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Effects of Nb_2O_5 and UO_2 Powder Types on Sintered Density and Grain Size of the UO_2 Pellet

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Abstract

The variation of sintered density and grain size in ex-AUC, ex-ADU and granulated ex-ADU UO_2 pellets in which 0.1~1.0wt% Nb_2O_5 were doped were examined. Pellets were sintered in an atmosphere of H_2 at 1700℃ for 4h. All the specimens tested showed more than 94% T.D.(Theoretical Density). Sintered density decreased with increasing the amount of Nb_2O_5. Powder types had little influence on the sintered density. Pore size distribution was shifted to the larger ones as Nb_2O_5 was added. The increase of total pore volume and grain growth due to the addition of Nb_2O_5 were thought to be the cause of the sintered density decrease. The largest grain size was seen in the 1.0wt% Nb_2O_5 doped ex-AUC UO_2 pellets. Their average size was 13.9 μm.

1. Introduction

The development programs of nuclear fuel for high burn-up and long term have been progressed with the aim of increasing the economics of the nuclear power station. The study to reduce the fission gas release which is thought to be the most serious problem for the high burn-up by growing the grain size of the pellet is one of these programs. This research has been carried out actively in the several countries[1-4]. There are two methods to grow the grain size. One is by changing the sintering conditions and the other is by adding dopant element. However, the former method increases the production cost and need new facilities. So the latter has been recognized as a reasonable method to grow the grain size. As dopant elements, Nb_2O_5, TiO_2, MgO and Cr_2O_3 are suggested by the researchers [5-10]. A lot of experiments have been performed on these elements. Especially, in Japan[11], Germany [13] and England[12], such studies are active and many patents related to dopant materials have been already registered.

Among the additives described earlier, Nb_2O_5 has been reported as the best promising element to increase the grain size of the UO_2 pellet with maintaining the integrity of the fuel pellet. The characteristics of the pellet differ in accordance with the kinds of the UO_2 powders as well as the sintering conditions and additives. Currently, ex-ADU(Ammonium DiUranate) UO_2 powder for the fuel of the CANDU type reactor and ex-AUC(Ammonium Uranyl Carbonate) for the fuel of the PWR type reactor are used in Korea. Because the ex-ADU UO_2 powder has small size and low flowability, it is used after pre-compacting process. Up to now, the study on the grain growth of the UO_2 pellet has mainly focused on the effect of the additives. The influence of UO_2 powder types has not been considered. This study has been performed to understand the effects of Nb_2O_5 contents and UO_2 powder types on the variation of sintered density of the pellet and grain size.

2. Experimental

For this study, three kinds of powder, ex-AUC UO_2 powder, ex-ADU UO_2 powder and granulated ex-ADU UO_2 powder, were used. These powders are currently used to fabricate commercial nuclear fuel. To obtain the data on the characteristics of each powder, apparent density, specific surface area and O/U ratio were measured. UO_2 powders were blended for 24 hrs after adding 0.1, 0.3, 0.5 and 1.0wt% Nb_2O_5 to each powder to get homogenized powder. The mixed powders were compacted in the 10 mm diameter of die hole with the pressure of 4 ton/cm^2 using hydraulic press. After compaction, the diameter, height and weight of the green pellet were measured. Green density was calculated using these values. Green pellets were sintered at 1700℃ for 4hrs in H_2 atmosphere using electric heater with the heating rate of 450℃/hr and the cooling rate of 400℃/hr. The water immersion method was used to measure the sintered density. The sintered pellets were cut in the longitudinal direction and observed their microstructure after polishing. The size and distribution of pore were measured using image analyser. Grain sizes were obtained by a linear intercept technique.

