

Microstructural Properties of the Insoluble Residue in a Simulated Spent Fuel

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Abstract

Chemical composition of the insoluble residue in a simulated spent PWR fuel(SIMFUEL) were studied. SIMFUELS were prepared by adding calculated amount of FP(fission product) elements with a burnup of 3.6% FIMA(fission per initial metal atom) to uranium in nitrate solution, evaporating the mixed solution to dryness, calcining at 900 °C in a stream of 4% H₂ + 96% He, and heating the pellet at 1400 °C under high and low oxygen potentials. Insoluble residue was obtained from the dissolution of the SIMFUEL with HNO₃(1:1). The chemical composition of the SIMFUELS and the insoluble residues was determined by EPMA(electron probe microanalysis), XPS(X-ray photoelectron spectroscopy) and by XRD (X-ray diffraction) measurements. All of the insoluble residues suspended and precipitated were composed mainly of Mo, Ru with a small amount of Zr, Rh, Pd and Cd. The amount of insoluble residue(<1 wt.%) and a Mo/Ru ratio decreased with increasing oxygen potential. Formation of the zirconium molybdate precipitate, ZrMo₂O₇(OH)₂(H₂O)₂, was observed in the residues. The possible role of Mo on the phase formation was discussed in regard to oxygen potential.

Key words: simulated fuel, insoluble residue, metallic phase

1. Introduction

The knowledge of the chemical state of steady-state operated PWR fuel is of great importance for the characterization of the fuel and the fission products as well as for the understanding of the cladding behaviour during the irradiation process. It is well known that insoluble materials remain unchanged during dissolution of spent nuclear fuel in nitric acid for post irradiation examination. The insolubles consist of metallic phases formed in the fuel during irradiation, reprecipitates from the

spent fuel solution, crud(radioactive corrosion products) adhering on the surface of fuel pin, and fine chips of cladding material formed during chopping of the fuel pins, etc[1].

Adachi et al.[2,3] have observed the formation of the zirconium molybdate precipitate, ZrMo₂O₇(OH)₂(H₂O)₂(zirconium dimolybdenum heptoxide dihydroxide dihydrate), in residues from the dissolution of fuel with a high burnup and a high oxygen potential. It has been shown that the amount and composition of the metallic particles in the dissolver residue are mainly dependent on

the fuel irradiation history, whereas the amount and composition of the oxidic precipitates are mainly influenced by the dissolution parameters, especially the molarity of the nitric acid.

Post irradiation examinations on the UO_2 with burnups of 3~5% FIMA revealed that most of the solid fission products are mainly incorporated into three phases : matrix fluorite, perovskite and metallic phases. In the matrix fluorite phase, the actinide and rare earth elements are incorporated as solid solutions. A part of Sr, Ba and Zr compounds is also soluble in this phase. The majority of BaO, however, appears to precipitate with SrO as the perovskite ($Ba,SrZrO_3$), in which minor amount of Cs, rare earth elements, U and Pu would be soluble[4,5]. Formation of the metallic phases seems to be considerably complex. The metallic phases produced in the fuel are a mixture of two or more phases, which mainly

consist of Mo, Tc, Ru, Pd and Rh. The amounts of Mo and Tc in the phases largely depend upon oxygen potential in the fuels[6-8].

To replicate the composition, chemical state and many of the microstructural features of used nuclear fuel, it is important to know how the amount of residue and its chemical composition are related to such parameters as burnup, oxygen potential and temperature during irradiation[9].

Muromura et al.[10] have prepared oxide and metallic phases by the reaction between UO_2 and simulated fission products of 5 to 30% FIMA in the temperature range 1000-2000 °C under various oxygen potentials. By X-ray diffraction, a hexagonal(ϵ -phase) and a cubic(α -phase) phases were identified in the simulated fuels before dissolution with nitric acid. After dissolution the α -phase was not observed in the residue, whereas the ϵ -phase still remained. However, a tetragonal

Table 1. Compositions of Simulated Spent Fuel

Element	Calculated(mg/5g-U)	Wt. %	Quantity added	
U	4794.125	95.884	UO_2	5438.67 mg
Ce	69.405	1.388	10000 ppm	6.941 mL
Nd	35.685	0.714	10000 ppm	3.569 mL
Cs	13.715	0.274	10000 ppm	1.372 mL
Rb	1.815	0.036	1000 ppm	1.815 mL
Ba	14.575	0.292	10000 ppm	1.458 mL
Sr	4.235	0.085	1000 ppm	4.235 mL
Zr	18.730	0.375	10000 ppm	1.873 mL
Mo	21.820	0.436	10000 ppm	2.182 mL
Ru	11.855	0.237	10000 ppm	1.186 mL
Rh	2.450	0.049	1000 ppm	2.450 mL
Pd	7.475	0.150	500 ppm	14.950 mL
Ag	0.415	0.008	1000 ppm	0.415 mL
Cd	0.605	0.012	1000 ppm	0.605 mL
Sn	0.485	0.010	1000 ppm	0.485 mL
Te	2.565	0.051	1000 ppm	2.565 mL
Total	5000.005	100.001		

Calculated : from ORIGEN2

Ce : Ce + Pr + Pu + Np + Am + Cm

Nd : Nd + La + Sm + Y + Eu + Gd + Pm

Mo : Mo + Tc

phase(δ -phase) was identified only in the insoluble residue derived from the fuel under the atmosphere of approximately -300 kJ/mol O_2 .

