

Phase relations and distribution of fission products in the Pu rock-like fuels with fluorite, spinel and corundum phases

Noriko Nitani ^{a,*}, Hiroto Yokoi ^b, Toshiyuki Yamashita ^a, Toshihiko Ohmichi ^a,
Tsuneo Matsui ^b, Tadasumi Muromura ^a

^a Japan Atomic Energy Research Institute, Tokai-mura, Ibaraki 319-11, Japan

^b Nagoya University, Department of Quantum Engineering, Furo-cho, Chikusa-ku, Nagoya 464-01, Japan

Abstract

Phase relations of fuel materials and simulated spent fuels in two $\text{ThO}_2\text{-MgAl}_2\text{O}_4\text{-Al}_2\text{O}_3$ and $\text{ZrO}_2(\text{Y, Gd})\text{-MgAl}_2\text{O}_4\text{-Al}_2\text{O}_3$ systems have been studied to confirm the formation of geologically stable fuels which consist of rock-like phases. The distributions of Pu and fission products (FPs) in fuel materials and simulated spent fuels were investigated by X-ray diffraction and electron probe micro-analysis. In both systems, the fuel materials consisted of three phases of fluorite, spinel and corundum, and Pu was solidified into the fluorite-type phase by making solid solutions. The simulated spent fuels consisted of five phases of fluorite, spinel, corundum, hibonite ($\text{MO} \cdot 6\text{Al}_2\text{O}_3$ and/or $\text{M}_2\text{O}_3 \cdot 11\text{Al}_2\text{O}_3$) and alloy. The lanthanide elements of Nd and Ce in FPs distributed into hibonite and fluorite phases. Alkaline earth elements were mainly solidified into the hibonite phase. © 1997 Elsevier Science B.V.

1. Introduction

In several years, the problem of disposing of excess plutonium (Pu) has become a critical issue. Inert matrix fuel free from UO_2 is one of feasible option for burning plutonium (Pu) and trans-uranium elements in light water reactors or fast reactors [1–4]. Rock-like fuels, which had multi-phase structures and were composed of the inert matrix materials and Pu, would be most effective one for annihilating excess Pu because of little reproduction of fissile elements as well as their high chemical stabilities. The fission products (FPs) of Pu are anticipated to be solidified into the mineral-like phases in the fuel, which are expected to be geologically stable for a long time. The spent fuels after almost complete burning of Pu could be disposed without further processing [1,5–7].

The phase relations of $\text{ThO}_2\text{-MgAl}_2\text{O}_4\text{-Al}_2\text{O}_3$ and $\text{ZrO}_2(\text{Y, Gd})\text{-MgAl}_2\text{O}_4\text{-Al}_2\text{O}_3$ systems have been investigated by the present authors to confirm the formation of chemically and geologically stable phases. We have pro-

posed [1,5] three candidates of inert matrix materials in the systems shown in Fig. 1: (1) two-phase mixture of fluorite and corundum, (2) three-phase mixture of fluorite, spinel and corundum and (3) two-phase mixture of fluorite and spinel. We have clarified the phase relations of two-phase

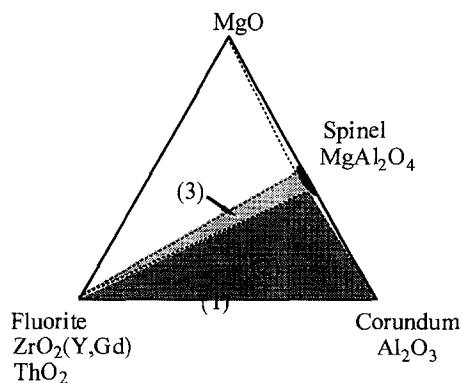


Fig. 1. Phase diagram of the quasi-three-component system of $\text{ZrO}_2(\text{Y, Gd})$ (or ThO_2)- Al_2O_3 - MgO at around 1400°C . (1) two-phase region of fluorite + corundum, (2) three-phase region of fluorite + spinel + corundum, (3) two-phase region of fluorite + spinel.

