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Microstructural Changes of AlOOH Doped UO_2 Pellet during the Annealing Process

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Microstructural changes of AlOOH doped UO_2 pellet after annealing up to 216 h have been observed and they were compared with those of the standard pellet. Grain and pore size of UO_2 pellet increased with the addition of AlOOH and its effect was still validated during annealing. Densification rate was reduced by the addition of AlOOH and it was attributed to coarsened pores with spherical shape. Grain and pore growth was stopped and density increase was the least after 144 h of annealing. The variation of pore size resulting from annealing has a linear relationship with that of grain size.

Key words: UO_2 pellet, Annealing, Densification, Pore, Grain

I. Introduction

In-pile densification of UO_2 pellet during the reactor operation has been a major concern to those who design nuclear fuel and operate atomic plant since it affects fuel rod integrity. W. Chubb[1] had reported in 1974 that densification was controlled by the microstructure of the fuel, particularly its pore size distribution and average pore size. He had concluded that sintering conditions determining the microstructure of pellet were the main factor that could control in-pile densification. In-pile densification has been believed to occur by the fission induced resolution of pores. The resolution of pores produces a dispersion of excess vacancies in the fuel and the migration of some of these excess vacancies to external surface results in local increase in density and corresponding dimensional changes. Therefore, it is important to control the microstructure of UO_2 pellet, especially, pores, to maintain the integrity of fuel rod during operation. As mentioned earlier, microstructure of UO_2 pellet strongly depends on sintering conditions. However, sintering variables such as temperature and time are directly related to the productivity so that other methods by which optimum microstructure of UO_2 pellet can be obtained without altering sintering conditions are highly recommended. The most promising way is to add dopant to UO_2. Up to now, massive studies on the effect of additives such as Nb_2O_5, MgO, TiO_2 and Al-compounds have been carried out.[2-5] Most of the studies have been concentrated on coarsening grain size of pellet since fission gas release is a prime concern to the researchers. Unlike other additives, Al-compounds have been used widely in commercial fuel since they are permitted to contain in UO_2 pellet as an impurity and their maximum allowable contents are higher than other elements. It has been known that Al-compounds increase grain size of pellet and decrease the amount of open porosity.[6] The effect of Al-compounds on grain growth is quite small compared to the other dopants and densification behavior of Al-compounds doped UO_2 pellet is little known. It is essentially needed to understand the microstructural changes of UO_2 pellet at the early stage of operation to predict densification. The densification behavior of UO_2 pellet during the reactor operation can be anticipated by observing the microstructural changes after annealing.

This work has been done to compare the densification behavior of AlOOH doped UO_2 pellet with that of the standard pellet. To do this, AlOOH doped UO_2 pellets were annealed up to 216 h at 1700°C. Densification behavior and microstructural changes during annealing were examined.

II. Experimental

1. Manufacturing of mixed powder

In this work, UO_2 powders produced by Dry Conversion process were used. The impurities and characteristics of undoped UO_2 powder were shown in Table 1 and 2. In order to simulate the commercial UO_2 pellet, U_3O_8, AZB as a pore former and zinc stearate as a lubricant were added as much as 12, 0.3 and 0.2 wt%, respectively. Mixing was carried out for 1.5 h in Turbula Mixer. The mixed powders including U_3O_8, pore former and lubricant were used as standard powders. When the standard powder was mixed with AlOOH powder, two-step mixing was performed to enhance the homogeneity. The standard powder was mixed with AlOOH with the ratio of 9 over 1 for 1.5 h in the first mixing, and in the second mixing step, the mixture was diluted with additional standard powder to get a final composition

Table 1. Characteristics of UO_2 Powder

Properties	Value
O/U ratio	2.046
Particle Size	<400 μm 100%
Specific Surface Area (m^2/g)	2.34
Apparent Density (g/cm^3)	1.1
Moisture Content (ppm)	1200

Table 2. Impurities Contents of UO_2 Powder

Impurity	Value (ppm)	Impurity	Value (ppm)
Al	0.8	Cr	1.3
B	0.2	Cu	<10
Bi	0.3	Fe	<20
Ca	<5	In	0.8
Cd	0.06	Mg	2.3
C	32	Mn	0.2
Cl	2	Mo	0.3
F	7	Ni	1.0
N	25	Pb	<5
Co	<5	Si	<20

and then mixed again for 1.5 h. AlOOH contents in the mixed powder were changed in the range of 0.06 to 5% by weight.

