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Effect of Ball-mill Treatment on Powder Characteristics, Compaction and Sintering Behaviors of ex-AUC and ex-ADU UO_2 Powder

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Abstract

The effects of ball-milling time(0~4 hrs) have been investigated on the change of powder characteristics, compaction behavior (compaction pressure range : 200~400MPa) and sinterability (1700℃ in H_2 atmosphere) of two different UO_2 powders (ex-ADU and ex-AUC) prepared by the wet process. It is observed that, while the ex-ADU UO_2 was little affected, the ex-AUC UO_2 was largely affected by the ball-milling treatment. This may be attributed to the characteristics of particle size formed during the preparation step, i.e., the former has a small average size of about 1.0㎛, while the latter has a relatively large average size of about 30㎛. It appeared that the effective size reduction by ball-milling treatment is limited to the particle size larger than 1㎛, and to the extent of maximum decrease in size of about 0.5㎛. In the case of ex-AUC UO_2, it is observed that the particle size decreased with ball-milling time and green density and sintered density of the pellets prepared from ball-milled powder increased compared with those of pellets prepared from the as-received powder under the same conditions. This may be attributed mainly to the fine particles formed during the ball-milling treatment.

Key Words : ball-milling, powder preparation, powder characteristics, sinterability, compaction

1. Introduction

UO_2 is the most widely used nuclear fuel for current nuclear power generation. The fabrication process of a UO_2 pellet is similar to general powder metallurgy. UO_2 powder is conventionally prepared by wet processes : ADU(Ammonium DiUranate)[1] and AUC (Ammonim Uranyl Carbonate)[2]. However, the characteristics of powders prepared from these two processes are different[3,4] and these different characteristics of UO_2 powders have a large influence on the compactiblity and sinterability[5-7]. As a step of development for nuclear fuel improvement, microstructure-controlled pelletizing technologies that can be produced to retain fission gases effectively within the pellet are continuously being developed to improve the performance of nuclear fuel in the reactor. There exist methods to control the microstructure of pellet and among others, mechanical milling of powder is one which is simple and easy to control. With this method, characteristics of powder and resultant compaction behavior and sinterabiltiy are properly controlled. Especially, in the case of MOX(Mixed OXide) fuel fabrication, an adequate homogenization step for MOX powder mixture is necessary because it influences not only the compactibility and sinterability of the powder mixture but also the homogeneity of the microstructure in the MOX pellet and hence, the powder milling technique has been widely used in this area. In this work, the effects of powder milling on the characteristics of powder, compaction and sintering behavior are investigated in detail.

It is in general well known that powder characteristics, especially the size and morphology of powder have an influence on the compaction behavior and sinterability of powders[8,9] Some mechanical milling methods to reduce a size of powder are reported[10]. However, in this experiment, two different as-received powders, ex-ADU and ex-AUC, are milled by ball mill, the most widely used techniques not only in UO_2 pelletizing process but also in other powder treatment. And some effects of these two ball-milled powders on the powder characteristics, compaction behavior and sinterability are investigated.

2. Experimental

Two different UO_2 powders, ex-AUC and ex-ADU, were used: the former was manufactured from UNH solution in KAERI and the latter was imported from CAMECO, Canada.

The revolving speed of a stainless steel mill jar is about 80rpm, calculated by Sundrica formula[11]. The type of mill jar is cylindrical and its diameter and length are 0.1m and 0.12m, respectively. Ball-milling was performed under an air atmosphere and the ball-milling time was varied from 0.5 to 4-hr, as it is observed that the ball-milling times of longer than 4-hr give adhesion of the powder mixture on the inner wall of the mill jar.

The input charges of powder and media(alumina ball, size ; 0.02m dia.) were 20vol% and 50vol% of jar inner volume, respectively. The ball-milled powder samples(20 ± 0.1g) were compacted with the compaction pressure range between 200 and 400MPa, and sintered at 1700℃ for 4-hr under a hydrogen atmosphere in order to investigate their compactibility and sinterability.

