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Thermo-chemical Characteristics of Powder Fabricated by Oxidation of Spent PWR Fuel

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***Abstract*—**Thermochemcial characteristics of powder fabricated using oxidation treatment of spent PWR fuel and SIMFUEL were evaluated for recycling of spent fuel such as DUPIC process. Especially, the influence of spent fuel burn-ups on the powder fabrication characteristics was experimentally evaluated, ranging from 27,300 to 65,000 MWd/tU. Densities of powder manufactured from an oxidation, OREOX and the milling processes at the same process conditions were compared as a function of the fuel burn-ups respectively. Also, based on chemical analysis results, homogeneity of fissile elements in oxidized powder was confirmed.

***Keywords*—**Spent PWR fuel, DUPIC, Oxidation, OREOX, Powder, Chemical analysis

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I. Introduction

A DUPIC process, which reuses spent PWR fuel as a raw material in CANDU reactors without any separation of the fissile materials and fission products, has been developing at KAERI.[1]-[2] In the fabrication of the DUPIC fuel, spent fuel pellets separated from the claddings of a spent LWR fuel are pulverized during a repeated oxidation and reduction, which is called the OREOX (oxidation and reduction of oxide fuel) process, due to the phase transformation and volume change between cubic UO_2(10.96 g/cm^3) and orthorhombic U_3O_8(8.3 g/cm^3). Using the spent fuel powder prepared from the OREOX process, fresh DUPIC fuels for CANDU reactors are remotely fabricated after compaction and sintering processes in a shielded hot cell. KAERI performed a series of remote fuel fabrication campaigns to produce DUPIC pellets and elements. Since 1999, DUPIC fuel has been fabricated using the normal burn-up spent PWR fuel discharged from Gori Nuclear Power Plant in 1986. In order to qualify the DUPIC pellet fabrication processes, a series of experiments were carried out and the optimum process flow sheets and parameters for the DUPIC fuel fabrication were established. [3]-[4]

Recently, the fuel discharge burn-up of PWRs has been extended to reduce the amount of spent fuel and fuel cycle cost. Considering this trend extending the fuel burn-up in PWRs, the DUPIC fuel fabrication technology should be improved to process high burn-up spent fuels by analyzing the effects of the spent fuel burn-up on the fuel fabrication. One of the key parameters influencing the fuel fabrication characteristics would be the amount of fission products contained in the spent fuel as impurities. As high burn-up spent fuel has a more amount of fission products than a low burn-up spent fuel, this characteristic would affects powder morphology fabricated from spent fuel oxidation. General observation of the oxidation rate with different fuel burn-ups is that the oxidation rate is decreasing with increasing fuel burn-ups [5].

In this work, in order to establish the optimized parameters of DUPIC process, the powder fabrication characteristics were experimentally evaluated with SIMFUEL (SIMulated FUEL) as a surrogate and an actual spent PWR fuel. Powder fabrication characteristics using SIMFUEL were analyzed for comparison of actual spent fuel data. Actual spent fuel burn-ups used in this study ranges from 27.3 to 65 GWD/tU. Also, homogeneity of fabricated powder was confirmed with a distribution of fissile elements content by chemical analysis.

II. Experimental

The spent PWR fuel with an average burn-up of the fuel rods ranging from 37 to 65 GWd/tU was used. The spent fuel burn-up was determined by the PIE test after its transportation to KAERI. DUPIC process parameters of each step were established from both the pre-qualification test and the qualification test [6], as shown in Fig. 1.

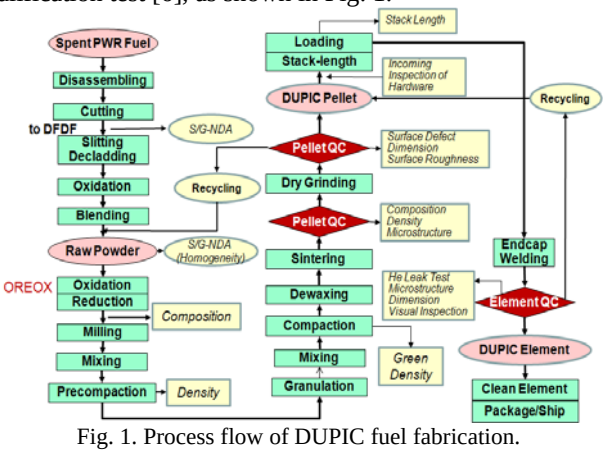


Fig. 1. Process flow of DUPIC fuel fabrication.

