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In-pile irradiation of plutonium rock-like oxide fuels with yttria stabilized zirconia or thoria, spinel and corundum

T. Yamashita [a,*], N. Nitani [a], H. Kanazawa [a], M. Magara [a], T. Ohmichi [b], H. Takano [a], T. Muromura [a]

[a] *Advanced Fuel Laboratory, Department of Nuclear Energy System, Japan Atomic Energy Research Institute, Tokai-mura, Ibaraki 319-1195, Japan*

[b] *Research Organization for Information Science and Technology, Tokai, Ibaraki 319-1195, Japan*

Abstract

In-pile irradiation and subsequent post-irradiation examinations have been performed for plutonium rock-like oxide (ROX) fuels with the ternary component system of yttria stabilized zirconia (YSZ) or thoria (ThO_2), spinel and corundum, to investigate the behavior of the ROX fuels under irradiation. Maximum neutron fluence was estimated to be $\sim 8.2 \times 10^{24}$ m^{-2} ($E < 0.6$ eV) and burnup was measured to be 21–28% of the initial plutonium atoms by destructive chemical analysis. Phase equilibria, element distribution over the phases and microstructure changes in the irradiated fuels were studied using X-ray diffraction, metallography, scanning electron microscopy and electron probe microanalysis. Relatively large swelling of the present fuels is discussed in connection with phase equilibria and microstructure changes. The measured isotopic compositions of Pu, Am and Cm in the irradiated fuels are also given. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

For the utilization of stock-piled plutonium, we have proposed plutonium rock-like oxide (ROX) fuels and their once-through burning in LWRs followed by direct disposal of spent fuels after cooling [1,2]. The ROX fuel is a multi-phase mixture of mineral-like (or rock-like) compounds such as stabilized zirconia, corundum, spinel and so on. Plutonium is incorporated in one of these compounds. Direct disposal of spent ROX fuels requires that the spent fuels must have high chemical, physical and geological stabilities to reduce environmental hazards. Effective and almost complete burning of fissile plutonium is also essential for proliferation resistance, environmental safety and economic points of view.

From a survey of physico–chemical properties of minerals and ceramics which have low neutron capture cross sections, we selected two systems of yttria stabilized zirconia (YSZ)–corundum (Al_2O_3)–spinel ($MgAl_2O_4$) and thoria (ThO_2)–corundum (Al_2O_3)–spinel ($MgAl_2O_4$) as candidates of the ROX fuel matrices. Plutonium added was assumed to incorporate with YSZ or ThO_2 by making solid solutions. Phase equilibria and element distributions over phases in the simulated spent fuels of these systems were examined by X-ray diffraction analysis (XRD), scanning electron microscopy (SEM) and electron probe microanalysis (EPMA). Uranium and stable isotopes of fission product (FP) elements were used as stand-ins. These studies have been made systematically in the two-phase mixture of YSZ (or ThO_2)–Al_2O_3 [1,3], the two-phase mixture of YSZ (or ThO_2)–$MgAl_2O_4$ [4], and the three-phase mixture of YSZ (or ThO_2)–$MgAl_2O_4$–Al_2O_3 [5] systems. From these studies, it was found that the simulated spent fuels consisted of five-phase mixture of a fluorite-type phase, spinel, corundum, hibonite and alloy. Plutonium and minor actinides were incorporated in fluorite phases (YSZ or ThO_2) by making solid solutions. Noble metals were precipitated as alloys with molybdenum. With the presence of excess Al_2O_3 in the fuel matrix, alkaline earth elements (Mg, Sr and Ba) and some rare earth elements formed a hibonite-type phase ($M^{2+}Al_{12}O_{19}$ and/or $M^{3+}M^{2+}Al_{11}O_{19}$).

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[*] Corresponding author. Tel.: +81-29 282 6951; fax: +81-29 282 5935; e-mail: yamasita@analchem.tokai.jaeri.go.jp

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Little is known, however, about the in-pile irradiation behavior of inert matrices [6,7]. No irradiation data are available for the composite ROX fuel. In order to obtain information on the in-pile irradiation behavior of Pu-ROX fuels, we irradiated the fuels in the Japan Research Reactor No. 3 (JRR-3) and performed post-irradiation examinations. In the present paper, we will focus on the phase equilibria, element distributions and microstructural changes of the irradiated fuels. The other phenomena observed in the present irradiation will be clarified after the on-going irradiation projects for ROX fuels. Because high grade plutonium (^{239}Pu content is more than 94%) was used for the ROX fuel, burnup and isotopic compositions of plutonium after the irradiation may supply valuable information on the nuclear database and development of burnup calculation. Results of the destructive chemical analysis are also briefly described.