2. *Pelletizing*

The prepared powders were pressed to have green densities of 5.95±0.05 g/cm^3. The green pellets were sintered in a tube furnace at 1730°C for 5 h. The sintering temperature and time were selected to simulate the sintering conditions of commercial plant. The furnace was heated at the rate of 5°C/min and held at 700°C for 1 h to burn the lubricant out. Pure hydrogen gas was blown to keep the interior of the furnace in a reduced atmosphere. The flowing rate of H_2 gas was 20 ml/min.

3. *Annealing*

After sintering, all the sintered pellets were annealed at 1700°C up to 216 h. Annealing process was performed on the same condition as the sintering process except temperature. One sample was taken out every 24 h to observe microstructural changes of the pellet.

4. *Measuring properties*

Sintered density and open porosity were measured using immersion method. In all cases the densities were reported as a percentage of the theoretical density of UO_2 (10.96 g/cm^3). One pellet from each condition was sectioned longitudinally and polished to observe microstructure. For measuring grain size, thermal etching was performed at 1250°C for 1.5 h. Pore size and distribution was measured using image analyzer(LECO 2000). The surface to spatial conversion of the measured two-dimensional pore size and distributions was made by application of the Saltykov[7] method for spherical particles with logarithmic size classification. Grain size was determined by a linear intercept method.

III. Results and Discussion

Fig. 1 shows the density variation of AlOOH doped UO_2 pellet as a function of AlOOH contents. Density decreased with increasing AlOOH content and the reduction rate was greater in the pellet including AlOOH below 0.1 wt% than the others. In case of 0.06 wt% AlOOH doped pellet, density was reduced as much as 0.5 wt% in comparison with the standard pellet. It is thought that the main cause of density decrease is the difference of theoretical density between AlOOH and UO_2. Another important factors to decide pellet density are the size and amount of pores existed in the sintered pellet. Pore content and size of pellet have made a decisive role to determine the in-pile densification behavior of pellet during the operation. It has been identified from this experiment that AlOOH has influenced on changing

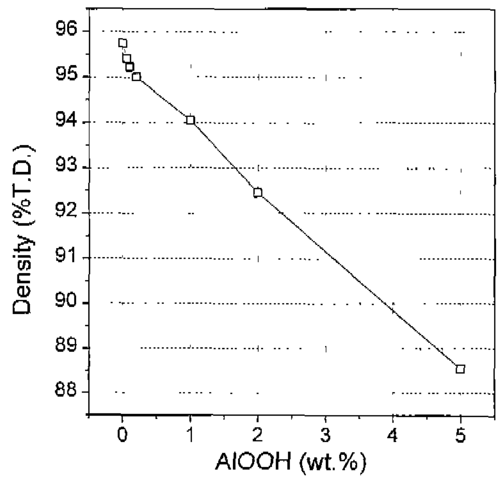

Fig. 1. Effect of AlOOH addition on sintered density of UO_2 pellet.

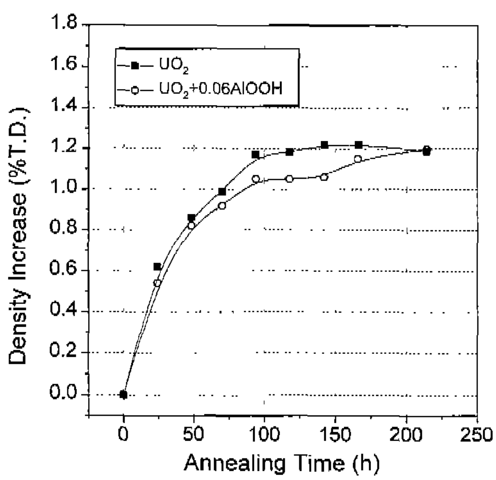

Fig. 2. Variation of density with annealing time.

pore size of UO_2 pellet. By the addition of 0.06 wt% AlOOH, pore grew to 3.9 μm from 3.1 μm. Therefore, pore growth is also contributed to decrease density.