In this study, the SIMFUELS have been prepared by the reaction between UO_2 and simulated fission products corresponding to PWR fuel with a burnup of 3.6% FIMA(35000 MWD/MTU) at 1400°C under high and low oxygen potentials. These SIMFUELS were dissolved in nitric acid solution, and the elemental composition and chemical properties of the insoluble residue were examined by several surface analysis techniques of XRD, EPMA, XPS and SEM(scanning electron microscopy), and by the chemical analyses of dissolved solution.

2. Experimental

2.1. Composition of SIMFUEL

The elemental compositions of the fuel for 3.6%

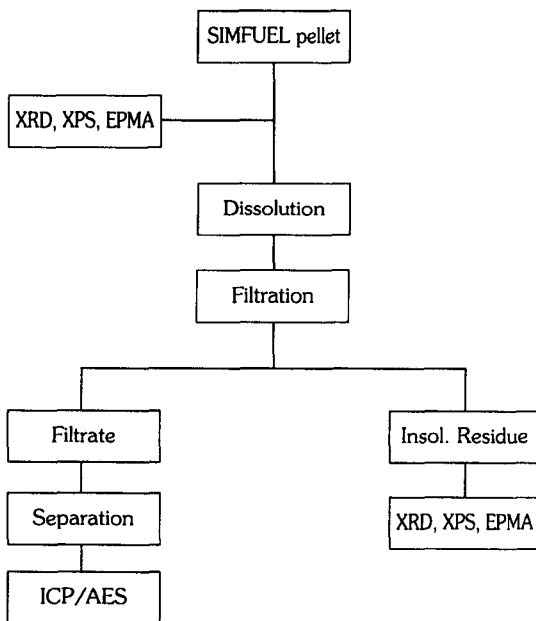


Fig. 1. Experimental Procedures for the Identification of the Insoluble Residue

FIMA was calculated using the ORIGEN2 code[11]. The compositions were simplified using some chemical stand-ins : The amounts of the transuranium elements and Pr, other rare earth elements and Tc were substituted by those of Ce, Nd and Mo, respectively. Volatile fission products and those with low fission yield(In, Sb, etc.) were neglected. The compositions of 16 elements thus determined are shown in Table 1.

2.2. Preparation of SIMFUEL

Stoichiometric amounts of starting materials were dissolved in 2M HNO_3 respectively(Table 1). The mixed solutions were prepared by mixing each metal solution in Alumina crucible. They were dried up on a hot plate and the residues were calcined at 900°C for 2 hours in a stream of 4% $\text{H}_2 + 96\% \text{He}$ to avoid vaporization loss of Ru and Mo. The calcined powder were pressed into pellets of 8 mm in diameter and about 1 g in weight. They were then heat-treated at 1400°C for 2 hours in a stream of 4% $\text{H}_2 + 96\% \text{He}$ (SIMFUEL A1, B1, A2 and B2), or He(SIMFUEL A3, B3, A4 and B4) in a Rapid Temp furnace(CM BLOOMFIELD N,J, USA). The temperature of the furnace was increased and cooled by a rate of $200 \pm 5^\circ\text{C}$ per hour.

2.3. Surface Analysis of SIMFUEL

Sample pellets(A1, A4, B1 and B4) were analyzed by XRD(GIMENS 500, Germany) using $\text{Cu-K}\alpha$ radiation. The phases were identified using powder diffraction files. The XPS(VG, ESCALAB. 220i, England) and EPMA(JEOL, JXA 8600 Japan) were also used to identify the chemical state of the elements in SIMFUEL.

