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A Study on the Characteristics of AlOOH Doped UO_2 Pellet

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Abstract

Characteristics of AlOOH doped UO_2 pellet have been examined. Sintered density decreased linearly with increasing the contents of AlOOH added. Open porosity was also reduced due to the addition of AlOOH but it was independent upon the quantity of AlOOH. AlOOH increased the grain size of UO_2 pellet up to about 10.4 μm. However, more addition of AlOOH than 0.06wt% didn't lead to further coarsening of grain. The degree of densification of AlOOH doped UO_2 pellet resulting from annealing for 216 hr was similar to dopant free UO_2 pellet as 1.2% T.D.. Pores of UO_2 pellet containing AlOOH had grown and turned into spherical shape after annealing. The maximum grain was obtained after annealing for 144 hr and its size was 25 μm.

1. Introduction

The experiments regarding the effect of additives on UO_2 pellet which has been used in atomic reactor as a fuel have been carried out since long time ago. Additives such as TiO_2[1], Nb_2O_5[2], MgO[3] and Al compounds[4,5] are known to have beneficial effect on the pellet. Especially, Nb_2O_5 and Al compounds had been considered as the most promising dopant due to their roles in the pellet to increase the creep rate which is very helpful to prevent PCI(Pellet Cladding Interaction) and to reduce the open porosity, respectively, as well as coarsening the grain.[1,2] BNFL had conducted massive studies on the niobia doped UO_2 pellet since 1970s and obtained positive results.

Different from other additives, Al compound has been used to produce commercial UO_2 pellet. Siemens had substituted ADS for conventional lubricant, zinc-stearate to enhance the properties of UO_2 pellet as well as to reduce defect pellets which occurred in the process of compacting. In case of Gadolinia-Urania pellet used as a burnable absorber in the PWRs and BWRs, Al compounds are essential additives not only to increase the sintered density but also to coarsen the grain size. In particular, Germany and Japan have been actively performed the experiments on the Al compound. Nowadays, they are deeply concerned with the effect of secondary additive on the Al compound doped UO_2 pellet such as SiO_2. In contrast to other countries, only a Lab studies were made and there was no attempt to apply Al compound to produce commercial UO_2 pellet in our country. In order to use Al compound in the UO_2 pellet as a dopant, a lot of basic data about the effect of Al compound on the UO_2 pellet should be accumulated. Experimental results obtained by other countries can be reference but can not directly apply to our manufacturing process. In addition, most of the data were acquired from ex-AUC UO_2 powder, so they would be much different from ex-DC(Dry Conversion) UO_2 powder.

This work has been undertaken to understand the influence of AlOOH on DC UO_2 pellet. Characteristics of UO_2 pellet as a function of AlOOH content such as sintered density, open porosity and microstructure were examined. To observe the microstructural stabilities of AlOOH doped UO_2 pellet caused by thermal energy, annealing test at 1700°C for 216 hr was carried out and analyzed the variation of the pellet properties due to annealing.

2. Experimental

In this study, UO_2 powders manufactured by DC process in KNFC were used. AlOOH in the range of 0.06 to 5 wt% was added as a dopant in the UO_2 powder. Mixing was performed by the two steps in order to enhance the homogeneity of AlOOH in the UO_2 powder. The same amount of AlOOH with UO_2 powder was mixed in the first step for 30 minutes and the mixed powder was diluted with additional UO_2 powder for 90 minutes until final composition was obtained. The mixed powders were pressed to make green pellets having densities of $6.0\pm0.5 g/cm^3$. The green pellets were sintered in pure H_2 atmosphere at 1730°C for 5hr. Immersion method was used to measure sintered density and open porosity. Annealing tests were carried out at 1700°C in $50H_2$-$50N_2$ atmosphere up to 216 hr. One pellet was taken in every 24hr to observe the microstructural change of pellet caused by annealing. One pellet of each condition was mounted, polished and examined ceramographically. Thermal etching was performed to see grain boundary in CO_2 atmosphere at 1300°C for 90 minutes. Grain size was measured by image analyzer.

3. Results and Discussion

The variation of sintered density of UO_2 pellet as a function of AlOOH contents added is shown in Fig. 1. As expected, density decreased linearly with increasing AlOOH contents. Density of UO_2 pellet containing 5wt% AlOOH is reduced to 88.5%T.D. in comparison with 95.7%T.D. of UO_2 pellet without AlOOH. It is thought that this is attributed to lower theoretical density and partial evaporation of AlOOH.