The variation of density during annealing is shown in Fig. 2. It can be clearly seen that the densification behavior of AlOOH doped pellet is quite different from the standard pellet. The densification rate of AlOOH doped UO_2 pellet is lower than that of the standard pellet. Densification of pellet during the operation occurs mainly due to the removal of pores especially smaller than 1 μm. In the case of AlOOH doped UO_2, oxygen and hydrogen elements would be evaporated or moved into UO_2 matrix interestitially and the remaining part reside at the grain interior or boundary during sintering process. Remained part of AlOOH hampers the movement of pore and pores will be assembled. Pores have been coarsened by the coalescence of these small pores. It can be seen from Fig. 3 that pores growth during annealing is proceeded. Pore growth rate is slightly higher in AlOOH doped UO_2 pellet than in the standard pellet due to Al-bearings of AlOOH which impede the movement of small pores and facilitate the coalescence of pores. Average pore size of UO_2 pellet containing 0.06 wt% after annealing for 144 h is 9 μm, compared to 6.5 μm of the standard pellet. Pore size and morphology changes due to annealing are shown in Fig. 4 and 5. It can be clearly seen the effect of AlOOH doping on pore size and shape of the pellet. In addition to increase pore size, AlOOH doping changes pore shape to spherical. With regard to densification, pore with spherical shape is more favorable than any other shape pore because it is hard to be removed.

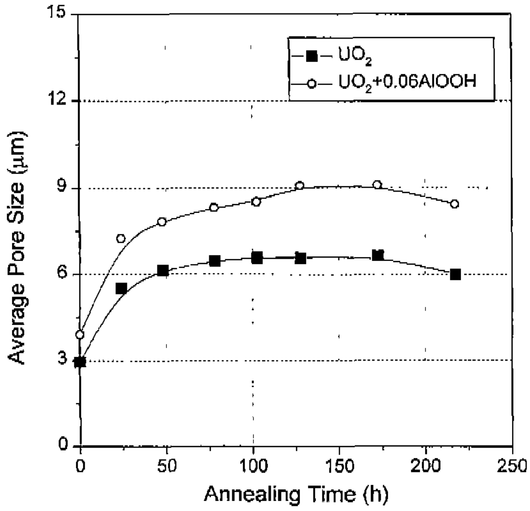

Fig. 3. Variation of average pore size of UO_2 pellet with annealing time.

AlOOH doping has also effect on increasing grain size of pellet. However, its effect was not greater than expected,

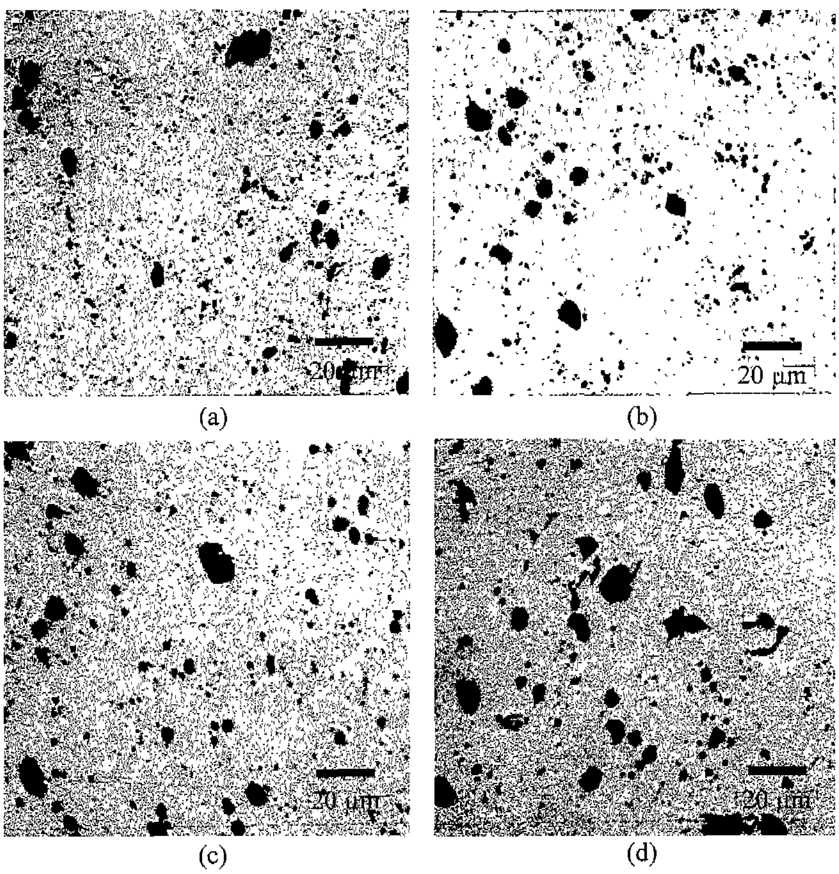

Fig. 4. Microstructure of the standard UO_2 pellet with various annealing times. (a) as sintered, (b) 24 h, (c) 96 h and (d) 144 h.