2. Experimental

2.1. Fuel fabrication

Two types of ROX fuels were prepared: one is Zr-type and the other is Th-type. The chemical compositions of the ROX fuels are shown in Table 1.

An inert matrix material of Zr-type was prepared as follows. Reagent grade of $ZrO(NO_3)_2 \cdot 2H_2O$, Y_2O_3, Gd_2O_3, $Al(NO_3)_3 \cdot 9H_2O$ and MgO were weighed and dissolved in a diluted nitrate solution. After drying up the solution, the residue was calcined at about 1000 K in air for 3 h to decompose the nitrate mixture. The obtained oxide mixture was then heated at 1670 K for 10 h in air. A Th-type inert matrix material was also prepared in a similar way.

Weighed amounts of the inert matrix material and PuO_2 powders were mixed thoroughly in an agate mortar and pressed into pellets. These pellets were heated at 1670 K in a vacuum of 0.1 Pa and pulverized again in an agate mortar. After several repetitions of the heating and pulverizing process, powders were pressed into disks and sintered at 1670 K for 5 h in Ar/8% H_2 gas stream. The average size of sintered disks was 3.25 mm in diameter and 1 mm in thickness.

Table 1
Chemical compositions (in mol%) of ROX fuels

Materials	Zr-type	Th-type
PuO_2	10	10
YSZ [a]	15	–
ThO_2	–	15
Al_2O_3	65	65
MgO	10	10

[a] YSZ: 79.86 mol% ZrO_2 + 19.78 mol% $YO_{1.5}$ + 0.36 mol% $GdO_{1.5}$.

2.2. Characterization

Both Zr- and Th-type fuel disks were characterized before irradiation using XRD, SEM and EPMA. Phases identified and their lattice parameters are summarized in Table 2. Both Zr and Th-type fuels consist of four-phase mixture of fluorite, corundum, spinel and hibonite phases. Lattice parameters of the fluorite phases are different from those of the pure phases, 0.5150 nm for $(Zr,Y,Gd)O_2$ [5] and 0.55972 nm for ThO_2 [8], due to the substitution of Pu for Zr or Th in the fluorite lattice. Lattice parameters of the fluorite phases are expected to be 0.5251 and 0.5520 nm for Zr- and Th-type, respectively, under assumptions that all plutonium is dissolved in the fluorite phases and that the fluorite solid solutions are ideal. Observed lattice parameters of the fluorite phases are different from estimated ones, which indicates that a part of plutonium is dissolved in the fluorite phase and the rest may form the other compounds. EPMA of these fuels clarified the point. EPMA results showed that plutonium existed with zirconium or thorium, and that some plutonium also existed with aluminum, which suggested the formation of Pu-aluminate (i.e. Pu–hibonite). From the lattice parameters of fluorite phases, fractions of plutonium in the fluorite phases were deduced to be 30% and 75% of initially added plutonium for Zr-type and Th-type fuels, respectively. The lattice parameters of the corundum phase are comparable to the literature values of $a = 0.47628$ and $c = 1.30032$ nm [9]. Lattice parameter of the spinel phase was not determined because of weak diffraction peaks. Lattice parameters of the hibonite phase, which is identified in this study, are given in Table 2.

The average grain size and porosity were deduced from SEM images. The obtained results are shown in Table 2. Average grain size of Zr-type fuel is slightly larger than that of Th-type. Small grains of each phase were distributed homogeneously in the pellet and no

Table 2
Characteristics of the fresh fuels

Phase	Zr-type	Th-type
	Lattice parameter (nm)	Lattice parameter (nm)
Fluorite	$a = 0.5180$	$a = 0.5537$
Corundum	$a = 0.4750$	$a = 0.4760$
	$c = 1.280$	$c = 1.280$
Hibonite	$a = 0.5586$	$a = 0.5588$
	$c = 2.192$	$c = 2.191$
Spinel	tr.	tr.
Average grain size (μm)	8	5
Estimated porosity (%)	18.4	17.4

large agglomerates of a special phase were observed. Small pores were also distributed homogeneously. Porosity was evaluated by graphic treatment of SEM images. A relatively large porosity, 18.4% for Zr-type and 17.4% for Th-type, might be attributed to several sinterings to obtain homogeneous fluorite solid solutions and to insufficient powder milling.