3. Results and Discussion

Table 1 is a summary of the characteristics of each powder used in this study. The size of ex-AUC and granulated ex-ADU UO_2 powder were similiar to 10~50 μm but that of ex-ADU UO_2 powder was very small(most of it was under 4 μm). The apparent density of ex-ADU UO_2 powder was 1.47g/cm^3, and the smallest among the powders. The surface area of ex-ADU UO_2 powder showed slightly higher than the others. But its difference was small. Green density of these three powders showed similar values as 5.95$\pm$0.05 g/cm^3(53.8~54.7%T.D) Fig. 1 shows the variation of the sintered density with the amount of Nb_2O_5 and UO_2 powder types. There were no significant differences among these three kinds of powders and was a tendency to decrease with increasing the amount of Nb_2O_5. The sintered density variation by the addition of Nb_2O_5 was smaller in ex-AUC UO_2 powder than in the other two powders. The trend of the sintered density variation with the addition of Nb_2O_5 has not been clearly identified. Different results have been reported according to the researcher. Some researchers had reported that the sintered density increased with increase of the amount of Nb_2O_5 while the others told the contrary results[1,9,13,14,15].

K.C Radford[15] and a group of Mitsubisi Co. in japan[11] observed that the increase of the sintered density was about 0.25~8%T.D. when 0.1~1.0wt% Nb_2O_5 was added to the pure UO_2 powders. However, the other researchers such as J.B. Ainscough [9], H.Assmann[13] and J.C. Killen[1] reported the decrease of the sintered density by the addition of Nb_2O_5. As shown in Fig. 1, in this study, the sintered density decreased with increasing the addition of Nb_2O_5. However, all the Nb_2O_5 doped UO_2 pellets satisfied the limit values of the specification for the fabrication of commercial nuclear fuel(94% T.D.). Grain growth is greatly affected by the size and the distribution of the pore. According to W.D Kingery[16], the pore size distribution was shifted to the larger ones when large grains with small curvature grew by

Table 1. Properties of UO_2 Powders

	ex-AUC	ex-ADU	Granulated ex-ADU
Particle Size(μm)	10~50	<4	10~50
Apparent Density (g/cm^3)	2.31	1.47	2.34
O/U ratio	2.25	2.17	2.16
Specific Surface Area(m^2/g)	4.47	4.79	4.54

absorbing small grains. Pores located on small grain boundaries were combined together and became a large pore. If small pores combine together to become large pore and pore size distribution is shifted to the larger ones, total pore volume will increase and the sintered density decrease eventually. The variation of pore size distribution in accordance with the amount of Nb_2O_5 in the ex-AUC UO_2 sintered pellet is shown in Fig. 2. Large pore over 6μm is 0.87% in the pure UO_2 pellet, 1.09% in the 0.1 wt% Nb_2O_5 doped pellet, 1.5% in the 0.3 wt% Nb_2O_5 doped pellet, 1.63% in the 0.5 wt% Nb_2O_5 doped pellet and 2.19% in the 1.0wt% Nb_2O_5 doped pellet. It can be known that a large pore becomes dominant and the pore size distribution is shifted to the larger ones as increasing the amount of Nb_2O_5.

This trend can be identified more clearly from the two lines in Fig.2 which are the polynomial curve fits of pure UO_2 and 1.0%Nb_2O_5 doped UO_2 pellet. Fig.3 indicates the pore size distribution of ex-ADU UO_2 pellet. It shows similiar results to that of ex-AUC UO_2 pellet. In the case of 1.0wt% Nb_2O_5 doped ex-ADU UO_2 pellet, a larger pore than 6μm is 2.4% which is higher than 2.19% of ex-AUC UO_2 pellet. The width between fitting curves is wider than that in ex-AUC UO_2 pellet. It is coincident well with the results of the sintered density variation in Fig. 1. As shown in Fig. 4, the trend of the pore size distribution in the granulated ex-ADU UO_2 pellet is also simillar to that of ex-AUC UO_2 pellet. Fig. 5 shows the grain size variation of the pellets as the addition of Nb_2O_5. Grain size increases with increasing the amount of Nb_2O_5

