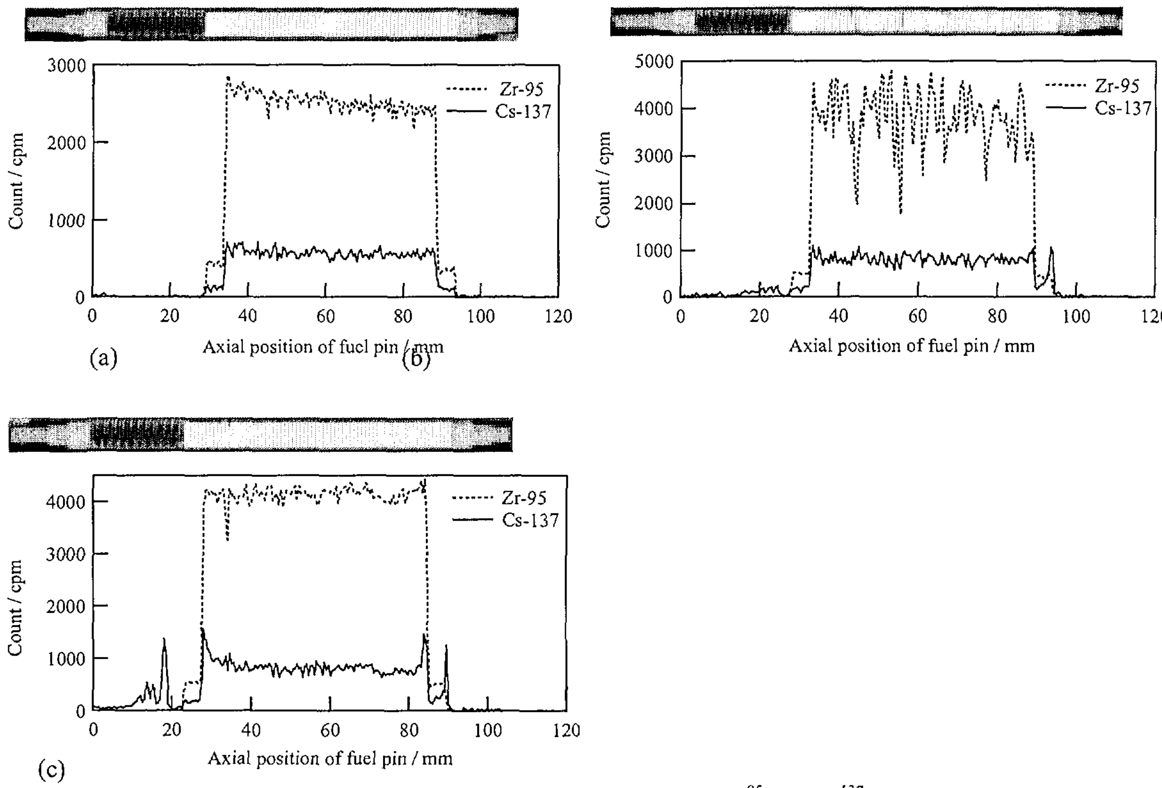



*Figure 1. X-ray photographs and γ scanning of $^{95}Zr$ and $^{137}Cs$*
*(a): Z (U-YSZ), (b): SD (U-YSZ+$MgAl_2O_4$, particle-dispersed),*
*(c): SH (U-YSZ+$MgAl_2O_4$, homogeneously-blended)*

