

Effects of Nb₂O₅ and UO₂ Powder Types on Sintered Density and Grain Size of the UO₂ Pellet

Ho Sik Yoo and Hyung Soo Kim

Korea Nuclear Fuel Company
150 Dukjin-dong, Yusong-gu, Taejeon 305-353, Korea

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Abstract

The variation of sintered density and grain size in *ex-AUC*, *ex-ADU* and granulated *ex-ADU* UO₂ pellets in which 0.1~1.0wt% Nb₂O₅ were doped were examined. Pellets were sintered in an atmosphere of H₂ at 1700 °C for 4h. All the specimens tested showed more than 94% T.D.(Theoretical Density). Sintered density decreased with increasing the amount of Nb₂O₅. Powder types had little influence on the sintered density. Pore size distribution was shifted to the larger ones as Nb₂O₅ was added. The increase of total pore volume and grain growth due to the addition of Nb₂O₅ were thought to be the cause of the sintered density decrease. The largest grain size was seen in the 1.0wt% Nb₂O₅ doped *ex-AUC* UO₂ 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, Nb₂O₅, TiO₂, MgO and Cr₂O₃ 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, Nb₂O₅ has been reported as the best promising element to increase the grain size of the UO₂ pellet with maintaining the integrity of the fuel pellet. The characteristics of the pellet differ in accordance with the kinds of the UO₂ powders as well as the sintering conditions and additives. Currently, *ex-ADU*(Ammonium DiUranate) UO₂ 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* UO₂ 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 UO₂ pellet has mainly focused on the effect of the additives. The influence of UO₂ powder types has

not been considered. This study has been performed to understand the effects of Nb₂O₅ contents and UO₂ 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 UO₂ powder, ex-ADU UO₂ powder and granulated ex-ADU UO₂ 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. UO₂ powders were blended for 24 hrs after adding 0.1, 0.3, 0.5 and 1.0wt% Nb₂O₅ 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/cm² 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°C for 4hrs in H₂ atmosphere using electric heater with the heating rate of 450°C/hr and the cooling rate of 400°C/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 UO₂ powder were similar to 10~50 μm but that of ex-ADU UO₂ powder was very small (most of it was under 4 μm). The apparent density of ex-ADU UO₂ powder was 1.47g/cm³, and the smallest among the powders. The surface area of ex-ADU UO₂ powder showed slightly higher than the others. But its difference was small. Green density of

these three powders showed similar values as 5.95 ± 0.05 g/cm³ (53.8~54.7%T.D) Fig. 1 shows the variation of the sintered density with the amount of Nb₂O₅ and UO₂ powder types. There were no significant differences among these three kinds of powders and was a tendency to decrease with increasing the amount of Nb₂O₅. The sintered density variation by the addition of Nb₂O₅ was smaller in ex-AUC UO₂ powder than in the other two powders. The trend of the sintered density variation with the addition of Nb₂O₅ 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 Nb₂O₅ while the others told the contrary results[1,9,13,14, 15].

K.C Radford[15] and a group of Mitsubishi Co. in Japan[11] observed that the increase of the sintered density was about 0.25~8%T.D. when 0.1~1.0wt% Nb₂O₅ was added to the pure UO₂ 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 Nb₂O₅. As shown in Fig. 1, in this study, the sintered density decreased with increasing the addition of Nb₂O₅. However, all the Nb₂O₅ doped UO₂ 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 UO₂ 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 Nb₂O₅ in the ex-AUC UO₂ sintered pellet

is shown in Fig. 2. Large pore over 6μm is 0.87% in the pure UO₂ pellet, 1.09% in the 0.1 wt% Nb₂O₅ doped pellet, 1.5% in the 0.3 wt% Nb₂O₅ doped pellet, 1.63% in the 0.5 wt% Nb₂O₅ doped pellet and 2.19% in the 1.0wt% Nb₂O₅ 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 Nb₂O₅.

