

Effects of High Temperature Treatment and Subsequent Oxidation and Reduction on Powder Property of Simulated Spent Fuel

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Abstract

The simulated spent PWR fuel pellet which is corresponding to the burnup of 33,000 MWD/MTU is prepared by adding 11 fission-product elements to UO_2 . The simulated spent fuel pellet is treated at 400°C in air (oxidation), at 1100°C in air (high-temperature treatment), and at 600°C in hydrogen (reduction). The product is treated through additional oxidation and reduction up to 3 cycles. Pellets are completely pulverized by the first oxidation, and the high-temperature treatment causes particle and crystallite to grow and surface to be smooth, and thus particle size significantly increases and surface area decreases. The reduction following the high-temperature treatment decreases much the particle size by means of the formation of intercrystalline cracks. The particle size decreases a little during the second oxidation and reduction cycle and then remains nearly constant during the third and fourth cycles. Surface area of powder increases progressively with the repetition of oxidation and reduction cycles, mainly due to the formation of surface cracks. The degradation of surface area resulting from high-temperature treatment is restored by two subsequent resulting oxidation and reduction cycles.

1. Introduction

The UO_2 pellet is broken up into fine powder during its oxidation to U_3O_8 , since the volume of U_3O_8 lattice is much larger than that of UO_2 lattice. This fact has commercially been applied to the recycle of pellet scrap. Spent UO_2 fuel pellet containing fission products shows the same behavior during the oxidation, which can also be applied to the recycle of spent fuel. The process called AIROX [1,2,3] was developed in 1960's, in which spent fuel pellets were treated through oxidation and reduction cycles up to 5 times to make sinterable powder. This recycled powder could be utilized through compacting and

sintering. Since then, several studies on thermal process have been reported [4,5], and it is generally recognized that sinterable powder can be obtained under the condition that oxidation at 400~500°C in air and reduction at 550~700°C in hydrogen are repeatedly performed.

Most fission products generated during irradiation remain in spent fuel, and the types of their existence are classified into 4 groups [6]; solid solution, metallic precipitates, oxide precipitates and volatile elements. Recently C.E.L. Hunt et al. [7] reported that volatile (Xe, Kr, and I) and semi-volatile (Ru) elements were substantially released from the spent fuel pellet at 1100°C in air. The removal of semi-volatile

elements from the spent fuel powder is desirable since the recycled powder has less poison materials. So it is necessary to incorporate high temperature treatment in the oxidation and reduction treatments of spent fuel pellets.

Since spent fuel emits high-energy rays, its handling is very complicated and requires special facility. In order to avoid such experimental difficulties simulated spent fuel containing only stable fission products can be substituted for the real spent fuel. Previous works using simulated spent fuel include identification of phases [8], oxygen potential [9] and thermal conductivity [10], showing that properties of the simulated spent fuel are similar to those of the real spent fuel.

This report is to investigate the effect of high-temperature treatment of simulated spent fuel powder on particle size, surface area and particle morphology and is to describe how these properties are changed by subsequent oxidation and reduction treatments.

2. Experimental Procedure

2.1 Preparation of a simulated spent fuel pellet

The fission-product contents of irradiated UO_2 fuel are determined by its initial enrichment, irradiation history and cooling period. The typical condition of spent PWR UO_2 fuel was selected; initial enrichment : 3.2wt%, burnup : 33,000MWD/MTU and cooling period : 10years. The ORIGEN-2(Oak Ridge Isotope Generation and Depletion) code [11] was used to calculate fission-product inventories. If volatile elements such as Xe, Kr, I, and Cs are not considered, eleven elements listed in Table 1 represent major solid fission-products in the spent UO_2 fuel.

The simulated spent fuel powder contains many additives. Preliminary experiments showed that sintered density would be low and that inhomogeneous microstructure would develop if the powder was not well mixed and milled. Uniform microstructure and sintered density were mainly considered in the preparation of simulated spent fuel pellets in this work.

Table 1 Concentrations of additives for simulated spent fuel corresponding to 33 MWD/kgU

Elements	Concentration (ppm/g U)	Form
U	balance	UO_2
Ce(+ Pu, + Np)	11760	CeO_2
Nd(+ Sm, + Pr)	5450	Nd_2O_3
Mo	3220	MoO_3
Zr	3450	ZrO_2
Ru(+ Tc)	3160	RuO_2
Ba	1390	BaCO_3
La	1220	La_2O_3
Sr	910	SrO
Pd	1210	PdO
Y	470	Y_2O_3
Rh	420	Rh_2O_3
total	32660	

The most promising method for the preparation of the simulated fuel pellet determined from several trials is as follows :

The additives whose forms are shown in Table 1 were mixed and milled in a mortar. Then the additives and the UO_2 powder derived from ADU(Ammonium Diuranate) and were mixed in the 'Turbula'. This powder was subsequently milled for 1 hr under a wet condition in the attritor, of which details was described elsewhere [12]. The resulting slurry was dried at 40°C in an oven.