Table 2. Separation of Metal Ions from Uranium and Elements Determined in the Different Fractions

Method	Solvent	Eluent/Extractant	Fraction	Element determined
Anion exch.-1	12M HCl	12M HCl	45mL	Ag, Ba, Ce, Cs, Nd, Rb, Rh, Sr, Te
		5M HCl	50mL	Zr
		0.3M HCl	50mL	U
Anion exch.-2	8M HNO ₃	8M HNO ₃	40mL	Ag, Ba, Cd, Ce, Cs, Mo, Rb, Rh, Sn, Sr, Te, Zr
		H ₂ O	40mL	U
Solvent extr.	8M HNO ₃	TEHP/Heptane(org.)*	50mL × 2	discard
		8M HNO ₃ (aq.)	20mL	Ba, Cd, Ce, Mo, Pd, Rh, Ru, Sn, Sr, Zr

* : TEHP-heptane solution(1:1 v/v) purified immediately before use[15]

2.4. Dissolution of SIMFUEL and Filtration of the Insoluble Residue

Experimental procedures for the identification of the insoluble residue from SIMFUEL are shown in Fig. 1. Sintered SIMFUEL pellets were dissolved in HNO₃(1:1) at 90~95 °C for 9h. The dissolution was continued for 9h under the same condition. The resultant solution was filtered through a 0.1 μm millipore filter with suction after 24 hours and over the end of the dissolution procedure. The insoluble residue was vacuum-dried and weighed.

2.5. Analysis of the Insoluble Residue and Dissolved Solution

XRD was used to identify the phases in the insoluble residues. XPS and EPMA were also used to determine chemical compositions. The filtrates were diluted to a definite volume and analyzed using inductively coupled plasma atomic emission spectrometer(ICP/AES, Jobin Yvon 38 PLUS and 50 P) and atomic absorption spectrophotometer(AAS, Perkin Elmer 5100 PC). The separation of the elements Ce, Nd, Cs, Rb, Ba, Sr, Zr, Mo, Ru, Rh, Pd, Ag, Cd, Sn and Te from

U was achieved by anion exchange chromatography and solvent extraction(Table 2). The first separation method is based on anion exchange separation(φ 1.4cm × 17cm) on AGMP-1 200/400 mesh resin using 12M and 5M HCl as eluents[12,13]. The second separation method is based on anion exchange separation(φ 1.4cm × 17cm) on AGMP-1 200/400 mesh resin using 8M HNO₃ as eluent[14]. The third separation method is based on solvent extraction using TEHP[tri(2-ethylhexyl) phosphate] diluted with heptane [15]. For the determination of chemical yield, the standard solutions having the same chemical composition with SIMFUEL are evaporated to dryness and separated at the same time.

3. Results and Discussion

3.1. Preparation of SIMFUEL

In this study, the burnup is designed with 3.6% FIMA for PWR fuel, and a high and a low oxygen potential of -160 and -540 kJ/mol O₂, controlled by He and 4% H₂ + 96% He, respectively. The range of two oxygen potentials are so wide

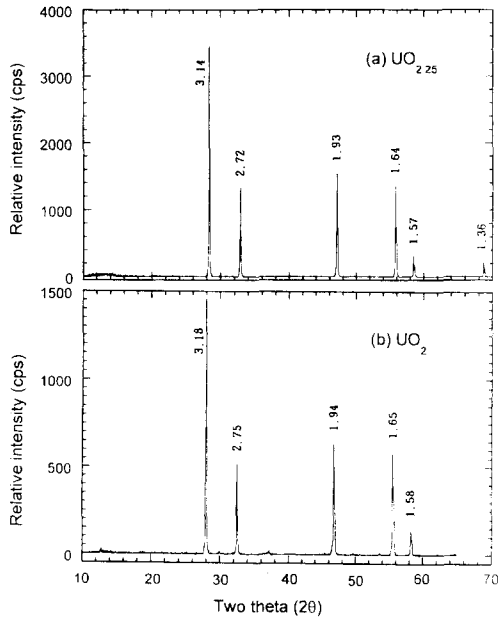


Fig. 2. XRD Patterns of Uranium Oxide in SIMFUEL
(a) A4 heat-treated in a stream of He
(b) A1 heat-treated in a stream of 4% H₂ + 96% He

compared with those of the real spent fuel, but these conditions would bring about some advantage for the identification of the phases in SIMFUELS. The SIMFUEL pellets after calcination and sintering were little decreased in weight compared with those before heat treatment (< 0.03g).

3.2. Chemical Properties of SIMFUEL

3.2.1. Formation of Oxide Phases

Fig. 2 shows the XRD spectrum of SIMFUEL A4 and A1. The O/U ratio of UO₂ powder used for the preparation of SIMFUEL was 2.04. The surface oxidation of U in the SIMFUEL A1 and B1 is very close to that in the UO₂ powder [Fig. 2(b)]. However, the surface oxidation of U in the