The fraction of open porosity in the UO_2 pellet decreased with the addition of AlOOH as shown in Fig. 2. Although absolute quantities of reduced open porosity is quite small, it must be true that AlOOH is effective to decrease open porosity. It seems that AlOOH contents have no great influence on decreasing open porosity. There is no much difference in the fraction of open porosity between 0.06 and 0.2wt% AlOOH doped UO_2 pellet. As shown in Fig. 3, the grain size of UO_2 pellet containing 0.06wt% AlOOH has grown to 10.4 ㎛ compared to 7.56 ㎛ of UO_2 pellet. Addition of AlOOH more than 0.06wt% was not contributed to more grain growth. UO_2 pellet including 0.2wt% AlOOH has similar grain size as 0.06wt% AlOOH doped pellet. Therefore, it can be concluded that small addition of AlOOH is sufficient to improve the microstructural properties of UO_2 pellet. Since Al element is permitted to include in the commercial UO_2 pellet up to 250 ppm as an impurity, the applicability of Al compounds as a dopant in the pellet is much higher than other additives.

Thermal stability of UO_2 pellet is important since UO_2 pellet is burnt at high temperature during operation. Accordingly, observing microstructural change of the pellet after annealing is very useful to predict the behavior of the pellet during operation. The commercial pellets are required to meet the UO_2 specification in which resintered density of UO_2 pellet should not exceed ceratin value. Density variation of the pellet with annealing time is shown in Fig. 4. Density increases exponentially until the annealing time of 144 hr in both specimens. But, in case of the pellet containing 0.06wt% AlOOH, densification was not proceeded from 144hr and it could not be seen further density increase by annealing. On the contrary, additive free UO_2 pellet was densified continuously with annealing time over 144 hr. Fig. 5 shows the degree of densification with annealing time. Both specimens were densified up to about 1.2% T.D. after 216 hr. The densification behavior of the pellet is thought to be closely connected with pore morphology. As can be seen in Fig. 7, pores of 0.06wt% AlOOH doped UO_2 became large and turned into spherical shape from irregular as annealing was proceeded. Spherical pore is more stable than other shape of pore so it is hard to remove by annealing. In general, pore removing is the main cause of densification. Therefore, it is thought that pore coarsening and morphology change of pore to spherical shape due to annealing were attributed to a halt of densification which could be seen in AlOOH doped UO_2 pellet after annealing time over 144 hr as can be seen in Fig.5.

The grain size variation of the pellets with annealing time is shown in Fig. 7. Grain growth can be seen and the maximum grain was obtained in UO_2 pellet containing AlOOH after annealing for 144 hr. The maximum size was 25 μm in comparison with 20 μm of UO_2 without AlOOH and further annealing did not lead to more increase the grain size of the pellet. Grain growth occurred by the movement of grain boundary and grain would stop coarsening if there were inhibators which prevented grain boundary from moving. It has been known[6] that pore controls grain growth in UO_2 and its mobility is reciprocal to $(\text{pore radius})^2$. Therefore, pore growth would retard the movement of grain boundary as can be seen in Fig. 8. Pore growth due to annealing, consequently, results in ceasing the grain growth.

4. Conclusion

1) The density of UO_2 pellet decreased linearly with increasing the contents of AlOOH added.
2) AlOOH had an effect on reducing open porosity and coarsening the grain of the UO_2 pellet but they were not dependent upon the contents of AlOOH.
3) As a result of annealing test, it was revealed that AlOOH made UO_2 pellet more stable in longer annealing time through the change of pore morphology to sphere.
4) Grain of the pellet had coarsened by annealing and the largest grain was obtained after annealing for 144 hr.
5) From the above results, it can be deduced that AlOOH has a beneficial effect on the in-pile behavior of UO_2 pellet

5. References

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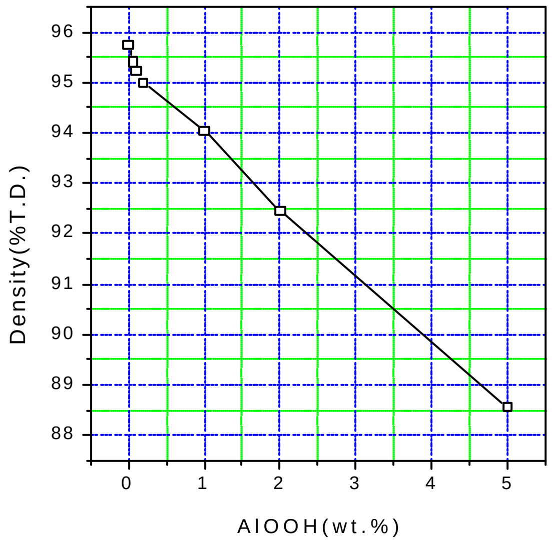