2.3. Irradiation

Five fuel disks separated by Nb/1 wt% Zr alloy sheets were loaded in a Nb/1 wt% Zr alloy case with an inner diameter of 4 mm and an outer diameter of 6 mm, sealed in a platinum sleeve and finally encapsulated in a Nb/1 wt% Zr alloy cladding with an inner diameter of 6.8 mm and an outer diameter of 10 and 90 mm long. Both Pt-sleeves and Nb/1 wt% Zr claddings were filled with He gas.

Six fuel pins, three for Zr-type and three for Th-type, were irradiated in an outer core region of JRR-3 in Japan Atomic Energy Research Institute (JAERI) during four reactor cycles (97 full power days). The neutron fluence was monitored using Al-Co wire flux monitors. Temperature of each fuel pin was measured by a thermocouple positioned close to the cladding. Fuel No., neutron fluence and average irradiation temperature are summarized in Table 3.

2.4. Post-irradiation examinations

Post-irradiation examinations were performed at the Real Fuel Examination Facility in JAERI under the standard procedure using the following techniques: X-ray photography, XRD, gamma scanning, metallography and SEM&EPMA. Irradiated fuel disks were embedded in a sample holder with epoxy resin, polished with diamond pastes and subjected to XRD at room temperature. They were also used for metallography and SEM&EPMA.

Chemical analysis of irradiated fuels was made to determine the burnup of the fuels. Two samples from Zr-type fuels, Zr-6 and Zr-7, and one sample from Th-type fuels, Th-2, were subject to chemical analysis. The amount of samples was 16.7, 18.6 and 34.9 mg for Zr-6, Zr-7 and Th-2, respectively. Prior to the chemical analysis, they were dissolved with aqua regia (a mixed solution of conc. HNO_3 and HCl with volume ratio of 1:3) with a few drops of HF at 420 K using a pressurized vessel with a Teflon inner crucible. Chemical separations were carried out using the standard procedure and isotopic ratios of neodymium, uranium and plutonium were determined by mass spectrometry. Enriched ^{150}Nd, ^{242}Pu and natural uranium were used as spikes to determine isotopic ratios by the standard isotopic dilution procedure. Fractions of americium and curium against plutonium were also determined by alpha spectrometry. Detailed procedures of the sample dissolution and chemical analysis are described elsewhere [10].

Table 3
Irradiation conditions

Fuel location	Bottom	Middle	Top
Fuel no.	Zr-5 Th-1	Zr-6 Th-2	Zr-7 Th-3
Neutron fluence (m^{-2})			
($E < 0.6$ eV)	$\sim 6.1 \times 10^{24}$	$\sim 8.2 \times 10^{24}$	$\sim 6.8 \times 10^{24}$
($E > 1$ MeV)	$\sim 2.5 \times 10^{24}$	$\sim 3.4 \times 10^{24}$	$\sim 2.8 \times 10^{24}$
Irradiation temperature (K)	1040 ± 50	1270 ± 10	980 ± 50

Irradiation period: 97 full power days in JRR-3.

3. Results

Results obtained for Zr-type fuels were mainly described here, because those for Th-type fuels were basically the same as those for Zr-types.

3.1. Gamma scanning test

The axial profiles of main FPs in the platinum capsule were determined by measuring radio-activities through a thin slit placed in front of a Ge(Li) detector. Solid FPs such as ^{106}Rh and ^{144}Ce were observed only at the fuel disk region. Most of ^{134}Cs and ^{137}Cs, which are known as semi-volatile FP, were observed at the fuel disk region and a part of them were also observed at the colder parts of the platinum capsule. No clear dependence was observed between irradiation temperature and the amount of Cs moved to colder regions, because the irradiation temperatures (980, 1040 and 1270 K) were higher than the boiling temperature of Cs (951 K) [11]. No radioactivity from FP was observed outside of the Pt sleeve.