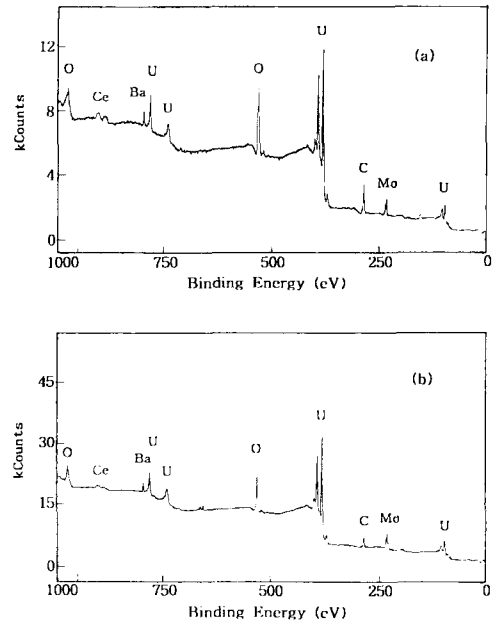


Fig. 3. Low-resolution Survey XPS Spectra of SIMFUEL
(a) B1 heat-treated in a stream of 4% H₂ + 96% He
(b) B4 heat-treated in a stream of He

SIMFUEL A4 and B4 is somewhat different and the O/U ratio was 2.25, i.e. UO_{2.25} or U₄O₉ [Fig. 2(a)]. The UO₂ phase with fluorite structure is observed as the only oxide phase, and the other secondary phases in the fluorite were impossible to be identified by XRD.

Fig. 3 shows low-resolution survey XPS spectra for the SIMFUEL B1 and B4 which was heat-treated at different oxygen potentials. These spectra were recorded over the range 0~1000 eV. The spectrum (a) is consistent with the spectrum (b) except the Mo region of binding energy around 230 eV. The XPS spectra for the SIMFUEL showed just the characteristic peaks of U, Ce, Ba and Mo in SIMFUEL. The spectrum of the U region for B4 is typical of U₄O₉, and very close to that in UO₂ for B1. Ba binding energy indicates that this element is present in the 2+

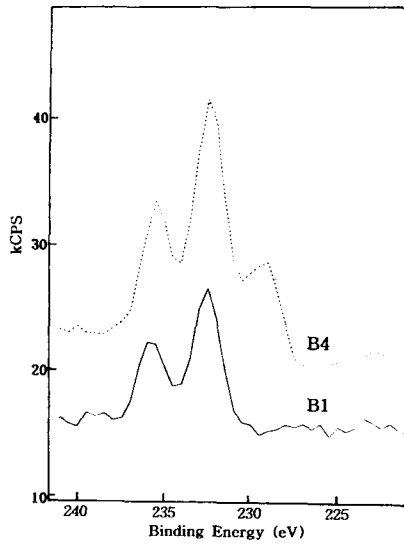


Fig. 4. High-resolution XPS Spectra for the Mo-rich Region in SIMFUEL B1 and B4

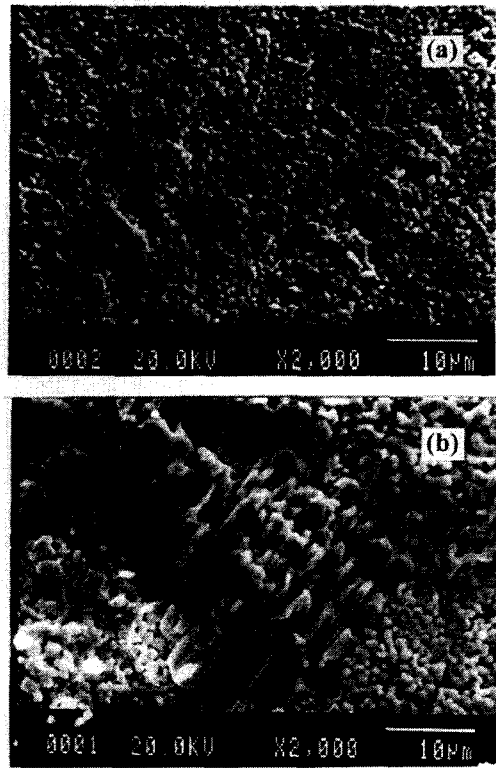


Fig. 6. SEM Image for SIMFUEL Surface
 (a) B1 showing the homogenous microstructure
 (b) B4 showing clusters of Mo-rich single crystals

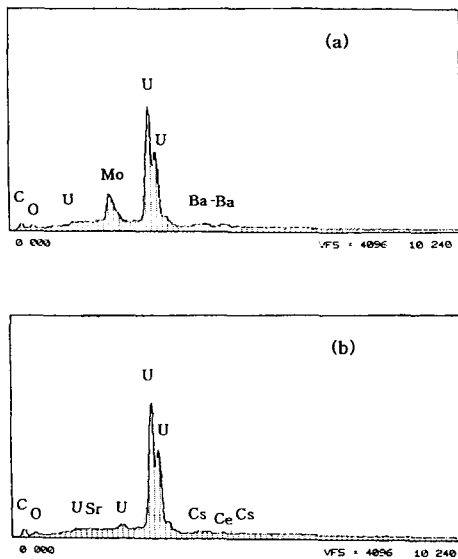


Fig. 5. Scan of X-ray Spectra Emitted by SIMFUEL
 (a) B4 heat-treated in a stream of He
 (b) B1 heat-treated in a stream of 4% H₂ + 96% He