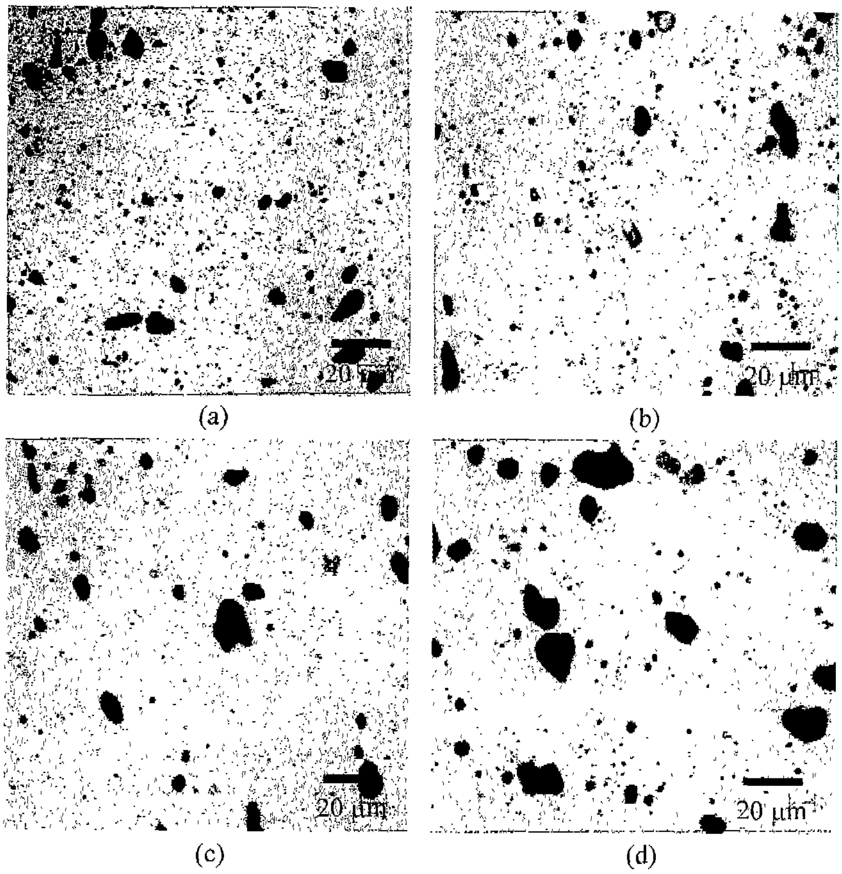

Fig. 5. Microstructure of 0.06 wt% AlOOH doped UO_2 pellet with various annealing times. (a) as sintered, (b) 24 h, (c) 96 h and (d) 144 h.

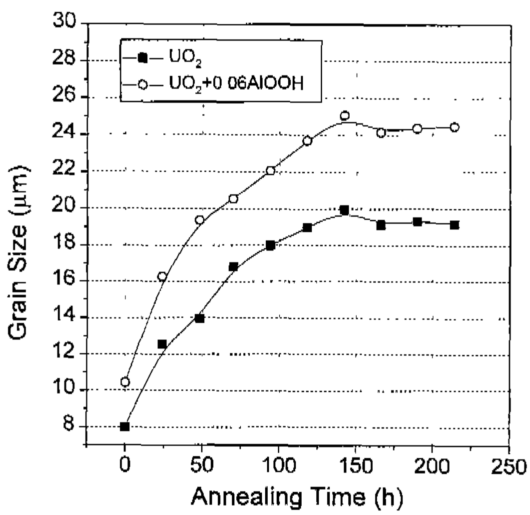

Fig. 6. Variation of grain size of UO_2 pellet with annealing time.

only a small increase of grain size can be observed. It is believed that oxygen atoms dissociated during sintering lead to grain growth by increasing the concentration of uranium vacancies through schottky equilibrium. Fig. 6 shows the grain size variation of pellet during annealing. As like in pore growth, AlOOH doped UO_2 pellet shows higher grain growth rate than the standard pellet. No further grain growth could be seen after annealing for 144 h. Grain was coarsened up to 25 µm in case of 0.06 wt% AlOOH added. Grain growth of AlOOH doped UO_2 pellet in accordance with annealing is shown in Fig. 7. It can be clearly seen in this picture that pore of the pellet including AlOOH has