The particle size and its distribution of ball-milled powder were measured with a laser type particle size analysis system(Malvern Co., UK, Model ; Mastersize/E). The specific surface area and O/U ratio of ball-milled powder were determined from BET and by gravimetric methods, respectively. The bulk density of ball-milled powder specimens was measured with the Hall flowmeter(ASTM B-329), and the green density and sintered density were measured by the geometrical and immersion method, respectively. The pore size and its distributions of the powder specimens and green pellet specimens were measured with a mercury porosimeter(Micromeritics Co., USA, Model ; Poresizer 9320).

3. Results and Discussion

3.1. Effects of Ball-mill Treatment on the Characteristics of UO_2 Powder

The results of variations in the powder characteristics, that is, specific surface area, O/U ratio, bulk density, particle size and its distribution and pore size and its distribution of green pellets

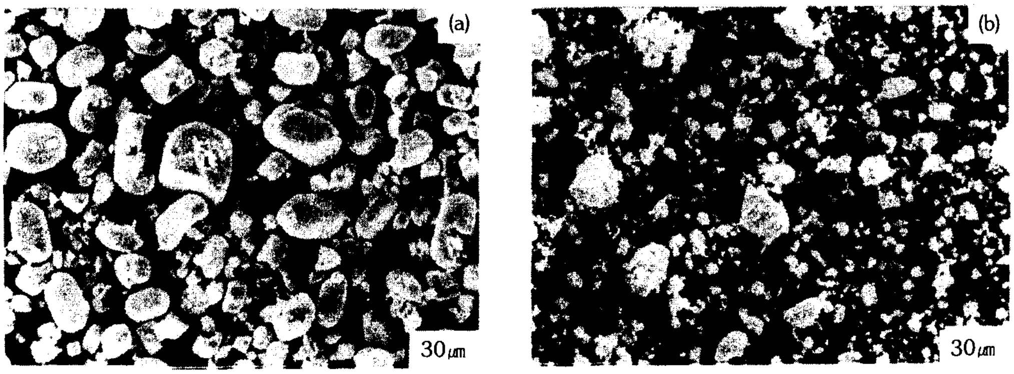

Fig. 1. Typical particle morphology of UO_2 powder (a) ex-AUC UO_2(KAERI) and (b) ex-ADU UO_2(Canada)

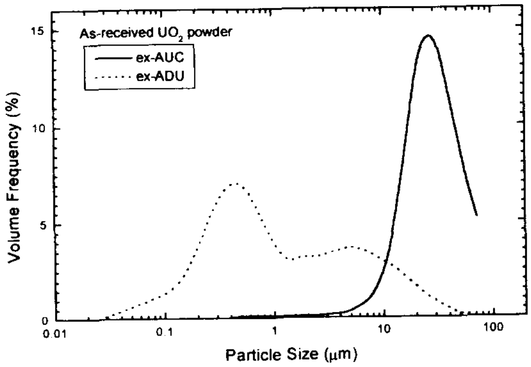

Fig. 2. Particle Size Distribution of As-received Powders of ex-AUC and ex-ADU UO_2

as a function of ball-milling time were summarized in Table 1. It can be observed in the Table that the chemical properties of two different as-received powders(ex-AUC and ex-ADU UO_2) are similar, but their physical properties, especially their average particle size and bulk density are largely different. For example, the average particle size of the ex-AUC UO_2 powder was markedly larger than that of ex-ADU UO_2 powder. Figs. 1 (a) and 1(b) show the morphologies of ex-AUC and ex-ADU UO_2 as-received powder, respectively, which reveal that ex-AUC UO_2 particles were relatively large and of round type, while ex-ADU UO_2 consists of irregular and agglomerated fine particles.