* Corresponding author. Tel.: +81-29 282 5495; fax +81-29 282 6097; e-mail: nitani@analchem.tokai.jaeri.go.jp.

Table 1
Composition and phases in the fluorite-spinel-corundum system

System	(A) Matrix compound		(B) Fuel material		(C) Simulated spent fuel	
	composition (mol%)	phase lattice const. (nm)	composition (mol%)	phase lattice const. (nm)	composition (mol%)	phase lattice const. (nm)
ThO ₂ - MgAl ₂ O ₄ - Al ₂ O ₃	ThO ₂ = 21.1, Al ₂ O ₃ = 68.4, MgO = 10.5	(1) fluorite <i>a</i> = 0.5600(1), (2) corundum <i>a</i> = 0.4764(1), <i>c</i> = 1.3004(2) (3) spinel <i>a</i> = 0.8039(2)	PuO ₂ = 10.0, ThO ₂ = 15.0, Al ₂ O ₃ = 65.0, MgO = 10.0	(1) fluorite <i>a</i> = 0.5537(1), (2) corundum <i>a</i> = 0.476(1), <i>c</i> = 1.28(1), (3) spinel <i>a</i> = 8.04(3)	FPs = 9.5, ThO ₂ = 19.0, Al ₂ O ₃ = 61.4, MgO = 9.4, UO ₂ = 0.7	(1) fluorite <i>a</i> = 0.5580(1), (2) corundum <i>a</i> = 0.476(1), <i>c</i> = 1.2999(2), (3) spinel <i>a</i> = 0.8032(3), (4) hibonite <i>a</i> = 0.556(1), <i>c</i> = 2.18(1), (5) alloy
ZrO ₂ (Y, Gd)- MgAl ₂ O ₄ - Al ₂ O ₃	ZrO ₂ (Y, Gd) = 21.1, Al ₂ O ₃ = 68.4, MgO = 10.5	(1) fluorite <i>a</i> = 0.5151(1); (2) corundum <i>a</i> = 0.4761(1), <i>c</i> = 1.2997(2), (3) spinel <i>a</i> = 0.8036(5)	PuO ₂ = 10.0, ZrO ₂ (Y, Gd) = 15.0, Al ₂ O ₃ = 65.0, MgO = 10.0	(1) fluorite <i>a</i> = 0.5180(1), (2) corundum <i>a</i> = 0.475(1), <i>c</i> = 1.28(1), (3) spinel <i>a</i> = 8.03(3)	FPs = 7.5, ZrO ₂ (Y, Gd) = 19.5, Al ₂ O ₃ = 63.3, MgO = 9.7	(1) fluorite <i>a</i> = 0.5150(1), (2) corundum <i>a</i> = 0.476(1), <i>c</i> = 1.2999(2), (3) spinel <i>a</i> = 0.8022(3), (4) hibonite <i>a</i> = 0.5585(1), <i>c</i> = 2.196(1), (5) alloy

mixture of fluorite and corundum [1] and that of fluorite and spinel [8].

In the present work, the phase relations were studied by X-ray diffraction (XRD) for three-phase mixture of fluorite, spinel and corundum (the region (2) in Fig. 1) containing Pu (fuel materials) or FPs (simulated spent fuels). The distribution of FPs was also examined by electron probe micro-analysis (EPMA) for the simulated spent fuels. The observed distribution of FP elements was discussed thermodynamically.

2. Experimental

2.1. Preparation of samples

Two kind of solutions containing the constituent elements for matrix compounds were prepared: one is ThO₂, MgO and Al₂O₃ (ThO₂-type) and another is ZrO₂ (Y, Gd), MgO and Al₂O₃ (ZrO₂-type), where the ZrO₂ (Y, Gd) is composed of 88.8 mol% ZrO₂, 11.0 mol% Y₂O₃ and 0.2 mol% Gd₂O₃. The chemical composition is listed in the left halves of column (A) of Table 1. After dried up the solutions, the residues were calcined at 800°C and sintered at 1400°C in air.