3.2. Metallography and SEM observations

Few irradiated specimens kept their original circular disk shapes: some had large cracks and the others were broken into small pieces. The high linear heating rate of 40 kW/m, which was estimated by burnup calculation of the fuels, may have caused the fragmentation of the disks. They also showed apparently volume increases and porous surface appearance. Because of the large cracks, it was impossible to determine the precise sizes of the irradiated disks. Rough measurements showed that the diameter of the disk irradiated at 980 K was about 3.6 mm and that of the fresh fuel disks was about 3.25 mm; about 10% increase in diameter.

Fig. 1 shows SEM images of the fresh fuel, Zr-7 and Zr-6. These images were taken at the central part of the disks. In the fresh fuel, small grains of fluorite (gray), hibonite (dark gray) corundum/spinel (black) are

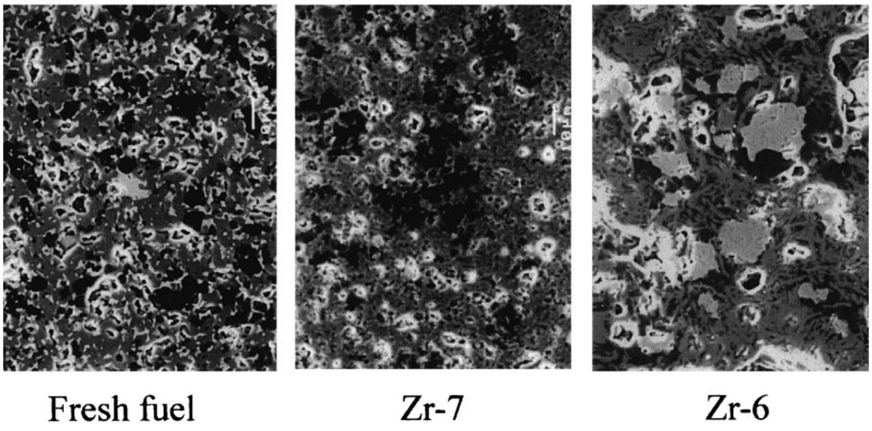

Fresh fuel Zr-7 Zr-6

Fig. 1. Microstructures of Zr-type fuels obtained by SEM. Left: fresh fuel; Middle: Zr-7, irradiated at 980 K; Right: Zr-6, irradiated at 1270 K.

distributed homogeneously. In the Zr-7 disk, some agglomerates of corundum are observed, and size and number of pores do not increase appreciably compared with the fresh fuel. On the other hand, large pores and grains of the fluorite phase are observed in the Zr-6 disk. Porosity of the Zr-6 disk is deduced to be 45.4% from the graphics treatment of the SEM image. Formation of hibonite phases in corundum phase is also clearly observed.

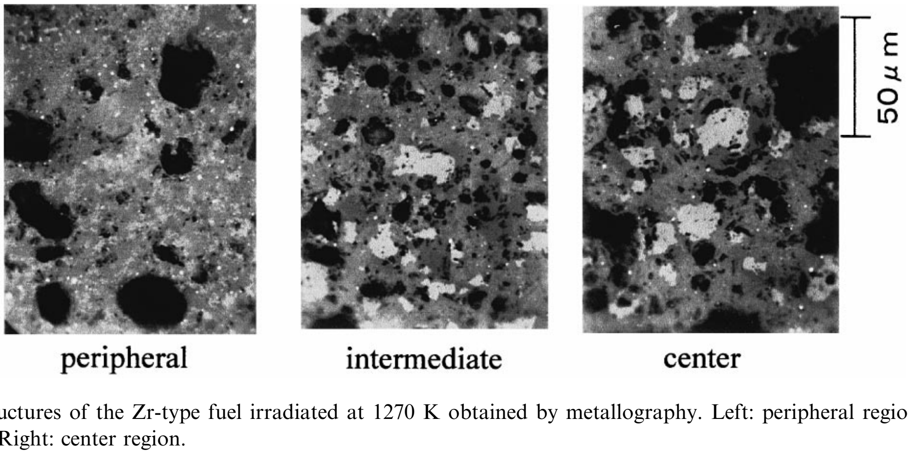
Fig. 2 shows microstructure changes of the Zr-6 disk. These are peripheral, intermediate and central parts of the disk. Alloy phases (white) can be seen as very fine precipitates. Such elements as ruthenium, palladium and molybdenum were observed in the precipitates by EMPA. At the peripheral region, no appreciable grain growth is observed but a large grain growth is clearly observed at the intermediate and central regions.