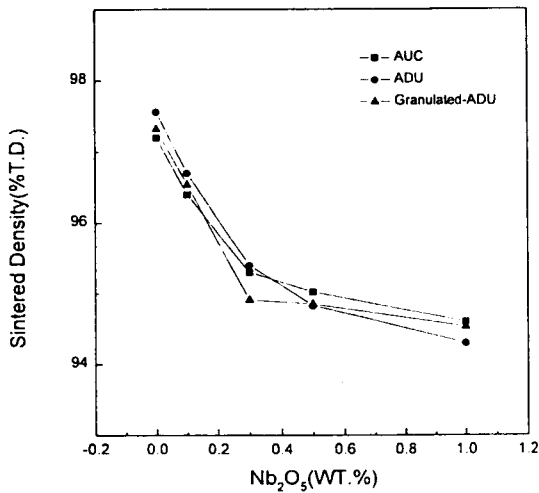


Fig. 1. Variation of the Sintered Densities of Nb₂O₅ Doped UO₂ Pellets

This trend can be identified more clearly from the two lines in Fig.2 which are the polynomial curve fits of pure UO₂ and 1.0%Nb₂O₅ doped UO₂ pellet. Fig.3 indicates the pore size distribution of ex-ADU UO₂ pellet. It shows similar results to that of ex-AUC UO₂ pellet. In the case of 1.0wt% Nb₂O₅ doped ex-ADU UO₂ pellet, a larger pore than 6 μm is 2.4% which is higher than 2.19% of ex-AUC UO₂ pellet. The width between fitting curves is wider than that in ex-AUC UO₂ 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 UO₂ pellet is also similar to that of ex-AUC UO₂ pellet. Fig. 5 shows the grain size variation of the pellets as the addition of Nb₂O₅. Grain size increases with increasing the amount of Nb₂O₅