The simulated spent fuel powder was compacted under the pressure of 3 ton/cm² with die-wall lubrication, and then sintered at 1700°C for 4hrs in flowing hydrogen. Sintered density was measured by water immersion method. For the examination of microstructure pellets were sectioned longitudinally, ground, and polished. Grain boundary was chemically etched, and grain size was measured by a linear intercept method.

2.2 Thermal treatments of simulated spent fuel pellets

The outline of 5 thermal treatments studied in this

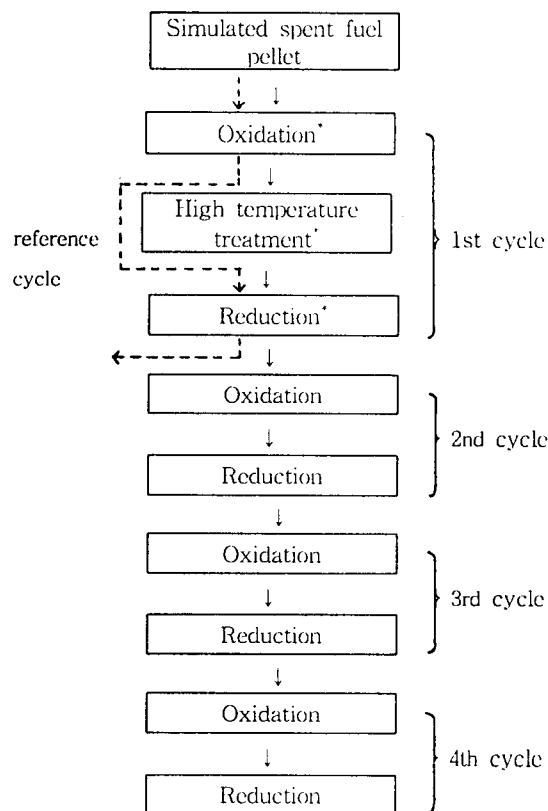
work is schematically shown in Fig. 1. The first cycle consists of following steps: 1) the oxidation of the simulated spent fuel pellets (UO_2) at 400°C in flowing air for 2 hrs, 2) the high-temperature treatment of U_3O_8 simulated fuel powder at 1100°C in air for 2 hrs, 3) the reduction of U_3O_8 simulated fuel powder at 600°C in flowing hydrogen for 2 hrs to convert it into simulated UO_2 powder. The second, third and fourth cycles mean that specimens were treated with one, two, and three additional cycles of the oxidation and reduction, respectively, after the first cycle. The durations of the oxidation and the reduction were determined from the respective weight gain and loss. A separate cycle was performed, in which the simulated fuel pellet was oxidized at 400°C for 2 hrs in flowing air and reduced at 600°C for 2 hrs in flowing hydrogen, so the high-temperature treatment was not involved in this cycle (reference cycle). Powder property of the reference cycle was compared with those of the other cycles in order to study the effect of the high-temperature treatment on powder property.

Particle size distribution was measured by laser light scattering method, and mean particle size was determined by the size occupying 50vol% in size distribution. The specific surface area of powder was measured by BET method.

3. Results and Discussion

Sintered densities of simulated spent fuel pellets range from 10.41 to 10.43g/cm^3 , and such densities are in good agreement with those of real spent PWR fuel pellets [13]. The microstructure appears uniform, but the grain size of about $1\mu\text{m}$ is much smaller than that of spent fuel ($6\sim 8\mu\text{m}$).

Fig. 2 shows mean particle sizes of the powders from all cycles. The mean particle size is about $3\mu\text{m}$ after the first oxidation and increases to over $10\mu\text{m}$ due to the high-temperature treatment. The mean particle size substantially decreases due to the subsequent reduction and then decreases slightly during



*oxidation : treated at 400°C for 2hrs in air reduction : treated at 600°C for 2 hrs in hydrogen high-temperature treatment : treated at 1100°C for 2 hrs in air

Fig. 1. Schematic outline of powder treatments.

the second oxidation and reduction cycle. However, the size remains nearly constant during the third and fourth cycles.