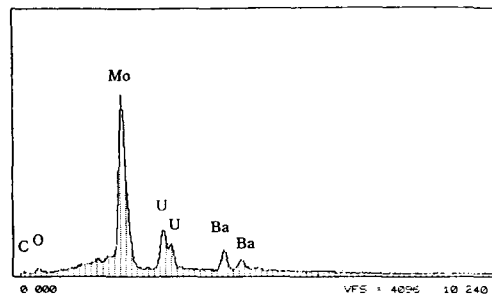


Fig. 7. Scan of X-ray Spectrum of Clusters of Mo-rich Single Crystals

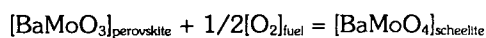
state. A very weak feature at 882 eV in the survey spectrum is close to the binding energy of the Ce band for CeO₂[16].

Fig. 4 shows high-resolution spectra for the Mo regions with double and triple peak from SIMFUEL B1 and B4, respectively. It is believed that the double peak around 232 and 236 eV in both spectra indicate the Mo in the metallic state, i.e. MoM_y, and the additional peak on the low-binding energy side in the spectrum B4 indicate that in the oxide state, i.e., (MoO₄)_xM_y, which is estimated as scheelite phase, BaMoO₄.

Fig. 5 shows X-ray spectra emitted from SIMFUEL B1 and B4 examined by EPMA. The spectrum (b) indicates that the fragment of SIMFUEL B1 is composed of UO₂ matrix and trace amounts of Cs, Ce and Sr. However, the spectrum (a) indicates that the fragment of SIMFUEL B4 contains a large amount of Mo and a small amount of Ba.

Fig. 6 shows SEM images of SIMFUEL B1 and B4, respectively. SIMFUEL B1 seems to have a homogeneous microstructure as shown in Fig. 6 (a). In case of SIMFUEL B4 in Fig. 6 (b), the bulk cluster over 30 μm is observed at measurement point. The EPMA spectrum of this bulk material shows that it is composed mainly of Mo and contains the smaller amounts of U and Ba(Fig. 7). It is therefore believed that SIMFUEL B4 consist of the metallic Mo compound and scheelite phase of BaMoO₄.

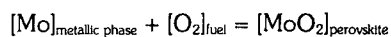
Formation of scheelite phase would be due to oxidation of Mo. MoO₃ would react with BaO in UO₂ and/or in the perovskite, and the scheelite phase, BaMoO₄ would be formed in the fuel.



Therefore, as the oxygen potential becomes greater than -190 kJ/mol O₂ of the BaMoO₃ -

BaMoO₄ equilibrium, the amount of the perovskite would rapidly decreases in the SIMFUEL[10]. Accordingly, in the present study, the scheelite phase would be formed in SIMFUEL B4(∼-160 kJ/mol O₂), when prepared under higher oxygen potential than -190 kJ/mol O₂. On the other hand, the phase would not be formed in the SIMFUEL B1(∼-540 kJ/mol O₂), when prepared under lower oxygen potential than -190 kJ/mol O₂.

The Mo(IV) would be formed by the oxidation of the metallic phases under high oxygen potential by the reaction.



The oxygen potential of the Mo - MoO₂ equilibrium at 1400 °C is about -300 kJ/mol O₂[10]. Accordingly, it is likely that Mo(IV) is not formed in SIMFUEL B1, when prepared under the oxygen potential lower than that of the Mo - MoO₂ equilibrium.

3.2.2. Formation of Metallic Phases

It has been reported that the hexagonal phase(ε-phase) and the cubic phase(α-phase) are found in SIMFUEL before dissolution with nitric acid solution, and after dissolution, the hexagonal phase is still remained but the cubic phase is totally disappeared. On the other hand, the tetragonal phase(σ-phase) was detected only in the insoluble residue derived from the SIMFUEL, when produced in an atmosphere of around -300 kJ/mol O₂ at 1400 °C[2,10]. In the present study, the metallic phases formed in SIMFUEL were not identified by XRD analysis. However, it was identified by the XPS and EPMA that the Mo is present in the metallic state, whereas Sr, Ba, Cs and Ce exist as oxides in SIMFUEL.

3.3. Separation of Insoluble Residue

After dissolution, the suspended insoluble residue was distinguished from the precipitated one by its colour, i.e., white to grey in the former and grey to black in the latter. Therefore, for the determination of chemical composition of the suspended and precipitated insoluble residue, they were filtered at different site on the same membrane filter.