The optimized process conditions were applied for producing the OREOX (Oxidation and Reduction of Oxide fuel) powder and pellet. The spent fuel pellet was oxidized at 500 ^oC for 5 hrs to convert UO_2 pellet to U_3O_8 powder. And the oxidized powder was treated by the OREOX process which is composed of 3 cycles of a oxidation at 450 ^oC in air and a reduction at 700^oC in 4%H_2/Ar. Both oxidized powder and OREOXed powder were characterized with various parameters,

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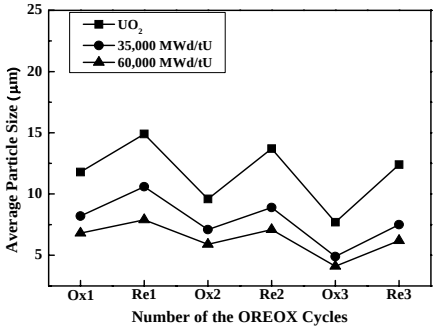
such as weight gain by oxidation, pour and tap density, particle size distribution. Powder samples for homogeneity analysis were prepared by ASTM method and these samples were chemically analyzed for obtaining U and Pu contents. After milling and precompaction steps, the green pellet was prepared with a pressure range from 88 MPa to 150 MPa. The sintering conditions were re-evaluated by changing its temperature and soaking program.

The ORIGEN (Oak Ridge Isotope Generation and Depletion) Code was used to calculate the fission product inventories to be added into the UO_2 powder for preparing the SIMFUEL pellets. The fifteen elements were selected as the major fission products except for the volatile elements. The additives milled by a mortar were mixed with the UO_2 powder in a Turbular mixer. A wet attrition milling was used to obtain a homogeneous powder mixture. The powder mixture was pressed into green pellets at 300 MPa and sintered at 1700 ^oC for 6 hours in an atmosphere of Ar-4%H_2. For the preparation of the powder from the SIMFUEL, the repetition of an oxidation and reduction step, called the OREOX process, was applied. The oxidation step was performed at 500 ^oC in air and the reduction step at 700 ^oC in Ar-4%H_2. Passivation was conducted at 70 ^oC in Ar-2%O_2. Two kinds of powders, 1 cycle-OREOX powder and 3 cycles-OREOX powder, were prepared for this experiment. The 1 cycle-OREOX powder was produced by only one cycle of an oxidation and reduction, whereas the 3 cycles-OREOX powder was made by 3 cycles of an oxidation and reduction. An attrition mill with a jar volume of 1.5 L was used to break the OREOX powder into a finer powder. The milling medium was zirconia balls with a 5 mm diameter. The OREOX powder was poured into the milling jar at a constant ball-to-powder weight ratio (40:1) and milled at 150 rpm. The millings of the 1 cycle-OREOX powder and 3 cycles-OREOX powder were performed for 120 minutes and 15 minutes, respectively.

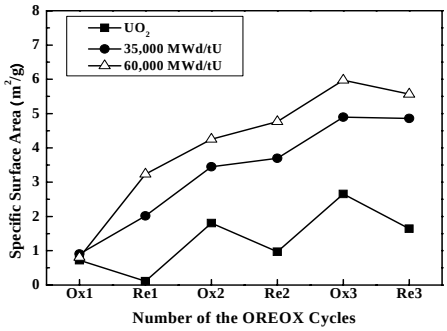
III. Results and Discussion

Fig.2 shows the average particle size and specific surface area of the SIMFUEL and pure UO_2 powders with the number of OREOX cycles. In a reduction step of the oxidized pure U_3O_8 powder, the specific surface area was decreased as the particle size increased. However, the specific surface area of the SIMFUEL powder was increased with an increasing particle size at the first and second reduction steps.