3.3. X-ray diffraction analysis

Phase relations and lattice parameters of phases in irradiated disks are summarized in Table 4. All irradiated fuels consist of five-phase mixture of the fluorite-type phase, hibonite, corundum, spinel and alloy, which is consistent with the results of the simulation experiments [1,3–5]. Although the alloy phase was not observed by XRD, small precipitates of alloy were found by SEM&EPMA.

The lattice parameter of the fluorite phase in Zr-6 was smaller than that of the phase in Zr-7, which indicated that the amount of plutonium in the fluorite phase of Zr-6 was smaller than that in the fluorite phase of Zr-7. EPMA results support this finding; much smaller intensity of plutonium in the fluorite phase of Zr-6 was observed than that in the fluorite phase of Zr-7.

A corundum phase was observed in the Zr-7 sample. In the Zr-6 sample, the corundum phase was faint, and instead, relative intensities of the hibonite phase increased and a spinel phase appeared. Lattice parameters of these corundum, spinel and hibonite phases were almost the same as those in the fresh fuel. It is well known that the corundum (Al_2O_3) phase suffers heavy irradiation damage from fission fragments and becomes



peripheral intermediate center

Fig. 2. Microstructures of the Zr-type fuel irradiated at 1270 K obtained by metallography. Left: peripheral region; Middle: intermediate region; Right: center region.

Table 4
Phase relations and distribution of plutonium in irradiated fuels

	Fluorite		Corundum		Spinel		Hibonite		Alloy	
	L.P.	Pu	L.P.	Pu	L.P.	Pu	L.P.	Pu	L.P.	Pu
Zr-7	$a = 0.5180$	++	$a = 0.475$ $c = 1.29$	–	tr.	–	$a = 0.5582$ c = 2.207	+++	ND	–
Zr-6	$a = 0.5153$	+	tr.	–	$a = 0.807$	–	$a = 0.5581$ $c = 2.202$	+++	ND	–
Th-3	$a = 0.5588$	–	$a = 0.474$ $c = 1.27$	–	tr.	–	$a = 0.5579$ c = 2.199	+++	ND	–
Th-2	$a = 0.5600$	–	tr.	–	tr.	–	$a = 0.5575$ $c = 2.198$	+++	ND	–

Lattice parameters (L.P.) are given in nm. Plutonium distributions are given in relative amounts: (+++) high; (++) medium; (+) low; (–) not observed.

amorphous [6]. The fact that the diffraction peaks of corundum were observed in the Zr-7 fuel, which were not so sharp, indicates that amorphization of the corundum phase might be recovered partially during irradiation due to high irradiation temperature.

3.4. Electron probe microanalysis

Element distributions over the phases in irradiated fuels were examined by EPMA. Relative intensities of plutonium are shown in Table 4. Plutonium was observed in the fluorite and hibonite phases and observed intensities of plutonium from the hibonite phase were higher than those from the fluorite phase. Some FP elements such as ruthenium, palladium and molybdenum were observed in fine alloy precipitates but alkaline earth and rare earth elements were not clearly detected probably due to low relative concentrations of these elements.

3.5. Chemical analysis

After separation of uranium, plutonium and neodymium by an anion exchange method using the HNO_3-methanol system, these eluted fractions were subjected to mass separation analyses. Table 5 shows the isotopic compositions of plutonium in fresh, Th-2, Zr-6 and Zr-7 fuels. The amount of ^{239}Pu decreases by irradiation and those of ^{240}Pu, ^{241}Pu and ^{242}Pu increase considerably.

Burnup ratio (B.U.) of irradiated fuels were calculated through

$$\text{B.U. } (\%) = \frac{\text{F}}{\text{P} + \text{F}} \times 100,$$

where F is the number of fission which is obtained by dividing the number of ^{148}Nd atoms by its fission yield (1.642115%) of ^{239}Pu by thermal neutrons [12], and P is the number of plutonium atoms in the irradiated fuels. Calculated B.U. are 27.95%, 27.90% and 20.75% of the initial plutonium atoms for Th-2, Zr-6 and Zr-7 fuels, respectively.