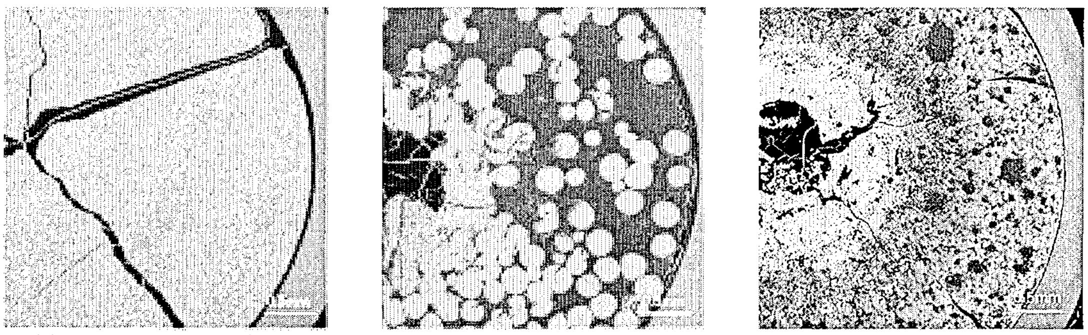
Fission product gas release is one of the key parameters for fuel irradiation performance. Gases in the fuel pin were collected and analyzed through the puncture test. Measured isotopic abundance of Kr and Xe using mass spectrometry were compared with the calculated results. Total yield and isotopic abundance of Kr and Xe were obtained from the burnup calculation using the SRAC95 code. The results of measured FP gas quantity and calculated total FP gas yield are shown in Table 3. The released Xe/Kr gas ratios were measured to be about 7.2, which agreed well with the calculated results. The smaller Xe/Kr ratio of the Z fuel might come from experimental difficulties because very small amount of gas was available for the determination.

Table 3. Measured and calculated Xe and Kr volume and FP gas release late

| Fuels | | Z | SD | CD | SH | CH |
|---|---|---|---|---|---|---|
| Measured volume of | Kr | 0.004 | 0.083 | 0.050 | 0.050 | 0.016 |
| released FP gas / $cm^3$ | Xe | 0.021 | 0.601 | 0.364 | 0.359 | 0.111 |
| Xe/Kr ratio | | 5.4 | 7.3 | 7.2 | 7.2 | 7.0 |
| Calculated volume of | Kr | 0.131 | 0.219 | 0.234 | 0.229 | 0.199 |
| produced FP gas / $cm^3$ | Xe | 0.936 | 1.57 | 1.68 | 1.65 | 1.42 |
| Xe/Kr ratio | | 7.1 | 7.2 | 7.1 | 7.2 | 7.2 |
| FP gas release rate / % | | 2.4 | 38.2 | 21.6 | 21.8 | 7.8 |

The release rate of FP gas is the ratio of the measured and calculated FP gas volumes. They are also shown in Table 3. The FP gas release rates of the particle dispersed type fuels (SD, CD) were higher than these of the homogeneously-blended type fuels (SH, CH). The microscopic crack generation may cause the high gas release rate of particle dispersed type fuels. Since thermal expansion of the U-YSZ particle is higher than that of the matrix, the cracks are generated in the matrix near the grain boundary. The grain size of particle dispersed type fuel was one order of magnitude larger than that of homogeneously-blended type fuel. So the thermal stresses concentrated, and cracks were generated easily. The produced FP gas might be escaped through the cracks generated in the grain boundary of U-YSZ particle. Similar behavior was observed in EFFTRA-T3 irradiation experiment [6, 7]. The FP gas release rate of large fissile inclusions (150μm) dispersed type fuel was remarkably higher than that of small fissile inclusions (<1μm) dispersed type fuel, and many cracks were observed in the matrix of large fissile inclusions dispersed type fuel. It is expected that the stress on grain boundary is reduced by having a small gap around the particle in fuel fabrication process. Furthermore, the distribution of the U-YSZ particle in particle dispersed type fuel used in this study was not so uniform, therefore, the fuel temperature is supposed to be locally higher. Form these points, it is important to fabricate the fuel that the small gap around the particle exists and the particle is uniformly dispersed, for good irradiation performance of particle dispersed type fuels.