Fig.3 shows the SEM micrographs of the cyclic OREOX powders. The powders from the first oxidation step (Fig.2.(a)-(1), (b)-(1), (c)-(1)) show a generally coarse and angular shape with large cracks. After the first reduction step, surface of the UO_2 particles (Fig.2.(a)-(2)) was still coarse, whereas that of the SIMFUEL particles (Fig.2.(b)-(2), (c)-(2)) became rougher with an increasing amount of impurities. The 3 cycles-OREOX powders for the SIMFUEL (Fig.2. (b)-(3), (c)-(3)) showed sponge-like particles shapes with internal pores.



(a) Average particle size



(b) Specific surface area

Fig. 2. Average particle size and specific surface area of SIMFUEL and UO_2 powders produced by the number of OREOX cycles.

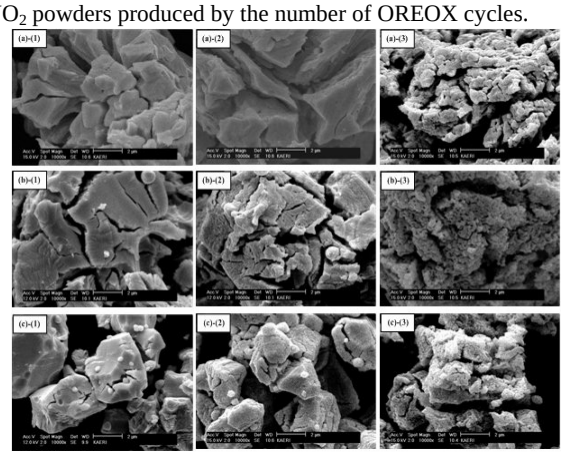


Fig. 3. Morphologies of the OREOX powder with the number of OREOX cycles; (a-1) 1st oxidation, (a-2) 1st reduction, and (a-3) 3rd reduction for UO_2; (b-1) 1st oxidation, (b-2) 2nd reduction, and (b-3) 3rd reduction for 35,000 MWd/tU SIMFUEL; (c-1) 1st oxidation, (c-2) 2nd reduction, and (c-3) 3rd reduction for 60,000 MWd/tU SIMFUEL.

The physical properties of the simulated DUPIC powder produced by a milling after 3 cycles of the OREOX treatment of the SIMFUEL pellet are shown in Table I.

TABLE I
CHARACTERISTICS OF SIMULATED DUPIC POWDER

Properties	35,000 MWd/tU		60,000 MWd/tU	
	As produced	After milling	As produced	After milling
Average particle size (μm)	7.6	0.6	6.2	0.4
Specific surface area (m^2/g)	4.86	5.38	5.57	6.21
Bulk density(g/cm^3)	0.71	1.63	0.72	1.95
Tap density (g/cm^3)	1.87	3.05	1.83	3.12

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The average particle size of the OREOX powders are larger than 2.91 μm of the UO_2 powder from the ADU (ammonium diuranate) process.[7] For the specific surface area, the OREOX powder for the SIMFUEL of 35,000 MWd/tU burn-up is lower than 5.27 m^2/g of the UO_2 powder. However, the OREOX powder for that of 60,000 MWd/tU has a slightly higher value than the UO_2 powder. The specific surface area of the OREOX powders was significantly increased by an attrition milling due to a reduction of the particle size into the submicron range, thus resulting in an improvement of the powder sinterability. The bulk and tap densities of the OREOX powders were considerably increased after a milling process. Therefore, it is expected that a higher packing density of the cyclic OREOX powder during a compaction would be obtained.

As for the DUPIC fuel fabrication process, the spent PWR fuel is first disassembled and then decladed to retrieve the fuel material.[8] Mechanical slitting method using the push-rod technique was applied to separate the fuel material from the spent fuel rod-cut which was about 25 cm in length. It was identified that the retrieval efficiency of the spent fuel material from the rod-cut was over 99.8% by using the DSNC (DUPIC Safeguard Neutron Counter) equipment. However, some amount of fuel material after a mechanical slitting was observed inside the cladding tube among a few of the high burn-up fuel rod-cuts. Therefore, an oxidation of the slitted cladding tube at 700°C for 5 hrs was required to completely retrieve the spent fuel material. After an oxidative treatment of the cladding tube, the retrieval efficiency of the spent fuel material was over 99%. As represented in Fig. 1, 3 cycles of the OREOX treatment of U_3O_8 powder was applied to produce a sinterable fine powder, and the milling process followed to break up the OREOXed powder into a submicron sized powder. Tap density values as the typical characteristics of these powders obtained from the spent fuel material with different burn-ups are shown in Fig. 4 ~ 6.