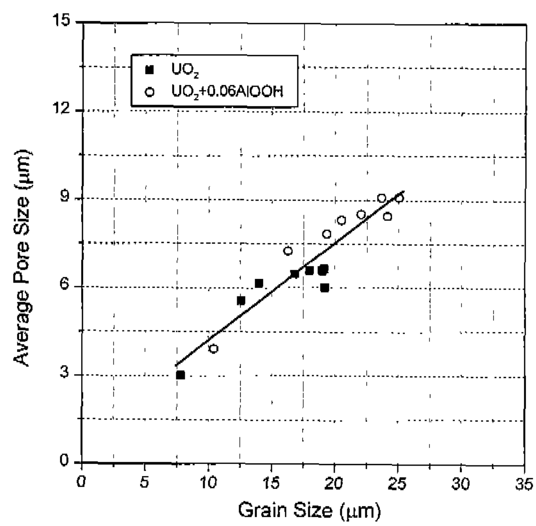

Fig. 8. Relationship between average pore and grain size in undoped UO_2 and 0.06 wt% AlOOH doped UO_2.

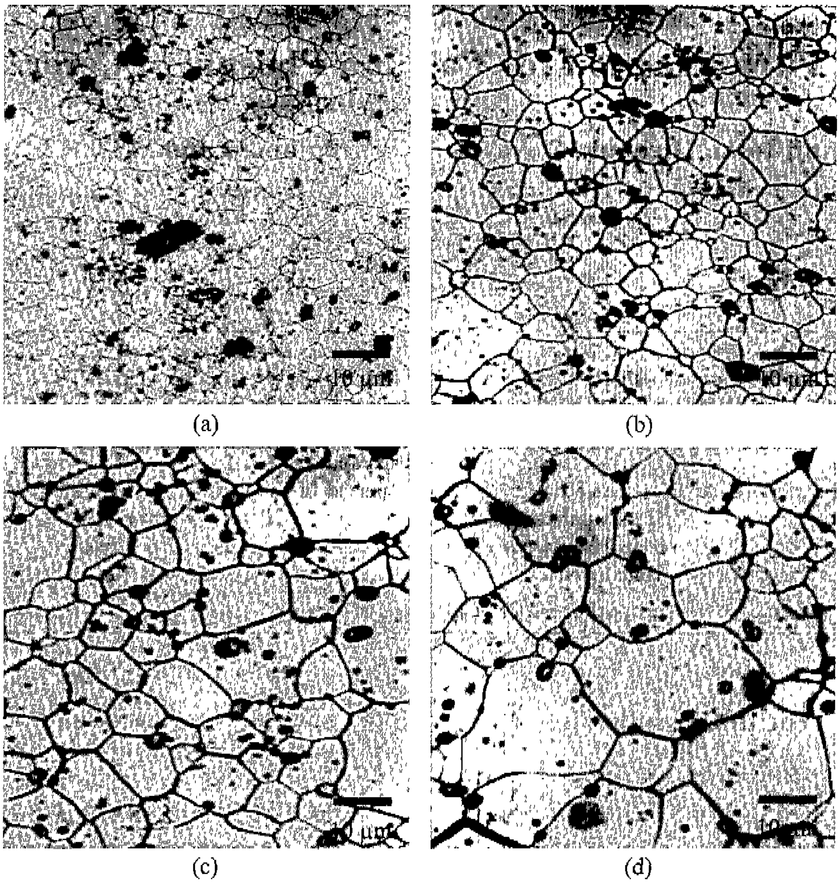

Fig. 7. Microstructure of 0.06 wt% AlOOH doped UO_2 pellets with various annealing times. (a) as sintered, (b) 24 hr, (c) 96 hr and (d) 144 hr.

round shape and most of them are located in the grain. It is thought that there must be a close relation between pore and grain growth. In order to find the relationship between pore and grain, each step of pore and grain size which were classified by annealing time were compared as shown in Fig. 8. As expected, pore size has a linear relationship with grain size. Coarsening of grains is considered as the process of coalescence of grains and combining of pores should be followed during this process. Accordingly, grain growth leads to pore growth.

It can be concluded from the above results that AlOOH facilitate the coarsening of pore and grain of the pellet and its effect is still validated during annealing.

IV. Conclusion

AlOOH doped UO_2 pellet was annealed for up to 216 h and the following results were obtained.

1. Densification was stopped after 144 h of annealing due to pores existed at the interior of grain.

2. Densification rate was reduced by the addition of AlOOH and it was ascribed to the coarsened pores with spherical shape which were more resistant to dissolve than small pores with irregular shape.

3. The behavior of pore during annealing was closely connected with that of grain and their size had a linear relationship.

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