Relative amounts of ^{241}Am, ^{242}Cm and ^{244}Cm to ^{239}Pu were determined by alpha spectrometry. Since the isotopic ratio of ^{239}Pu was determined by the mass spectrometry, these values were easily calculated. Calculated atom ratios of ^{241}Am, ^{242}Cm and ^{244}Cm against initial plutonium in irradiated fuels are given in Table 5.

Table 5
Isotopic composition (%) of plutonium, ^{241}Am, ^{242}Cm and ^{244}Cm in fresh and irradiated fuels (atom ratios of ^{241}Am, ^{242}Cm and ^{244}Cm are given against initial plutonium in fresh fuels)

Fuel	^{238}Pu	^{239}Pu	^{240}Pu	^{241}Pu	^{242}Pu	^{241}Am	^{242}Cm	^{244}Cm
Fresh	0.008 (0.0003)	94.606 (0.0008)	5.289 (0.0005)	0.081 (0.0003)	0.016 (0.0004)	–	–	–
Th-2	0.022 (0.0006)	75.494 (0.002)	19.818 (0.002)	4.281 (0.0007)	0.385 (0.0007)	$3.226 \cdot 10^{-3}$	$3.124 \cdot 10^{-6}$	$4.839 \cdot 10^{-6}$
Zr-6	0.020 (0.0002)	75.491 (0.003)	20.073 (0.003)	4.046 (0.0008)	0.370 (0.0004)	$3.046 \cdot 10^{-3}$	$2.985 \cdot 10^{-6}$	$3.988 \cdot 10^{-6}$
Zr-7	0.016 (0.0005)	79.812 (0.002)	17.118 (0.002)	2.841 (0.001)	0.212 (0.0003)	$2.355 \cdot 10^{-3}$	$1.832 \cdot 10^{-6}$	$2.012 \cdot 10^{-6}$

Values in parentheses indicate errors in the measurements.

4. Discussion

4.1. Phase equilibria and elements distribution

Estimated volume fractions of the phases in Zr-type fuels are summarized in Table 6. These values are obtained by considering the results of XRD and EPMA as well as mass balances of the fuel and plutonium fission yields. In the estimations, the amount of plutonium in the fluorite phase was estimated from the lattice parameter of the fluorite phase at first. The rest of the plutonium and trivalent FPs such as rare earth elements were supposed to form the hibonite phase. Increases of the hibonite fraction in irradiated fuels are mainly due to additional hibonite formation by FPs, which results in the decrease of the corundum fraction. Based on the fact that the spinel phase was clearly observed in the Zr-6 fuel by XRD, a high value of the spinel volume fraction was given, though the reason why the spinel phase appeared distinctly in this fuel was unclear.

Although the fresh fuel consisted of the four-phase mixture of fluorite, corundum, spinel and hibonite phases, the formation of plutonium–hibonite was not expected. Any indication of the Pu–hibonite formation was not observed for either preliminary surveys of reactions between PuO_2 and Al_2O_3 in vacuum or simulation experiments. At the last step of the fuel preparation, fuel disks were sintered at 1670 K in 8% H_2/Ar atmosphere and some Pu^{4+} were considered to be reduced to Pu^{3+}. Presence of trivalent plutonium may be essential for the formation of the hibonite. A weak signal of magnesium was also observed from this phase by EPMA. Gasperin et al. [13] studied $LaM^{2+}Al_{11}O_{19}$ systems and pointed out that the $LaAl_{11}O_{18}$ type compounds were meta-stable and they could be stabilized by the introduction of divalent cations in the crystal lattice. They had the general formula $LnM^{2+}Al_{11}O_{19}$ where Ln = La to Gd, and M^{2+} = Mg, Mn, Fe, Co, Ni, Cu. On the analogy of rare earth hibonite compounds, the new Pu-hibonite may have a formula $PuMgAl_{11}O_{19}$.