Weight gain by the fuel oxidation to U_3O_8 at 500°C for 5 hrs showed a sharp decrease over 60,000 MWd/tU fuel burn-ups, as shown in Fig. 4. It was also observed that the oxidized powder with a fuel burn-up to 40 GWd/tU has about 3.3 g/ cm^3 in tap density, while a high burn-up fuel of 65 GWd/tU has a higher tap density. A higher density of the U_3O_8 powder made from spent fuel with 65,000 MWd/tU was probably attributed to an incomplete oxidation of the high burn-up spent fuel. Figure 5 shows that no significant difference in the tap density of the OREOX powder fabricated from all of the spent fuel materials with a range of 27.3 ~ 39.6 MWD/tU was observed. Regardless of the spent fuel burn-ups, the densities of the milled powder increased by about 3 times more than those of the OREOX-treated powder, as shown in Fig. 6. Particle size distribution of fabricated powder is very important for fabricating sound DUPIC pellet. Fig. 7 shows particle size distribution of oxidized and OREOX powders with fuel burn-ups. A lower fuel burn-up has finer particle size distribution than high burn-up fuel. This result would be contributed to incomplete oxidation due to higher fission products amount.

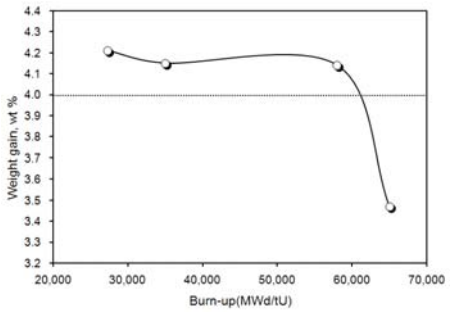


Fig.4. Variation in the weight gain of oxidized powder with the spent fuel burn-ups.

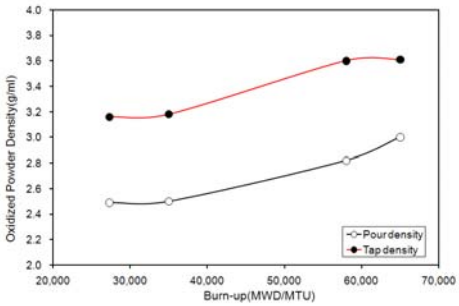


Fig. 5. Influence of the burn-ups on the densities of the oxidized powder.

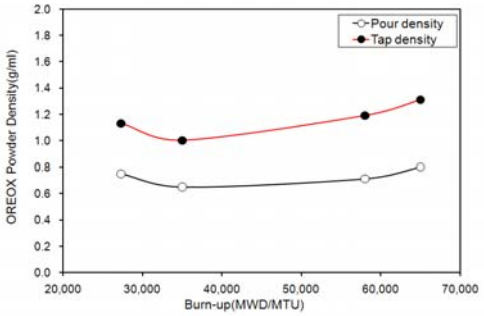


Fig. 6. Influence of the fuel burn-ups on the densities of the OREOX powder.

As a practical point of DUPIC fuel performance, distribution of fissile materials such as ^{235}U and Pu on DUPIC fuel is essential. Chemical analysis of oxidized powder using spent fuel with 27,300 MWd/tU burn-up was performed for analyzing homogeneity of fissile elements. Table II shows concentration of uranium and plutonium isotopes as a basis of initial uranium in four kinds of oxidized powders. ASTM method was used for typical sampling. Table III was difference from mean value for each sample based on concentration value in Table II. Measurements for the fissile elements, ^{235}U and ^{239}Pu showed that no individual value of either isotope was to differ from the mean value for that isotope by more than 2.5% of the mean value which is the design requirements. The ^{235}U contents difference from the mean value ranged from 0.62 to 1.7 %. The ^{239}Pu difference from the mean value ranged from 0.46 to 1.27 %.