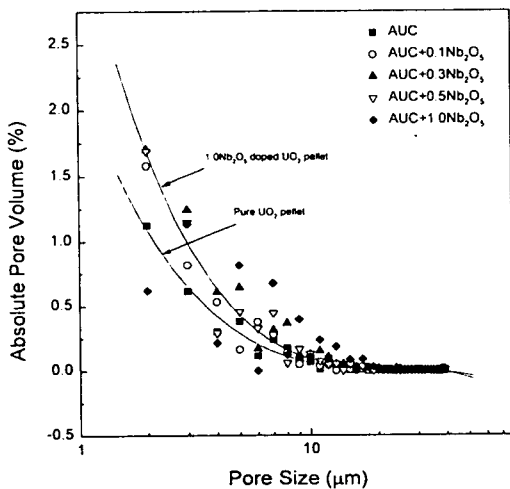


Fig. 2. Pore Size Distributions of UO₂ Pellets Produced by ex-AUC UO₂ Powder

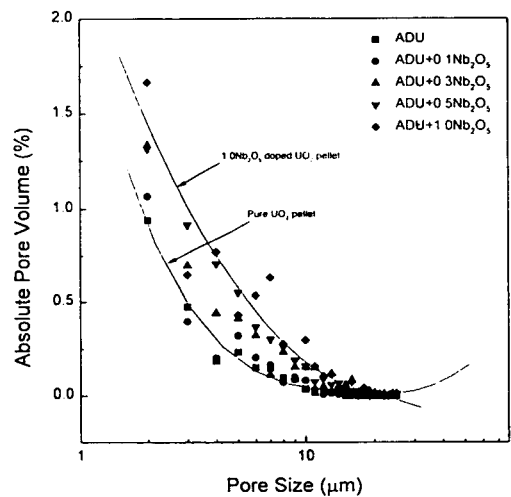


Fig. 3. Pore Size Distributions of UO₂ Pellets Produced by ex-ADU UO₂ Powder

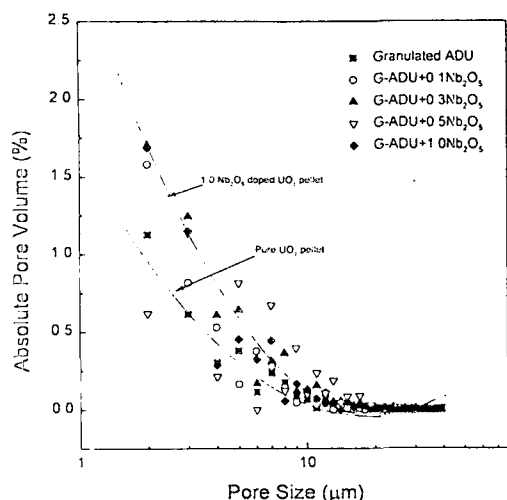


Fig. 4. Pore Size Distributions of UO₂ Pellets Produced by Granulated ex-ADU UO₂ Powder

but powder types are not influenced by the grain size greatly. Average grain size of 1.0wt% Nb₂O₅ doped ex-AUC UO₂ pellets is 13.9 μm which is slightly larger than that of ex-ADU and granulated ex-ADU UO₂ pellet, which are 11.6 and 11 μm, respectively. Judging from the experiment results that Nb₂O₅ doped ex-AUC UO₂ pellet showed the smallest sintered density variation and the largest grain growth as the addition of Nb₂O₅, it can be concluded that the sinterability of the ex-AUC UO₂ 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 Nb₂O₅ doped UO₂ 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 Nb₂O₅. According to the experimental results obtained by other researchers[11,15,17], the grain size of Nb₂O₅ doped UO₂ pellet is normally 20~30 μm. It is greater than the average grain size(13.9 μm) in this study. The grain growth of Nb₂O₅ doped UO₂ pellet is due to increase the point defects in the UO₂ pellet which make U-ion diffuse more rapidly. The prevail-

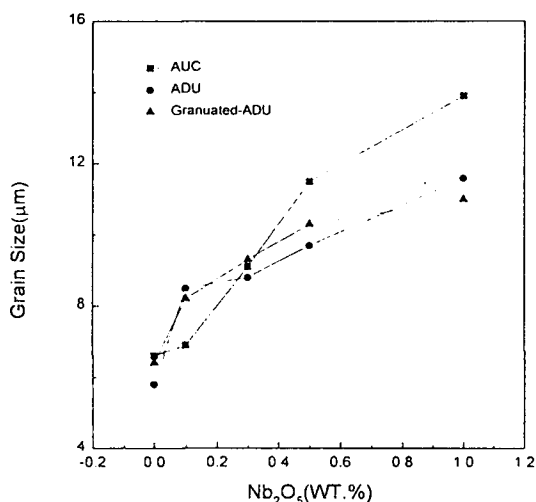


Fig. 5. Variation of the Grain Size of Nb₂O₅ Doped UO₂ Pellets

ing defects in UO₂ 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 Nb₂O₅. 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 Nb₂O₅ has a function to increase the grain size of UO₂ pellet, it also reduce the thermal conductivity of the fuel[18,19]. Therefore, it is very important to determine the optimum amount of Nb₂O₅ 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 Nb₂O₅ 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 UO₂ pellet sintered in an atmosphere of H₂ at 1700 °C for 4h are as follows.

- 1) The sintered density decreased with the ad-

dition of Nb₂O₅, but the powder types did not have influenced on it greatly.

- 2) As Nb₂O₅ was added, pore size distribution of all the pellets were shifted to the larger ones due to the grain growth of the UO₂ pellet. Consequently, this leads to the decrease of the sintered density.
- 3) The grain size of the pellet increased with increasing the amount of Nb₂O₅.
- 4) 1.0wt% Nb₂O₅ doped ex-AUC UO₂ pellet showed the largest grain size and average grain size was 13.9 μm.

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