The fuel pin was cut off, and resin was injected. After polishing the surface of pellets, the microstructure analyses by ceramography and electron probe micro analysis were carried out. The SEM images of Z, SD and SH fuels are shown in Figure 2. In the Z fuel pellet, several radial cracks existed, as observed in the LWR $UO_2$ fuel. The pellet showed uniform structure throughout the surface, though central region of the pellet revealed slightly porous microstructure. The aspect of pellet was analogous to LWR $UO_2$ fuel. From X-ray diffraction analysis, deformation of the diffraction peak and phase separation of the fluorite phase was not observed for the Z fuel. In the SD and SH fuel pellets, about 0.5mm diameter central holes existed (see Figure 2 (b) and (c)). The U-YSZ particles of the SD fuel were concentrated to the center of the pellet, and the particles were deformed. The behavior, the aggregation of U-YSZ grains, was also observed for the SH fuel. The fuel structures and components were varied concentrically, and lots of pores were generated in central and intermediate regions.



(a) (b) (c)

*Figure 2. The SEM images of (a) Z ($UO_2$-based YSZ), (b) SD ($UO_2$-YSZ+$MgAl_2O_4$, particle-dispersed) and (c) SH ($UO_2$-YSZ+$MgAl_2O_4$, homogeneously blended) fuels*

The line profiles of U, Zr, Al and Mg of the SH fuel are shown in Figure 3 with a SEM image. By comparing the distribution of Al and Mg, it was confirmed that Al existed not as spinel but as corundum in the region of middle toward the center of the pellet. The irradiated SH fuel pellet comprised roughly three regions; the center region consisted of only U-YSZ (about 0.5 - 1.2 mm from the center of the pellet); the middle region consisted of U-YSZ and corundum (about 1.2 - 1.7 mm); the outer region consisted of U-YSZ and spinel (about 1.7 mm - surface). The SD fuel pellet also consisted of similar structures, U-YSZ particle region, U-YSZ particle and corundum region, and U-YSZ particle and spinel region. The observed appearance changes by irradiation were little in the outer region of the SD fuel. Magnesium oxide was detected on the pellet surface and the cladding tube, for both of SD and SH fuels.

It is considered that the occurrence of corundum phase was caused by the decomposition of spinel by the fission damage and vaporization of MgO. The resistance of spinel to neutron irradiation is high [8], but that to fission fragment is not sufficient. The high irradiation temperature and the large temperature gradient (~ 200K/mm) caused the MgO vaporization. Because of high temperature and irradiation field, MgO produced by decomposition of the spinel was vaporized, and moved to the gap and deposited there at lower temperature. By the vaporization of the MgO, the spinel was transformed into the corundum. The volume of matrix decreased by the transformation. The central hole of the pellet was caused by migration of voids, which generated by the volume reduction of the matrix. The U-YSZ grains, which existed in central area in the pellet, were pushed out and were aggregated by central hole generation. The separation of fluorite phase was not observed by X-ray diffraction analysis; zirconium and uranium were distributed homogeneously, though the aspect of fuel pellet was changed by irradiation.