Fig. 3 shows the change in particle size distribution due to each treatment in the first cycle. The size distribution ranging from approximately 1 to $10\mu\text{m}$ after the first oxidation has changed into that ranging from 3 to $100\mu\text{m}$ after the high-temperature treatment. The size distribution of powder after reduction becomes similar to that of the first oxidation, and such distribution is virtually unaffected by further

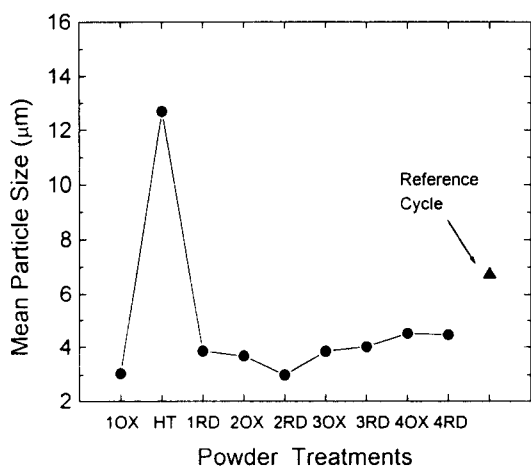


Fig. 2. Variation in particle size due to powder treatments.

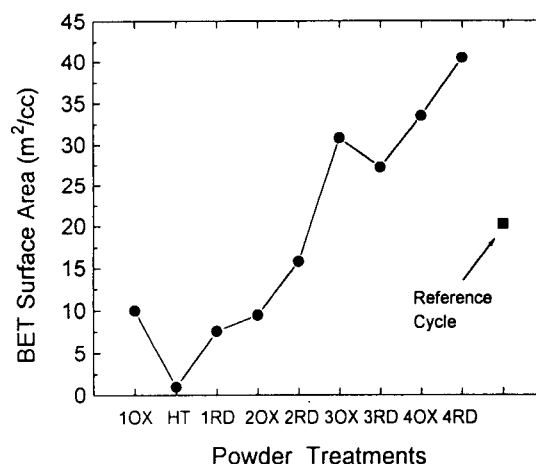


Fig. 4. Variation in surface area due to powder treatments.

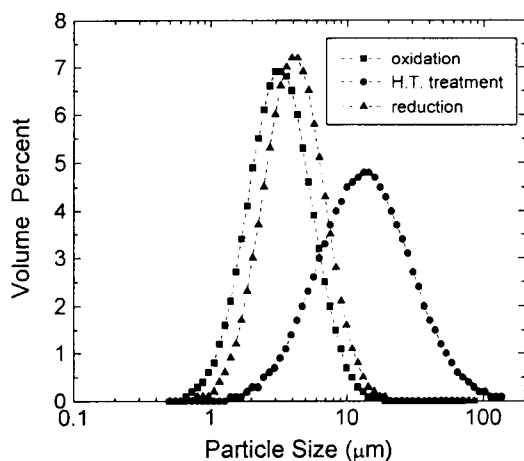


Fig. 3. Changes in particle size distribution due to powder treatments in the first cycle.

treatments from second to fourth cycles. The high-temperature treatment makes not only particle size bigger but size distribution broader.

The BET surface areas of powders processed by each treatment throughout the 4 cycles are shown in Fig. 4. Surface area diminishes significantly due to the high-temperature treatment and then increases progressively with the repetition of the oxidation and reduction cycle. The effect of the oxidation and re-

duction cycle is in good agreement with the results of Strausberg [1] and Kim et al. [14]. The surface area of the reference cycle is larger than that of the second cycle but smaller than that of the third cycle, which indicates that the degradation of surface area due to the high-temperature treatment is fully recovered by two additional oxidation and reduction cycles.

Figs. 5(a), 5(b), and 5(c) show morphologies of powders after oxidation, high-temperature treatment and reduction in the first cycle, respectively. Morphologies of powders after the second, third and fourth cycles are also shown in Figs. 5(d), 5(e) and 5(f), respectively. The particles produced from the first oxidation of simulated spent fuel pellets seem to consist of many crystallites (grains), that is, to be polycrystalline, and they have large cracks on surface. Fig. 5(b) shows the particle composed of well developed crystallites, which have significantly been grown by the high-temperature treatment. In addition particle surface appears smooth and perfectly free from cracks. The intercrystalline cracks running between crystallites are seen in Fig. 5(c) and are probably the main cause of particle disintegration by the reduction. Fig. 5(d) shows that particle surface is less smooth than