By irradiation of the fuels, almost all plutonium moved from the fluorite phase to the hibonite phase, especially at high irradiation temperature, as shown in Table 4. This fact suggests that the oxygen potential around fuels was low enough to allow the hibonite formation. The fuel disks were inserted in a Nb/1 wt% Zr alloy case and the estimated oxygen potential around fuel disks during irradiation was well below −800 kJ mol^{-1} at 1273 K, which was enough to reduce Pu^{4+} to Pu^{3+} [14]. The reaction between PuO_2 and $MgAl_2O_4$ was examined separately at 1670 K in 8% H_2/Ar atmosphere. No indication was observed for the formation of the Pu-hibonite compound. The Pu-hibonite phase formation can, therefore, be avoided by eliminating excess Al_2O_3 in the fuel matrix as well as extremely low oxygen potentials during fuel fabrication and irradiation. Further studies are now underway to establish chemical and physical properties of the new Pu–hibonite compound.

Here it is worthwhile to summarize the effects of excess Al_2O_3. Although it was well recognized that Al_2O_3 was not stable against irradiation, much attention was paid to the ability of Al_2O_3 for the retention of semi-volatile alkali metals within fuel matrices by forming alkali aluminate compounds. According to the results of gamma scanning tests, however, some Cs moved out from the disks. This means that the initial intention to retain semi-volatile FPs in the matrices is not successful. Disadvantages are high swelling rate, Pu-hibonite formation under very low oxygen potential and lower melting temperature by forming ternary eutectic compounds (YSZ–$MgAl_2O_4$–Al_2O_3). Therefore, we have concluded that the addition of excess Al_2O_3 is not favorable for ROX fuel. So far, the best composition of ROX is considered to be a composite of fluorite and spinel phases.

Table 6
Estimated volume fractions (%) of the phases in the Zr-type fuels

	Fluorite	Corundum	Spinel	Hibonite	Alloy
Fresh fuel	14	26	5	55	0
Irradiated					
Zr-7	13	16	5	66	tr.
Zr-6	13	3	16	68	tr.

4.2. Microstructure changes

The irradiated fuels showed considerable swelling, more than 30% in volume increase. Such swelling was brought out by the combination of gas bubble formation, irradiation damage, phase change and so on. Swelling due to irradiation damage is considered not to be so large (about 5%), because the volume fractions of the corundum and spinel phases are small (see Table 6) and because some damage annealing may occur due to high irradiation temperatures. Swelling due to phase change, which is a transformation from corundum to hibonite phases, was estimated from crystal volumes and molar fractions of phases under constraint of mass balance. Calculated results show that volume increases against fresh fuel are 3% and 9% for the Zr-7 and Zr-6 fuels, respectively. Therefore, most of the large volume increase observed for the present irradiated fuel may be caused from gas bubble formations. Exact mechanism for the formation of large gas bubbles in the fuels is not clarified yet, repetition of damage annealing processes and phase transformation from corundum to hibonite phase may enhance gas bubble movement in this fuel.

Because of the lack of information on the irradiation behavior of ROX fuels, some results obtained in this irradiation are not clarified yet. We have two additional plans for ROX fuels' irradiation. Results of post-irradiation examination of these ROX fuels will serve useful information to elucidate the irradiation behavior of ROX fuels.

5. Conclusions

In-pile irradiation and subsequent post-irradiation examinations were performed for plutonium ROX fuels with the ternary component system of the fluorite-type phase, spinel and corundum. Phase equilibria, element distribution and microstructure changes of irradiated fuels were studied using XRD, metallography, SEM and EPMA.

Phase equilibria and distributions of most of the elements were consistent with the results obtained using simulated spent fuel studies except for plutonium. A new hibonite-like compound containing Pu, Mg and Al was found to be formed under very low oxygen potentials. Existence of Pu^{3+} and free Al_2O_3 was essential for the formation of this compound the possible formula of which is $PuMgAl_{11}O_{19}$.

Most of the large swelling of the present fuels may be caused by gas bubble formation. The influences of irradiation damage and phase transformation from corundum to hibonite on the fuel volume increase were estimated to be small (about 5% each). However, repeated damage annealing processes and phase transformation from corundum to hibonite phase may enhance gas bubble movement in this fuel.

The existence of excess Al_2O_3 was found to cause unfavorable effects on ROX fuel, such as large swelling, hibonite formation and lower melting point. So far, the best composition of ROX is considered to be a composite of fluorite and spinel phases.

Measured isotopic compositions of Pu, Am and Cm in the irradiated fuels give valuable information for nuclear database and burnup calculations.

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