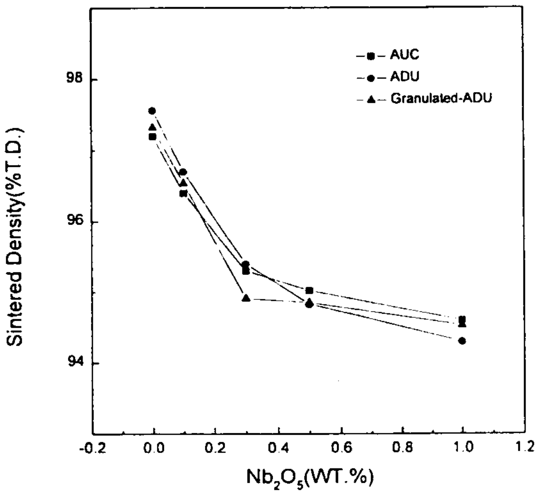

Fig. 1. Variation of the Sintered Densities of Nb_2O_5 Doped UO_2 Pellets

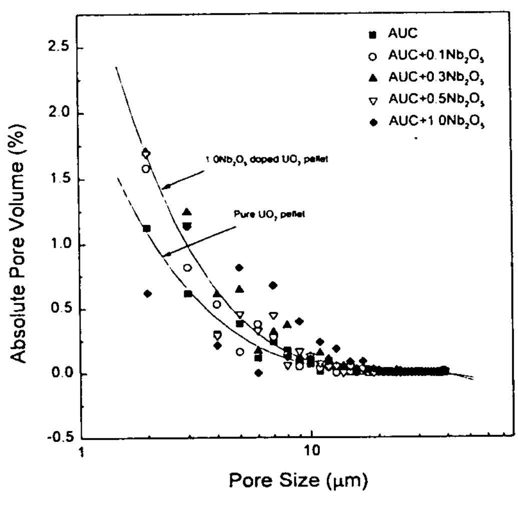

Fig. 2. Pore Size Distributions of UO_2 Pellets Produced by ex-AUC UO_2 Powder

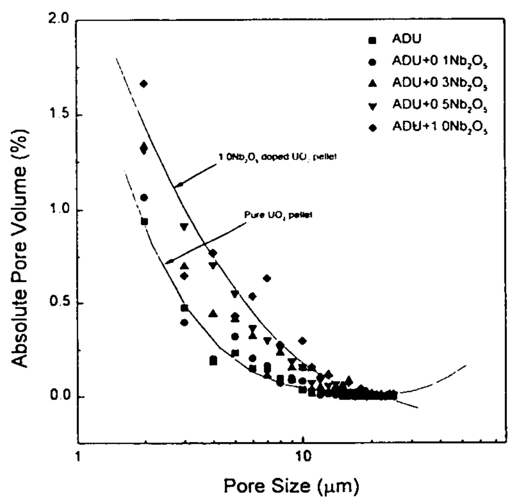

Fig. 3. Pore Size Distributions of UO_2 Pellets Produced by ex-ADU UO_2 Powder

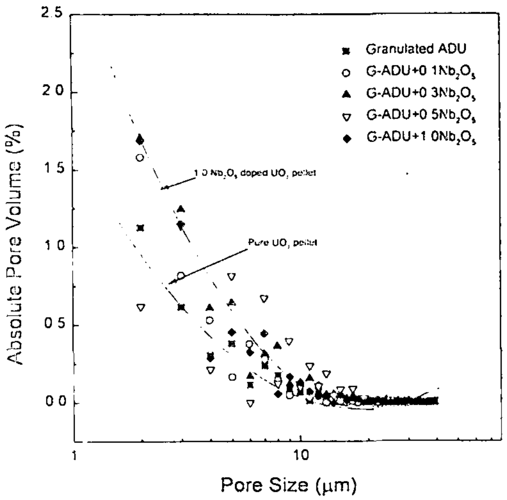

Fig. 4. Pore Size Distributions of UO_2 Pellets Produced by Granulated ex-ADU UO_2 Powder