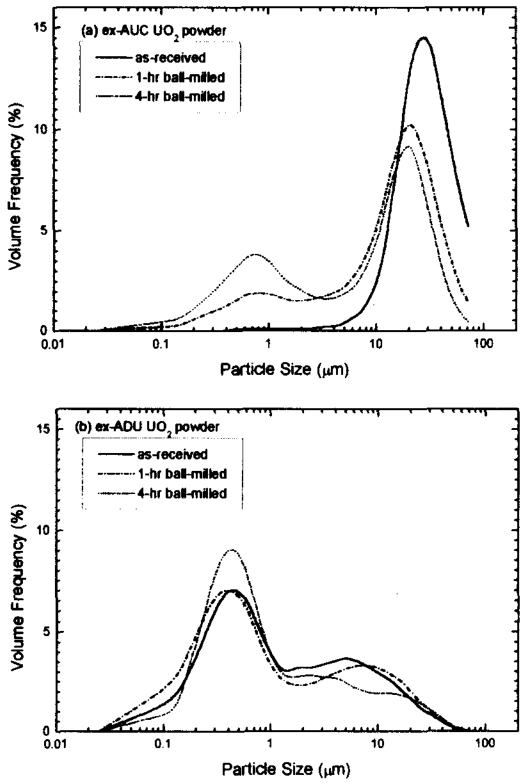

Fig. 3. Particle Size Distribution of Ball-milled Powder (a) ex-AUC UO_2 and (b) ex-ADU UO_2

Table 1. Characteristics of Powder Samples

characteristics \ milling time (hr) \ powder	ex-AUC UO_2					ex-ADU UO_2				
	0	0.5	1	2	4	0	0.5	1	2	4
Chemical										
O/U	2.19	2.21	2.21	2.21	2.21	2.14	2.15	2.15	2.15	2.15
moisture contents(%)	0.36	0.40	0.36	0.40	0.42	0.42	0.33	0.39	0.35	0.40
Physical										
specific surface area(m^2/g)	4.86	4.75	4.72	4.62	4.57	4.60	4.89	4.70	5.11	5.01
bulk density(Mg/m^3)	2.32	2.04	1.70	1.54	1.48	1.20	1.23	1.22	1.22	1.14
average diameter(㎛)	27.52	18.47	15.31	12.76	10.40	0.91	0.72	0.75	0.59	0.64

Fig. 2 compares the particle size distributions of two different as-received ex-AUC and ex-ADU UO_2 powders and shows that the size distribution of the ex-AUC UO_2 is a normal mono-modal type having a peak value at the size of 28㎛ but that of ex-ADU UO_2 is a bi-modal type(peak values ; at 0.5 and at 5㎛). Figs. 3(a) and 3(b) show the variations of particle size distribution of ex-AUC UO_2 and ex-ADU UO_2 with 1 and 4hrs of ball-milling times, respectively. In the case of ex-AUC UO_2, as the milling time increases, the particle size decreases and the shape of particle size distribution was changed from a mono-modal type to a bi-modal one(peak values ; about at 23㎛ and at 0.8㎛). However, in the case of ex-ADU UO_2, in spite of increasing ball-milling time, the shape remained bi-modal except that the peak value of the size was shifted from 5㎛ to 0.5㎛. It is considered that the size of as-received powder having a size range of 2~20㎛ is reduced by ball-mill treatment. Accordingly, it seems that the size reduction of powder by the ball-mill has an influence on the powders above, of at least 1㎛. In this experiment, it appeared that the least average particle size of powder that could be obtained by ball-mill was about 0.5㎛.

As shown in Table 1, it appeared that the chemical properties of powder, that is, the O/U ratio and moisture contents of both ex-AUC and ex-ADU UO_2 were not affected by ball-milling times. It is considered that the heat produced by dry ball-mill does not show any influence on the chemical properties of powder. On the other hand, only in the case of ex-AUC UO_2, the physical properties, that is, specific surface area, bulk density and average size of particle show markedly the effect of the ball-mill treatment.

Fig. 4 shows the variation of average particle size and bulk density of ex-AUC and ex-ADU powders as

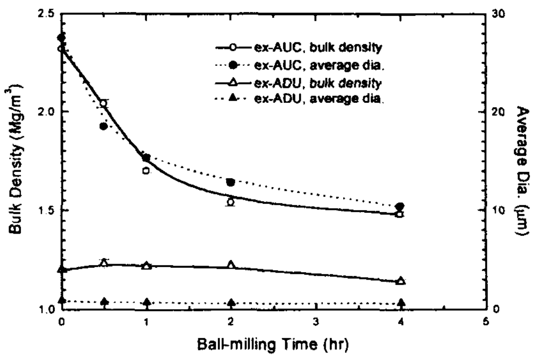

Fig. 4. Variations of Bulk density and Average Diameter of Particle as a Function of Ball-milling Time for ex-ADU UO_2 and ex-AUC UO_2 Powders