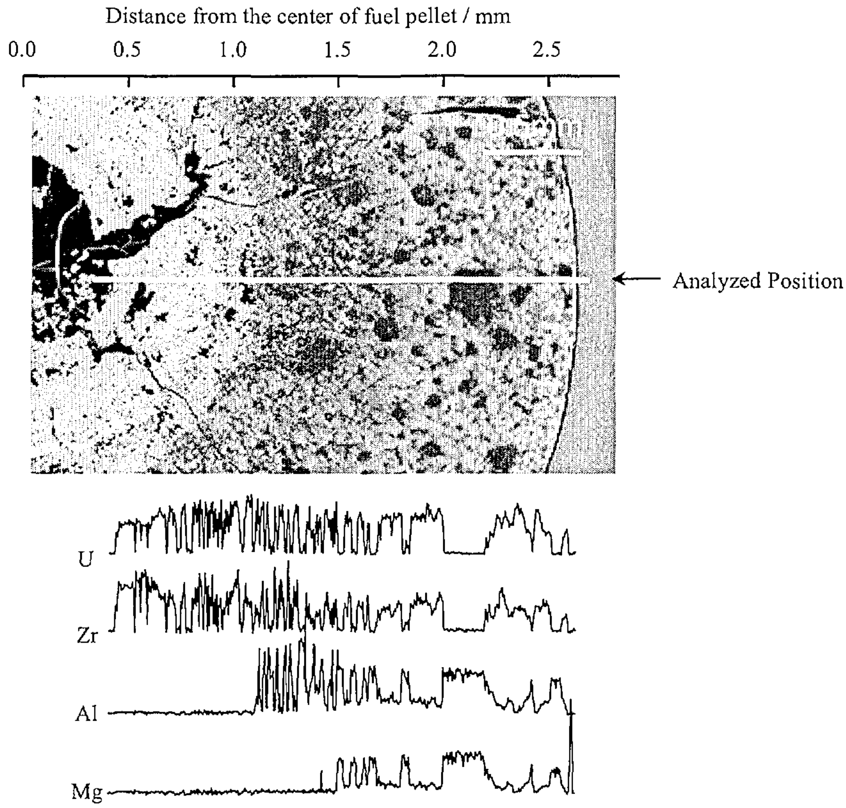



*Figure 3. The line profiles of U, Zr, Al and Mg of SD fuel, and SEM image corresponds to the position measurement was carried out.*

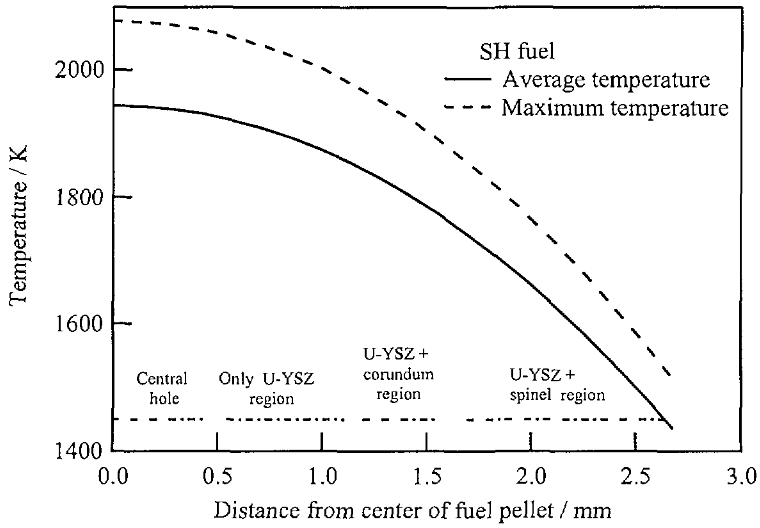


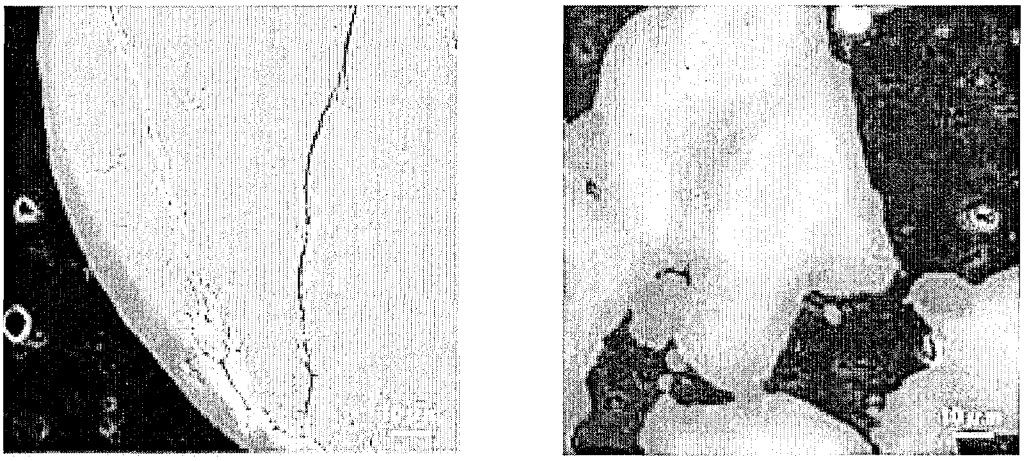

*Figure 4. The estimated temperature distribution in the SH fuel*

Figure 4 shows the estimated temperature distribution in the SH fuel pellet at the beginning of irradiation. By comparing the aspect of pellet surface and the temperature distribution, it is expected that the vaporization of MgO occurred in the area that average irradiation temperature was over about 1700K. The vaporization of MgO was not observed in an irradiation experiment on Spinel-$UO_2$ fuel with the temperature below 1000K [6, 7]. It is expected that the vaporization of MgO would be avoided by lowering the irradiation temperature.