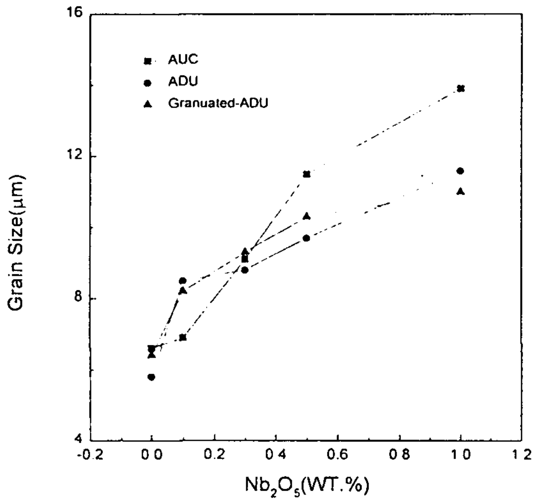

Fig. 5. Variation of the Grain Size of Nb_2O_5 Doped UO_2 Pellets

but powder types are not influenced by the grain size greatly. Average grain size of 1.0wt% Nb_2O_5 doped ex-AUC UO_2 pellets is 13.9 μm which is slightly larger than that of ex-ADU and granulated ex-ADU UO_2 pellet, which are 11.6 and 11 μm, respectively. Judging from the experiment results that Nb_2O_5 doped ex-AUC UO_2 pellet showed the smallest sintered density variation and the largest grain growth as the addition of Nb_2O_5, it can be concluded that the sinterability of the ex-AUC UO_2 powder is better than the other two powders. It seems that the granulating process has no effect on the grain growth.

The causes of sintered density decrease shown in the Nb_2O_5 doped UO_2 pellet are thought to be the increase of total pore volume and its size due to the coalescence of pore located at the grain boundary resulting from the grain growth by the addition of Nb_2O_5. According to the experimental results obtained by other researchers[11,15,17], the grain size of Nb_2O_5 doped UO_2 pellet is normally 20~30 μm. It is greater than the average grain size(13.9 μm) in this study. The grain growth of Nb_2O_5 doped UO_2 pellet is due to increase the point defects in the UO_2 pellet which make U-ion diffuse more rapidly. The prevailing defects in UO_2 pellet are oxygen vacancies and interstitials(an anti Frenkel-type defect structure) and the concentration of anion vacancies(oxygen vacancies) decrease with the addition of Nb_2O_5. This leads to increase the concentration of cation vacancies(Uranium vacancies) through Schottky equilibrium, which results in increasing the uranium diffusion coefficient and consequently the enhancement of grain growth. While Nb_2O_5 has a function to increase the grain size of UO_2 pellet, it also reduce the thermal conductivity of the fuel[18,19]. Therefore, it is very important to determine the optimum amount of Nb_2O_5 where the benefits is maximized while the side effect should be minimized. To do this, more concern and continuous study are required.

4. Conclusions

The effect of Nb_2O_5 in the range from 0.1 to 1 wt% on the sintered density and grain size of ex-AUC-, ex-ADU and granulated ex-ADU UO_2 pellet sintered in an atmosphere of H_2 at 1700℃ for 4h are as follows.

1) The sintered density decreasesd with the ad-

dition of Nb_2O_5, but the powder types did not have influenced on it greatly.

2) As Nb_2O_5 was added, pore size distribution of all the pellets were shifted to the larger ones due to the grain growth of the UO_2 pellet. Consequently, this leads to the decrease of the sintered density.

3) The grain size of the pellet increased with increasing the amount of Nb_2O_5.

4) 1.0wt% Nb_2O_5 doped ex-AUC UO_2 pellet showed the largest grain size and average grain size was 13.9 μm.

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