It has been reported that the particle size of insoluble residue grows larger with increasing standing time after dissolution[3]. In the present study, it is believed that the suspended insoluble residue with fine particles in the dissolved solution begin to coagulate during dissolution, and then settle down after 24 h to form larger particles. Hence, the membrane filter with 0.1 μm pore size would be enough to filtrate the insoluble residues. The amounts of the insoluble residue dried against the SIMFUEL dissolved are about 0.57 wt.% for A2 + B2 and 0.19 wt.% for A3 + B3, respectively. These results are compared with the amounts of insoluble residue(0.35 - 0.6 wt.%) from the spent PWR fuel with a burnup of around 3.6% FIMA[10, 17-19].

3.4. Structural Properties of Insoluble Residue

It has been reported that the phases identified in the residue after dissolution of SIMFUEL are hexagonal phase, tetragonal phase and the hydrated oxide phase[zirconium molybdate(ZM) phase, $\text{ZrMo}_2\text{O}_7(\text{OH})_2(\text{H}_2\text{O})_2$] [2,10]. In addition, the cubic phase was observed only in the SIMFUELS before dissolution with nitric acid solution. Neither the perovskite phase[(Ba,Sr)ZrO₃] nor the scheelite phase [(Ba,Sr)ZrO₄] were detected in residues by XRD. The metallic phases

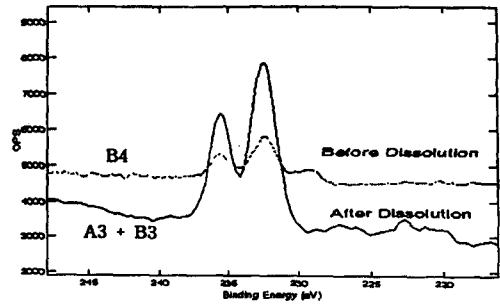


Fig. 8. Comparison of XPS Spectra for the Mo-rich Region in SIMFUEL B4 and in Insoluble Residue A3 + B3

found in the post irradiation studies of spent fuels were mostly the hexagonal phase, and it has been reported by many researchers that this phase is a Ru-based alloy, and that its main components are Ru, Mo, Tc and Pd[6, 7].

3.4.1. Oxide Phase

Fig. 8 shows high resolution XPS spectra for the Mo region of SIMFUEL B4 before dissolution and that of insoluble residue from SIMFUEL A3 + B3 after dissolution. The spectrum of the latter shows the strong doublet, while that of the former shows the weak triplet. In addition, these spectra indicate that the Mo in the SIMFUEL at a high oxygen potential, controlled by He, exists in the metallic and scheelite phase(triplet), but the Mo in the scheelite phase disappeared(doublet) after dissolution.

3.4.2. Zirconium Molybdate Phase

Adachi et al.[2] suggested that the zirconium molybdate(ZM phase) in the irradiated fuel may be the same as that observed in the SIMFUEL, although the formation condition was somewhat different. It is natural to consider that this

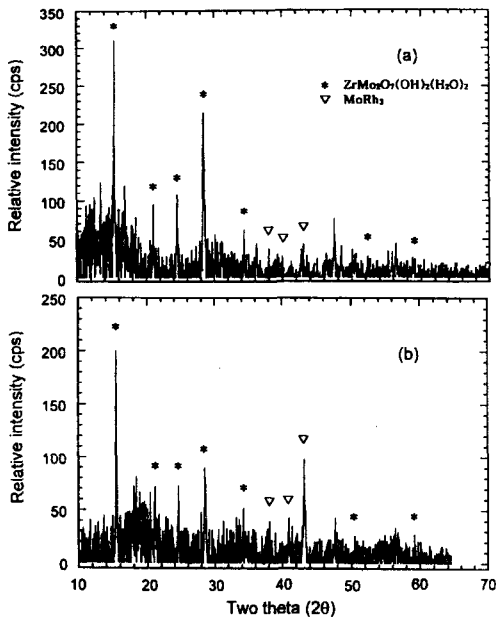


Fig. 9. XRD Patterns for Insoluble Residue from SIMFUEL A2 + B2
(a) suspended portion
(b) precipitated portion

zirconium molybdate should form in the solution during dissolution, because this compound is a hydrated phase and is not detected in the fuel before dissolution[2].