Fuel materials were obtained by heating mixtures of PuO₂ and matrix compound powders at 1400°C under vacuum of 0.1 Pa. The chemical composition is listed in the left halves of column (B) of Table 1; 10 mol% PuO₂ was added to matrix compounds in an attempt to examine the solid solubility of PuO₂ in the fluorite phase.

The solutions of simulated spent fuels were prepared by mixing those of matrix compounds and FPs. The chemical compositions of simulated spent fuels and FPs are listed in the left halves of column (C) of Table 1 and in Table 2, respectively. Addition of UO₂ and a slight increase in the amount of FPs in ThO₂-type system compared to that in ZrO₂-type system are made by taking into account of new production of ²³³U from ²³²Th during irradiation. After dried up the mixed solutions, the residues were calcined at 800°C and sintered at 1400°C in 8%H₂ + 92%He. The

Table 2

Composition of simulated FPs (Initial ²³⁹Pu content = 94%, ORIGEN-2, LWR, 1400 days)

Element	Atomic %	Stand-in role
Zr	10.3	-
Ba	6.5	Sr
Ce	15.5	Pr, Np, Pu
Nd	19.3	La, Pm, Sm, Eu, Y, Gd, Am, Cm
Mo	15.5	Tc
Ru	11.6	-
Rh	1.4	-
Pd	11.8	-

details of sample preparation for simulated spent fuel was described in the previous paper [8].

2.2. Measurement

A part of the products thus obtained were crushed into powder and subjected to XRD at room temperature using $\text{CuK}\alpha$ radiation. The phases were identified by means of the powder diffraction files compiled by JCPDS [9]. The analysis by EPMA was performed to determine the distribution of elements in the simulated spent fuels.

3. Results and discussion

3.1. Matrix compound

The results obtained by XRD are compiled in Table 1. The observed phases and their lattice parameters in the matrix compounds of ThO_2 -type and ZrO_2 -type systems are shown in the right halves of column (A). In both systems, the matrix compound consists of three phases of fluorite, spinel and corundum. The ZrO_2 (Y, Gd) phase is stabilized and has the fluorite structure with a lattice parameter of 0.5149 nm.

3.2. Fuel materials

The results of XRD are shown in the right halves of column (B) of Table 1. Three phases of fluorite, spinel and corundum are formed in the fuel materials, similarly to the matrix compounds. As can be seen from the table, the lattice parameters of the fluorite phase in fuel materials change noticeably by the addition of 10 mol% PuO_2 , indicating that PuO_2 mainly dissolves into the fluorite phase and that the solubility of Pu in corundum and spinel phases is small. Additionally, a few weak peaks from unidentified phase were observed in XRD patterns of fuel materials, which suggested the formation of a new phase by the reaction between lower valent Pu and matrix compounds under low oxygen potentials at high temperatures.



Fig. 2. Typical SEM image of the simulated spent fuel of ZrO_2 (Y, Gd)– MgAl_2O_4 – Al_2O_3 system. (1) fluorite, (2) corundum, (3) spinel, (4) hibonite, (5) alloys.

3.3. Simulated spent fuels

The obtained phases and their lattice parameters are shown in the right halves of column (C) of Table 1. In the simulated spent fuels, new phases of hibonite and alloys were formed in addition to the three phases observed in the matrix compounds and fuel materials.

Typical SEM image of the ZrO_2 -type simulated spent fuel is shown in Fig. 2. Several subregions are distinguished by the difference in shapes and brightness. The results of EPMA examination were as follows. The bright phase pointed by the arrow (1) in Fig. 2 was found to be the fluorite phase and to contain some amounts of lanthanides and actinides. The corundum phase is shown by the arrow (2). The dark area pointed by the arrow (3) is the spinel phase. The plate-like region pointed by the arrow (4) was found to be the hibonite phase which was newly formed in the simulated spent fuel by the reaction between Al_2O_3 and oxides such as Ce_2O_3 , Nd_2O_3 and BaO . The most bright region pointed by the arrow (5) is the alloy consisting of Ru based alloy and Pd based alloy.