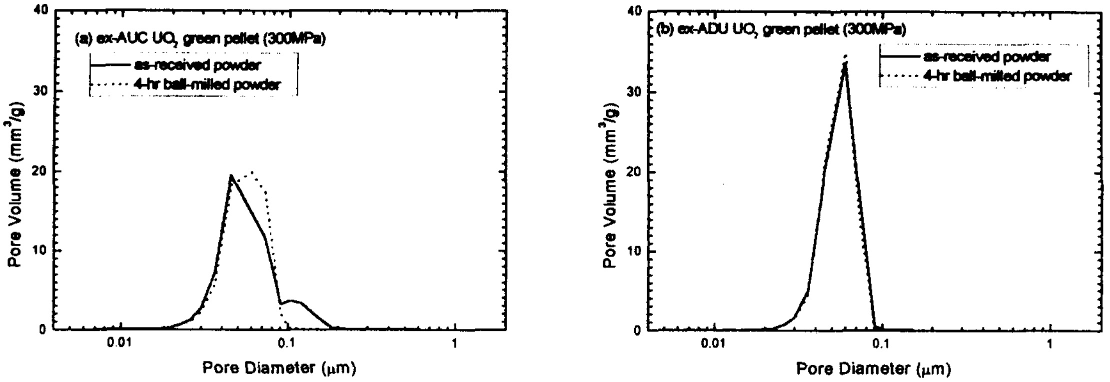

Fig. 5. Variations of Pore Size Distribution of UO_2 Green Pellets with a Compaction Pressure of 300MPa (a) ex-AUC UO_2 and (b) ex-ADU UO_2

a function of ball-milling time. It can be observed that the paricle size and bulk density of the ex-ADU UO_2 powder have changed little with increasing ball-milling time, while those of ex-AUC UO_2 decreased sharply until 3-hr of ball-milling and remained constant above that milling time. Therefore, it seems that ball-milling times longer than 3-hr do not contribute to the size reduction of powder and, also the decrease of bulk density with increasing ball-milling time showed a similar behavior to that of reduction of particle size. This may be attributed to bad flowability due to the increase in number of fine and irregular particles with increasing ball-milling time, indicating that the size and the morphology of particles have a close interrelation.

3.2. Effects of Ball-mill Treatment on the UO_2 Compaction

Figs. 5(a) and (b) compare, respectively, the pore volume distributions of ex-AUC and ex-ADU UO_2 green pellets compacted from as-received and 4-hr ball-milled powders with a compaction pressure of 300MPa. In the case of ex-AUC UO_2, the calculated total pore volumes per weight of green pellets which were compacted from the as-received powder and the 4-hr ball-milled powder were 73.3 and 70.2 mm^3/g, respectively, and those for ex-ADU UO_2 were 81.4 and 80.9 mm^3/g, respectively. Therefore, the total pore volume of the ex-ADU UO_2 green pellet was larger than that of ex-AUC UO_2 green pellet, and the calculated total pore volume of the green pellet from the ball-milled powder was larger than that of the green pellet from the as-received powder. As shown in Fig. 5(a), in the case of as-received powder, pore size distribution in the green pellet shows a bi-modal type having two peak values(at the first peak value, pore diameter and pore volume are 0.12μm and 3.5mm^3/g, respectively, and at the second peak value, pore diameter and pore volume are 0.043μm and 19.6mm^3/g, respectively). On the other hand, in the case of 4-hr ball-milled powder, pore size distribution in the green pellet shows mono-modal distribution(at the peak value, pore diameter and pore volume are about 0.06μm and 20mm^3/g, respectively). This may be attributed to a decrease of pore size due to finely milled particles which are rearranged and extruded into pores during compaction. In the case of ex-ADU UO_2, however, as shown in Fig. 5(b), both the as-received powder and the 4-hr ball-milled powder show similar normal distribution having same peak value(pore volume is about