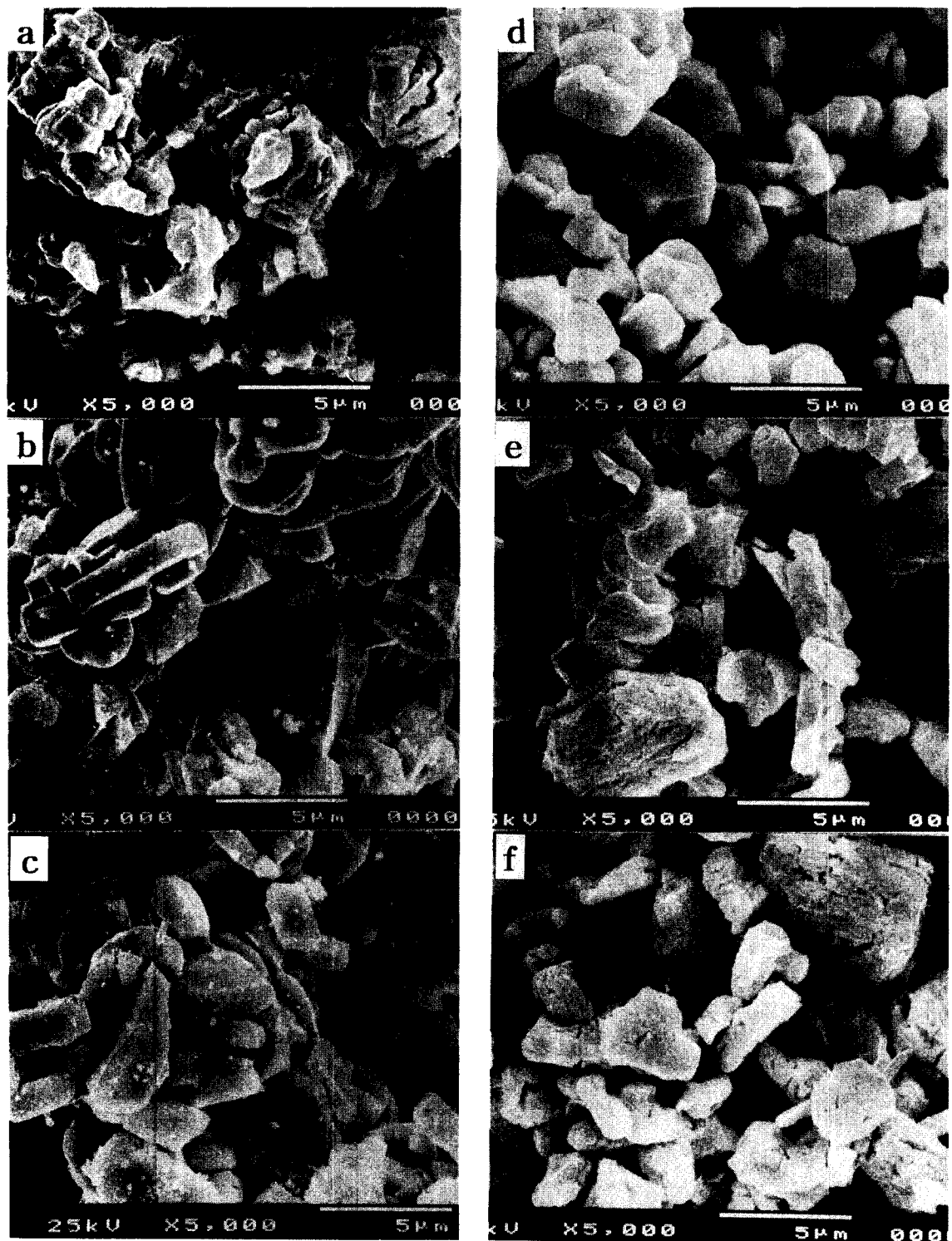


Fig. 5. SEM micrographs of powder morphologies after ; (a) first oxidation, (b) high-temperature treatment, (c) first reduction, (d) second oxidation and reduction cycle, (e) third oxidation and reduction cycle, (f) fourth oxidation and reduction cycle.

that of Fig. 5(c), and that most particles look like one grain after the second cycle, implying that intercrystalline cracks have developed to such an extent that they separate almost all of the crystallites during the second cycle. Fine cracks are formed on particle surface after the third cycle (see Fig. 5(e)). Fig. 5(f) shows that surface cracks are formed a lot more, and simultaneously some fine cracks has developed into large ones.