Heterogeneous distribution of Ba and the lanthanides in

Table 3
Distribution of actinides and FPs in spent fuels

Atoms	Phase				
	fluorite ($\text{ZrO}_2(\text{Y,Gd})$ (ThO_2))	spinel (MgAl_2O_4)	corundum (Al_2O_3)	hibonite ($\text{MO} \cdot 6\text{Al}_2\text{O}_3$) ($\text{M}_2\text{O}_3 \cdot 11\text{Al}_2\text{O}_3$)	alloys (Ru, Pd)
Actinide	⊙				
Lanthanide	○			⊙	
Alkaline-earth		○		⊙	
Mo, Tc					⊙
Platinum group					⊙

⊙ main distribution, ○ secondary distribution.

the hibonite phase was observed by EPMA. This suggests that two kinds of hibonite phases were formed, i.e., Ba-rich hibonite and (Ce, Nd)-rich one. A large difference in the lattice parameters between $\text{BaO} \cdot 6\text{Al}_2\text{O}_3$ ($a = 0.561$, $c = 2.29$ nm) and $\text{Ce}_2\text{O}_3 \cdot 11\text{Al}_2\text{O}_3$ ($a = 0.556$, $c = 2.20$ nm) was reported [9]. The lattice parameter of the hibonite phase obtained in the present study was close to those of $\text{Ce}_2\text{O}_3 \cdot 11\text{Al}_2\text{O}_3$. X-ray diffraction peaks from the Ba-rich hibonite phase were not clearly observed, possibly, due to less amount of the Ba-rich hibonite phase than that of the (Ce, Nd)-rich one as was expected from Table 2.

Similar results to the ZrO_2 -type simulated spent fuel were also obtained for ThO_2 -type.

The phase equilibria and distributions of actinides and FPs in the simulated spent fuels are summarized in Table 3. Actinides are mainly precipitated in the fluorite phase. Most of lanthanides and alkaline earth elements are consumed to form hibonite phases. Molybdenum, technetium and platinum group elements form alloys. It has been well known that all of these phases observed in the simulated spent fuels are geologically stable in igneous rocks for several million of years. [10,11]

3.4. Evaluation of phase equilibria in simulated spent fuels

Formation of possible compounds in the ZrO_2 -type simulated spent fuel was evaluated using a phase equilibrium calculation code [12]. We mainly focused on the precipitation of Sr as a stand-in of alkaline-earth in FPs.

On the precipitation of new phases in the simulated spent fuel, such compounds were taken into account as ZrO_2 (Y, Gd), SrZrO_3 , MgAl_2O_4 , SrAl_2O_4 , $\text{SrO} \cdot 6\text{Al}_2\text{O}_3$, Al_2O_3 , MgO , SrO and O_2 . Most of their thermodynamic data were obtained from the literature [13]. The free energy of formation of hibonite $\text{SrO} \cdot 6\text{Al}_2\text{O}_3$ was reported by Akolis et al. [14]. The values of SrZrO_3 and SrAl_2O_4 were estimated using the empirical law applicable to complex compounds [15].

The calculated results at 1200°C under low oxygen pressures showed that Sr first dissolved into the spinel phase up to solubility limit and then excess amount of Sr precipitated as hibonite $\text{SrO} \cdot 6\text{Al}_2\text{O}_3$. It was also found that the formation of perovskite SrZrO_3 was not possible in this system. These findings are in good accordance with the experimental results.

4. Conclusion

From the study on the phase relations and distribution of Pu and FPs in Pu rock-like fuels of fluorite-spinel-corundum phases, the following conclusions are obtained.

(1) Plutonium is solidified into the fluorite phase by making solid solutions.

(2) In the simulated spent fuels, the lanthanides in FPs distribute into hibonite and fluorite phases, and the alkaline earth elements mainly distribute into the hibonite phase. Noble metals form the metal alloy with Mo. The geological stability of all phases formed in the simulated spent fuels is well known.

(3) From the thermodynamic evaluation of phase equilibria, the formation of the hibonite phase was confirmed in the simulated spent fuel.

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