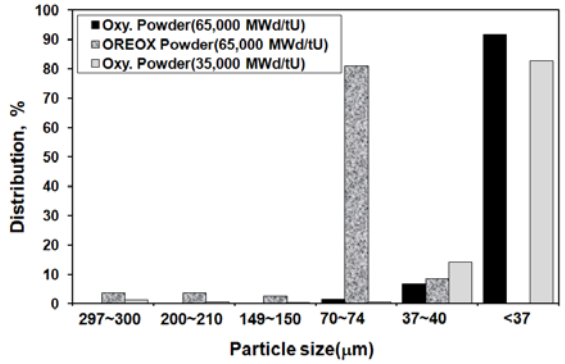


Fig. 7. Particle size distribution of oxidized and OREOX powders with different fuel burn-ups.

TABLE II
CONCENTRATION OF U AND PU ISOTOPES FOR EACH SAMPLE

Nuclide	Units	Sample 1	Sample 2	Sample 3	Sample 4	Average
U-Content	g/g-IU	0.93627	0.94639	0.96563	0.95832	0.951651
Pu-Content	g/g-IU	0.00828	0.00824	0.00837	0.00843	0.008332
U-234	g/g-IU	0.000178	0.000182	0.000181	0.000185	0.000181
U-235	g/g-IU	0.010120	0.010232	0.010458	0.010371	0.010295
U-236	g/g-IU	0.003545	0.003616	0.003434	0.003517	0.003528
U-238	g/g-IU	0.922426	0.932356	0.951556	0.944247	0.937647
Pu-238	g/g-IU	0.000155	0.000183	0.000136	0.000175	0.000162
Pu-239	g/g-IU	0.005205	0.005162	0.005279	0.005270	0.005229
Pu-240	g/g-IU	0.001984	0.001972	0.002014	0.002033	0.002001
Pu-241	g/g-IU	0.000552	0.000545	0.000558	0.000563	0.000555
Pu-242	g/g-IU	0.000386	0.000379	0.000386	0.000390	0.000385

TABLE III
DIFFERENCE FROM MEAN VALUE FOR EACH SAMPLE

Nuclide	Sample 1	Sample 2	Sample 3	Sample 4	DMV Av.
U-Content	1.61	0.55	1.47	0.70	1.083
Pu-Content	0.60	1.08	0.51	1.18	0.842
U-234	1.99	0.07	0.07	1.86	0.996
U-235	1.70	0.62	1.58	0.74	1.160
U-236	0.49	2.49	2.67	0.31	1.490
U-238	1.62	0.56	1.48	0.70	1.091
Pu-238	4.68	12.61	15.91	7.97	10.293
Pu-239	0.46	1.27	0.96	0.78	0.867
Pu-240	0.83	1.43	0.67	1.59	1.130
Pu-241	0.42	1.65	0.57	1.50	1.033
Pu-242	0.05	1.60	0.27	1.28	0.799

IV. CONCLUSIONS

Thermochemcial characteristics of powder fabricated using oxidation treatment of spent PWR fuel and SIMFUEL were evaluated for improving DUPIC fuel fabrication process. Especially, the influence of spent fuel burn-ups on the powder fabrication characteristics was experimentally evaluated. The fuel burn-ups used in this study range from 27,300 to 65,000 MWd/tU. Densities of the powder manufactured from an oxidation, OREOX and the milling processes at the same process conditions were compared as a function of the fuel burn-ups respectively. Weight gain by the fuel oxidation to U_3O_8 showed a sharp decrease over 60,000 MWd/tU fuel burn-ups. OREOX powder density increased up to 3.7 g/cm^3 for a high burn-up fuel, and the density of the milled powder represented almost a similar value of 3.2±0.2 g/cm^3 regardless of the fuel burn-ups. Based on chemical analysis results, homogeneity of ^{235}U and ^{239}Pu in oxidized powder showed the design requirement of ± 5%.

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