Fig. 9a and 9b show the XRD patterns of the suspended(H2F) and precipitated(H2P) insoluble residues from SIMFUEL A2 + B2, respectively. Fig. 10a and 10b show the XRD patterns of the suspended(He3F) and precipitated(He3P) insoluble residues from SIMFUEL A3 + B3, respectively. The characteristic peaks of the zirconium molybdate, $[\text{ZrMo}_2\text{O}_7(\text{OH})_2(\text{H}_2\text{O})_2]$, are shown in all spectra. On the other hand, it is indicated from spectra of (a) and (b) that the chemical states in the suspended and precipitated insoluble residues are somewhat different. The characteristic peaks in the H2P and He3P spectra indicate that ZM phase as well as metallic compound are matching to the

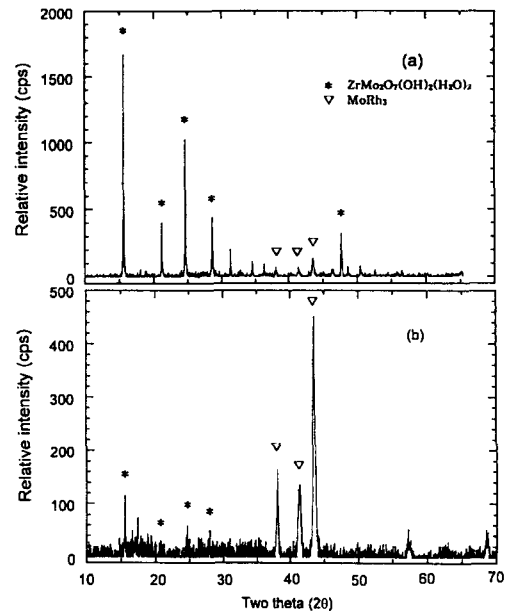


Fig. 10. XRD Patterns for Insoluble Residue from SIMFUEL A3 + B3
(a) suspended portion
(b) precipitated portion

XRD pattern of the imaginary MoRh_3 phase, which has not been reported yet as a real phase. In addition, the peak intensity of the imaginary MoRh_3 measured for He3P are much higher than that for H2P.

3.4.3. Tetragonal Phase

By Muromura et al.[10], the tetragonal phase was identified only in the insoluble residue of the SIMFUEL, when produced in an atmosphere of around -300 kJ/mol O_2 . In addition, they suggested that the tetragonal phase was not detected in the fuel before dissolution. The oxygen potentials used in the heat treatment of SIMFUELS in this study are higher or lower than -300 kJ/mol O_2 . It is therefore believed that the tetragonal phase is not formed in these SIMFUELS. In fact, the tetragonal phase was not detected by the XRD

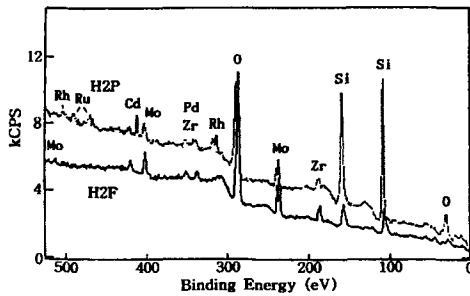


Fig. 11. Low-resolution Survey XPS Spectra from Insoluble Residue of SIMFUEL A2 + B2
H2F : suspended portion
H2P : precipitated portion

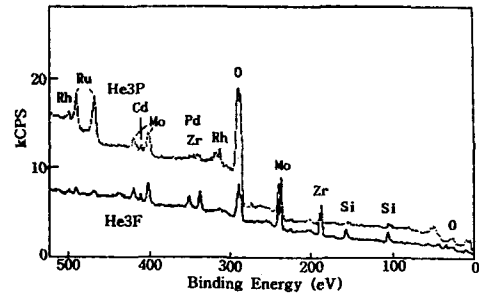


Fig. 12. Low-resolution Survey XPS Spectra from Insoluble Residue of SIMFUEL A3 + B3
He3F : suspended portion
He3P : precipitated portion

Table 3. Composition of the Metallic Phases Formed in Insoluble Residues from SIMFUEL A2 + B2 and A3 + B3

Element	Atom %			
	H2F	H2P	He3F	He3P
Mo	56.15	27.30	50.32	23.75
Zr	24.85	7.19	25.16	1.20
Ru	8.56	29.67	14.35	46.03
Rh	4.34	24.80	4.26	14.19
Pd	3.74	10.40	4.41	13.68
Cd	2.37	0.64	1.49	1.16
Total	100.01	100.00	99.99	100.01

H2F : suspended portion of insoluble residue from SIMFUEL A2 + B2

H2P : precipitated portion of insoluble residue from SIMFUEL A2 + B2

He3F : suspended portion of insoluble residue from SIMFUEL A3 + B3

He3P : precipitated portion of insoluble residue from SIMFUEL A3 + B3

analysis for all the SIMFUELS and the suspended and precipitated insoluble residues.