The change in mean particle size can be explained in terms of powder morphology. A simulated spent fuel pellet is completely broken up into powder by the first oxidation. According to the study on oxidation of pure UO_2 pellets [15,16], oxidation begins on grain boundary prior to matrix and preferentially forms intergranular cracks, which is consistent with the powder morphology in Fig. 5(a) showing that particle shape almost looks like grain shape. The intercrystalline cracks in Fig. 5(c) formed by the reduction suggest that the reduction might occur preferentially on crystalline boundary. Consequently, it can be proposed that grain and crystal boundaries are major crack paths in particle disintegration during not only oxidation but reduction. The important role of crystal boundary in particle disintegration is supported by the results that the mean particle size is decreased only by the first reduction and the second cycle where starting particles are polycrystalline (see Fig. 5(b) and 5(c)).

The particle size remains nearly constant during the third and fourth oxidation and reduction cycles. However, other works [1,14] reported that the oxidation and reduction cycles which did not include high-temperature treatment decreased particle size to below the grain size of an original pellet. The particle that has undergone the high temperature treatment has very smooth surface, and the residual stress caused by the first oxidation could be relieved by crystallite growth. Such particle will naturally be more resistant to cracking than the particle that has not been treated at high temperature, and actually the surface cracks formed during the third and fourth cycles are

not so large as to cause particle disintegration.

The surface area of powder is determined by particle size and open porosity, however, surface crack is more likely in this case than open porosity. Surface area increases directly with the amount of surface cracks and inversely with particle size. One of the ways to determine which of them is more influential to surface area is the roughness factor. The roughness factor is defined by S_b/S_p , where S_b is BET surface area and S_p the surface area calculated from particle size distribution assuming a spherical shape, and thus it approaches unity as surface becomes smooth. The values of the roughness factor are shown in Fig. 6, in which the roughness factor decreases to 1.5 after the high-temperature treatment, indicating that particle surface is very smooth. The roughness factor increases progressively with the repetition of the oxidation and reduction cycles. The increasing tendency of the roughness factor throughout all the treatments seems to be quite close to that of surface area in Fig. 4. Moreover, the variation in roughness factor are exactly consistent with the change in the morphology of powder shown in Fig. 5; the smooth surface after high-temperature treatment and the formation of fine surface cracks during the second to fourth cycles. Therefore, it can be concluded that the surface area of particle is increased predominantly by the forma-

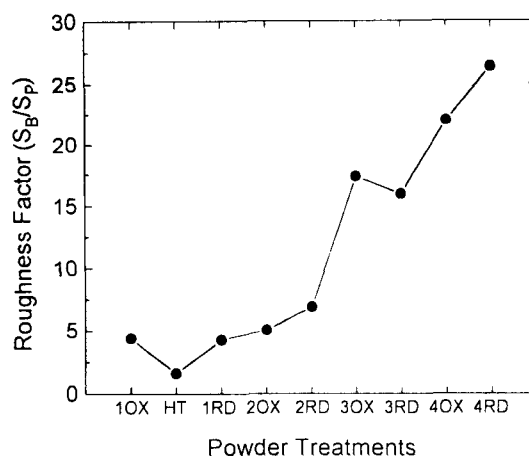


Fig. 6. Variation in the roughness factor of particle due to powder treatments.

tion of surface cracks.

According to Timmermans et al. [17], high temperature treatments of pure UO_2 powder increased particle size and decreased surface area, giving rise to the deterioration of powder sinterability. In this work the high-temperature treatment of simulated spent fuel powder has the same effects on both particle size and surface area, and those effects are expected to be detrimental to powder sinterability. However, the surface area of the reference cycle is smaller than those of the third and fourth cycles. Therefore, the degradation of surface area due to the high-temperature treatment can be recovered by two subsequent oxidation and reduction cycles.

4. Summary

The simulated spent fuel pellet is oxidized at 400°C in air, annealed at 1100°C in air (high-temperature treatment), and reduced at 600°C in hydrogen. The product is treated through additional oxidation and reduction up to 3 cycles. The high-temperature treatment substantially increases particle size and decreases powder surface area. It also causes crystallite growth and makes particle surface smooth. The subsequent reduction preferentially forms intercrystalline cracks, and thus significantly decreases particle size. The particle size decrease a little during the second cycle and then remains nearly constant during the third and fourth cycles.

The surface area of powder increases with the repetition of the oxidation and reduction cycles owing to the formation of fine surface cracks, and consequently the degradation of surface area caused by the high-temperature treatment can be recovered by two subsequent oxidation and reduction cycles.

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