In this experiment, the FP gas release rates of spinel-based fuels (SD, SH) were higher than those of corundum-based fuels (CD, CH). The decomposition of the spinel and the vaporization of MgO caused high FP gas release. It will be able to reduce the FP gas release of the spinel-based fuel by lowering the irradiation temperature, because spinel has essentially high irradiation resistance to neutron and high gas retention ability [9].

The SEM images of the U-YSZ particle (or grain) and matrix boundary on the SD and SH fuels are shown in Figure 5. Those are the images of the outer region where the vaporization of MgO did not occur. In the surface area of the particle (or grain), gray layer of about 10μm thickness was observed. The layer was composed of fine particles of spinel and U-YSZ. The thickness of the layer was comparable to mean range of fission fragments. The layer probably indicates the radiation damaged region. Since the surface area of U-YSZ contacted with spinel was larger in the SH fuel than in the SD fuel, the damaged region in the SH fuel was larger. It is considered that the larger radiation damage area was related to the larger swelling of the SH fuel. When the irradiation temperature is sufficiently low to avoid the vaporization of MgO, the radiation damage of spinel-based fuel may be reduced to this level throughout the fuel pellet.

There was no migration of the U-YSZ particle (or grain) for corundum-based fuels (CD, CH). It is known that the neutron resistance of corundum is inferior to that of spinel, and corundum becomes amorphous by fission damage. The amorphization causes a large volume swelling in low temperature region of the fuel [10]. In this work, the swelling of the fuel pellet was small, and no amorphization was observed by X ray diffraction pattern. It is considered that the damaged crystal structure recrystallized, because the irradiation temperature was high enough to anneal the corundum amorphous. The central holes in the fuel pellet were not observed on the CD and CH fuel pellets. Because the volume change by the irradiation of the corundum was smaller than that of the spinel in which MgO vaporization occurred, the amount of generated void in the corundum-based fuel was less than that in the spinel-based fuel.



(a) (b)

*Figure 5. The SEM images at interfacial region of U-YSZ particle (or grain) and spinel for (a) SD and (b) SH fuels*

## 4-CONCLUSION

Five kinds of ROX fuels were irradiated and post-irradiation examinations were carried out.

No significant swelling of fuel pellets was observed except the SH fuel.

FP gas release for all kinds of fuels were lower than the previous experiment using disk shaped fuels of 1 mm thickness. FP gas release rates of the particle-dispersed type fuels were higher than homogeneously-blended type fuels. It is supposed that the crack generation caused the high gas release rate for particle dispersed type fuels. So, it is necessary for particle dispersed type fuels to fabricate the fuels which can relax the thermal stress generated by difference of thermal expansion coefficients between the U-YSZ particle and the matrix. The Z fuel showed low FP gas release rate. The irradiation temperature of Z fuel was lower than that of other fuels. It is considered the lower irradiation temperature is an important factor for the lower FP gas release than other fuels.

The microstructures of fuels were analyzed by ceramography and EPMA. The aspect of the Z fuel pellet was analogous to LWR $UO_2$ fuels, and showed uniform structure throughout the pellet surface. It is confirmed that the decomposition of spinel and vaporization of MgO occurred by high temperature irradiation, for the spinel-based fuels. It is expected that the large amount of gas release and the vaporization of MgO are avoided by lowering the irradiation temperature less than 1700K. For corundum-based fuels, in this irradiation condition of sufficiently high irradiation temperature to anneal the corundum amorphous, significant appearance changes such as swelling and heterogeneity of fuel structures were not observed.

It is also confirmed that the regions suffering the irradiation damage of the particle dispersed type fuels were less than those of the homogeneously-blended type fuels.

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