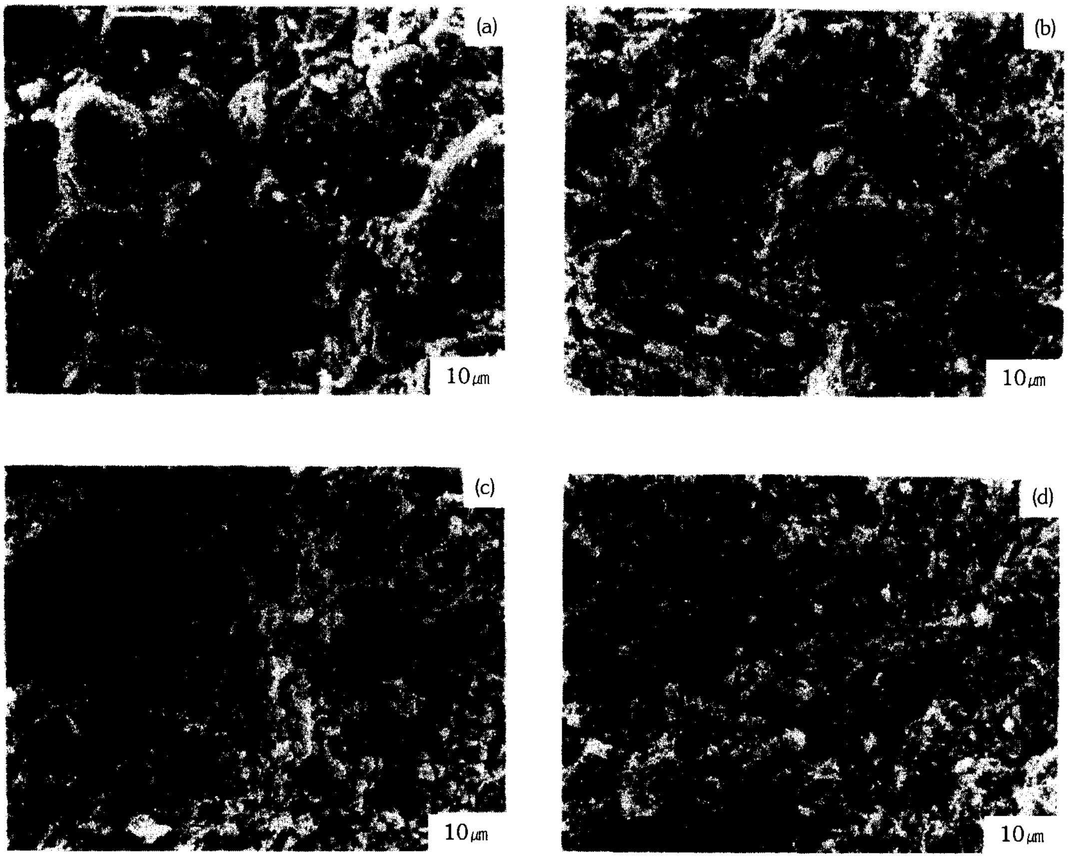

Fig. 6. Radial Fractographs of the Green Pellets Compacted with a Compaction Pressure of 300MPa (a) ex-AUC, as-received, (b) ex-AUC, 4-hr ball-milled, (c) ex-ADU, as received and (d) ex-ADU, 4-hr ball-milled

$35mm^3/g$ at the pore diameter of about $0.06\mu m$). Comparing Fig. 5(a) with Fig. 5(b), in the case of ball-milled powder, the pore size distribution of the ex-ADU UO_2 green pellet appears narrower than that of ex-AUC UO_2 green pellet. It seems that the relatively coarse particles are not entirely crushed and particles less than $1\mu m$ in diameter are little crushed by the ball-mill treatment.

Fig. 6 shows radial fractographs of green pellets which were compacted with a compaction pressure of 300MPa. As shown in Fig. 6(a), large particles remained unchanged and relatively large pores are formed between the particles, while, Fig. 6(b) shows only small pores exist because finely milled particles were filled into pores between particles which were not sufficiently finely milled. On the other hand, Figs. 6(c) and (d) show only small pores are uniformly distributed in the green pellet in both as-received and ball-milled powder.