3.4.4. Hexagonal Phase

Fig. 11 shows low-resolution survey XPS spectra for the suspended(H2F) and precipitated(H2P) insoluble residues from SIMFUEL A2 + B2. Fig. 12 shows low-resolution survey XPS spectra for the insoluble residues suspended(He3F) and precipitated(He3P) from SIMFUEL A3 + B3. The characteristic peaks of Ru, Rh, Zr, Mo, Pd and Cd

among the 16 elements used in this SIMFUEL preparation were observed. The intensity of Rh peaks in the precipitated insoluble residues is higher than those of the suspended insoluble residues. This supports the results observed in the XRD patterns presented above. In the XRD patterns for the precipitated portion, the peak intensity of the metallic MoRh_3 was higher than that for the suspended portion.

Table 3 shows the values(mean atom %) determined by EPMA for the major components in the surface region of the suspended and

Table 4. Mass Fraction of the Fission Products in the Insoluble Residue of Spent LWR Fuel and the Simulated Fission Products in Those of SIMFUELS

F.P (Sim.-F.P)	Residue/Yield (wt.%)		Residue/Quantity added (wt.%)	
	SPENT LWR*	SIMFUEL(A2+B2)	SIMFUEL(A3+B3)	
Sr	2	4.8	15.5	
Zr	5	43.1	27.5	
Mo	19	47.1	55.5	
Tc	25	-	-	
Ru	60	82.8	89.1	
Rh	51	34.4	45.0	
Pd	15	30.0	41.7	
Sn	75	30.0	<0.1	
Te	75	88.9	92.3	
Ba	8	42.4	39.9	

* : Data from ref. 18,
LWR UO₂ (3.2% ²³⁵U)
burnup : 55900 MWD/MTU
dissolution : 7M HNO₃, 115°C, 5h

precipitated insoluble residue. Silica from the dissolution vessel was ignored in the determination of the composition of the metallic phases. The EPMA results confirmed the presence of Pd in insoluble residues which was difficult to observe in the XPS spectra. That may be attributed to that the XPS signal of the sample is limited by the top few nanometres of the sample surface. The relative concentrations of Mo and Zr obtained in the suspended portions showed higher values than those obtained in the precipitated portions, whereas their relative concentrations in the precipitated portions are higher rather than those in the suspended portions in case of Ru, Rh and Pd.

Adachi et al.[2] studied on the effects of oxygen potential on the composition of insoluble residue in SIMFUEL. They showed that the Mo/Ru ratio decreases with increasing oxygen potential because the oxygen potential for Ru/RuO₂ equilibrium is much higher than that for Mo/MoO₂ equilibrium, and also explained that the amount of metallic Mo in the alloy phase should decrease at

higher oxygen potentials because Mo tends to be oxidized to MoO₂ at higher oxygen potentials.

The Mo/Ru ratios calculated from EPMA results for the suspended and precipitated portions of insoluble residues in the present study are as follows.

	H2F	He3F	H2P	He3P
Mo/Ru ratio	6.56	3.51	0.92	0.52

This result explains that the Mo/Ru ratios decrease with increasing oxygen potential for all the suspended and precipitated portion of the insoluble residue, and also agrees with the result of Adachi et al.[2].

Chemical analyses of the elements of the dissolved solution were carried out by ICP/AES after solvent extraction and anion exchange separation. The amounts of each element(in wt.%) in the insoluble residues irrespective of the chemical state are compiled in Table 4, together with the results obtained in the insoluble residue from spent LWR fuel by Kleykamp et al.[18]. The

order of the undissolved fraction for four noble metal elements in the insoluble residue from the SIMFUELS is $Ru > Mo > Rh > Pd$, compared with that from spent LWR fuel, $Ru > Rh > Mo > Pd$ [3,18]. The concentration of Te found in the dissolved solution by chemical analysis was very low, but Te was not detected in the insoluble residue by EPMA and XPS. Thus, it seems that it is necessary to dissolve that completely for the analysis of the insoluble residue. The total dissolution has been performed by means of a mixture of HCl/HNO₃(9/1) at 180°C for 16h in autoclaves[17].

4. Conclusions

- (1) All of the insoluble residues suspended and precipitated were composed mainly of Mo, Ru with a small amount of Zr, Rh, Pd and Cd.
- (2) The amount of metallic residue and the Mo/Ru ratio decreased with the increase in oxygen potentials. These results may be related to the oxygen potential for the Mo-MoO₂ equilibrium.
- (3) The formation of a zirconium molybdate precipitate, $ZrMo_2O_7(OH)_2(H_2O)_2$, was identified only in the residue. The phase was possibly formed during the dissolution process.
- (4) SIMFUEL could provide a convenient way to investigate chemical properties for the fuel compositions such as the oxides dissolved and metallic precipitates distributed in the UO₂ matrix.
- (5) In future, the chemical properties of the insoluble residue in various SIMFUELS should be studied in detail by considering burnup, oxygen potential and temperature during irradiation.

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