Fig. 7 shows a variation of green densities of ex-AUC UO_2 (as-received and 4-hr ball-milled) and ex-ADU UO_2 (as-received and 4-hr ball-milled) as a function of compaction pressure. The green density of ex-AUC UO_2 was higher than that of ex-ADU UO_2 under the same compaction pressure. The difference value was about $0.2Mg/m^3$ in the

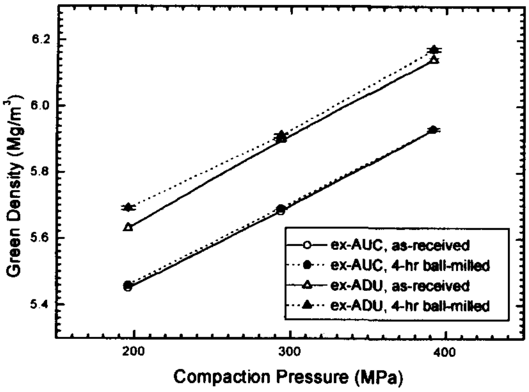

Fig. 7. Green Density vs. Compaction Pressure Relationship of ex-ADU and ex-AUC UO_2 Green

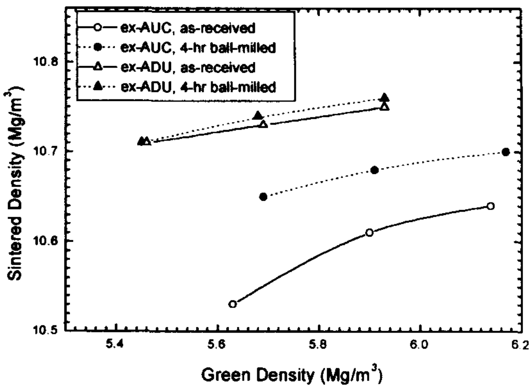

Fig. 8 Green Density vs. Sintered Density Relationship of ex-ADU and ex-AUC UO_2 Pellets with as Received and 4-hr Ball-milled Powders

range of compaction pressures applied in the experiment. In the case of ex-ADU UO_2, green densities were only slightly different between the as-received and ball-milled powder, while in the case of ex-AUC UO_2, the green density of as-received powder was slightly higher than that of ball-milled powder under the same conditions.

It can be revealed that in the ex-ADU UO_2 powder there is little effec by ball-milling on the decrease of size because of its fine particles, and that ex-AUC UO_2 powders which were finely milled by the ball-mill treatment are rearranged and forced to be filled into pores between less ball-milled particles. This, as mentioned above, agrees with the behavior of the variation in the pore volume of the green pellet. That is, in the case of the ex-ADU UO_2 green pellet, the difference of pore volume between the as-received and the ball-milled powder is small, while in the case of the ex-AUC UO_2 green pellets, the pore volume of the ball-milled powder is smaller than that of the as-received powder. The total pore volume of the ex-ADU UO_2 green pellet is markedly larger than that of the ex-AUC UO_2 green pellet, though the pore size of the former is smaller than that of the latter.

3.3. Effects of Ball-mill Treatment on the UO_2 Sintering

Fig. 8 shows the relationship between sintered density and green density of ex-AUC UO_2 (as-received and 4-hr ball-milled powder) and ex-ADU UO_2 (as-received and 4-hr ball-milled powder). The sintered density increased as the green density increased regardless of powder type. It also shows that the sintered density of the ex-ADU UO_2 pellet was markedly larger than that of the ex-AUC UO_2 pellet, though the green density of the former was smaller than that of the latter under the same compaction pressure(see Fig. 7). And in the case of ex-ADU UO_2, the ball-mill treatment had no effects on the increase of sintered density, while in the case of ex-AUC UO_2, the effects of ball-mill resulted in an increase of sintered density. It can be considered that the increase of sintered density has a closer relation with the pore size of the green pellet, indicating that ex-ADU UO_2 green pellets have fine pores which can easily be annihilated during sintering, while the ex-AUC UO_2 green pellets have relatively large pores which still remain after sintering.

4. Conclusions

Results of the experiments described in this work lead to the following conclusions :

1) There was no effect of ball-mill treatment on the size reduction for ex-ADU UO_2 powders having size of about 0.9 μm, indicating that efficiency of the ball-mill treatment is limited for size reduction less than 1 μm in UO_2 powder.
2) There are marked effects of ball-mill treatment on the powder having relatively large sizes as follows:
   i) Some characteristics of powder, that is, specific surface area, particle size and bulk density decreases as the ball-milling time increases.
   ii) The pore sizes of pellet are smaller and their distribution is narrower as the ball-milling time increases.
   iii) The green density and sintered density of a pellet increases as the ball-milling time increases.

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