Fig. 1. Density variation of UO_2 pellet with AlOOH content

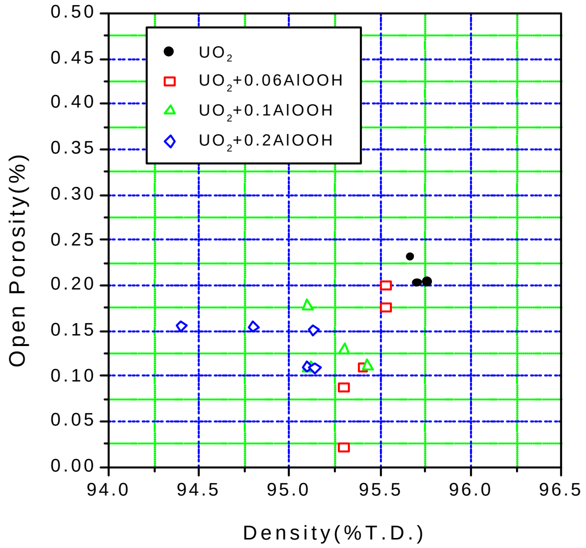

Fig. 2. Effect of AlOOH contents on open porosity

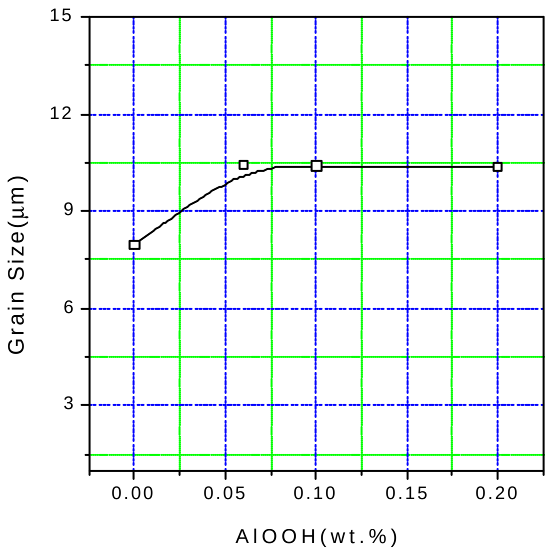

Fig. 3. Grain size variation of UO_2 pellet with AlOOH contents

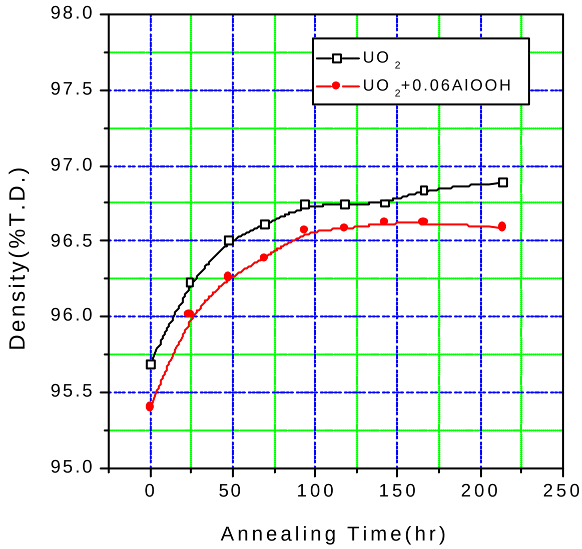

Fig. 4. Effect of annealing time on density of pellet

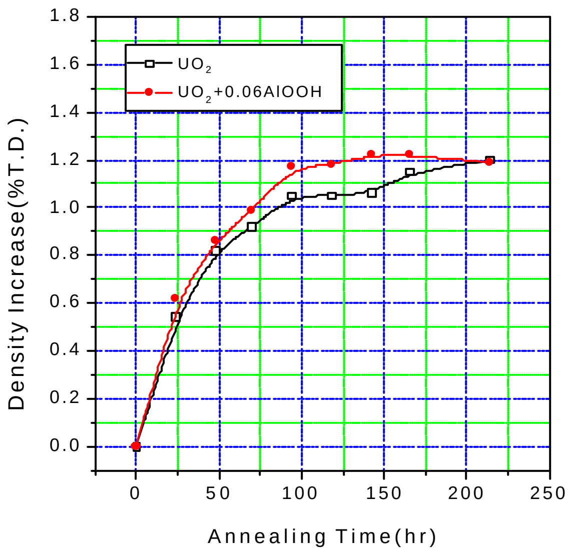

Fig. 5. Density increase with annealing time

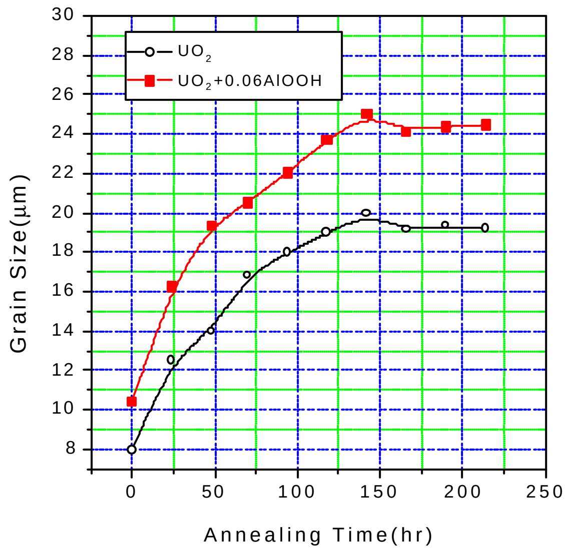

Fig. 6. Grain growth with annealing time

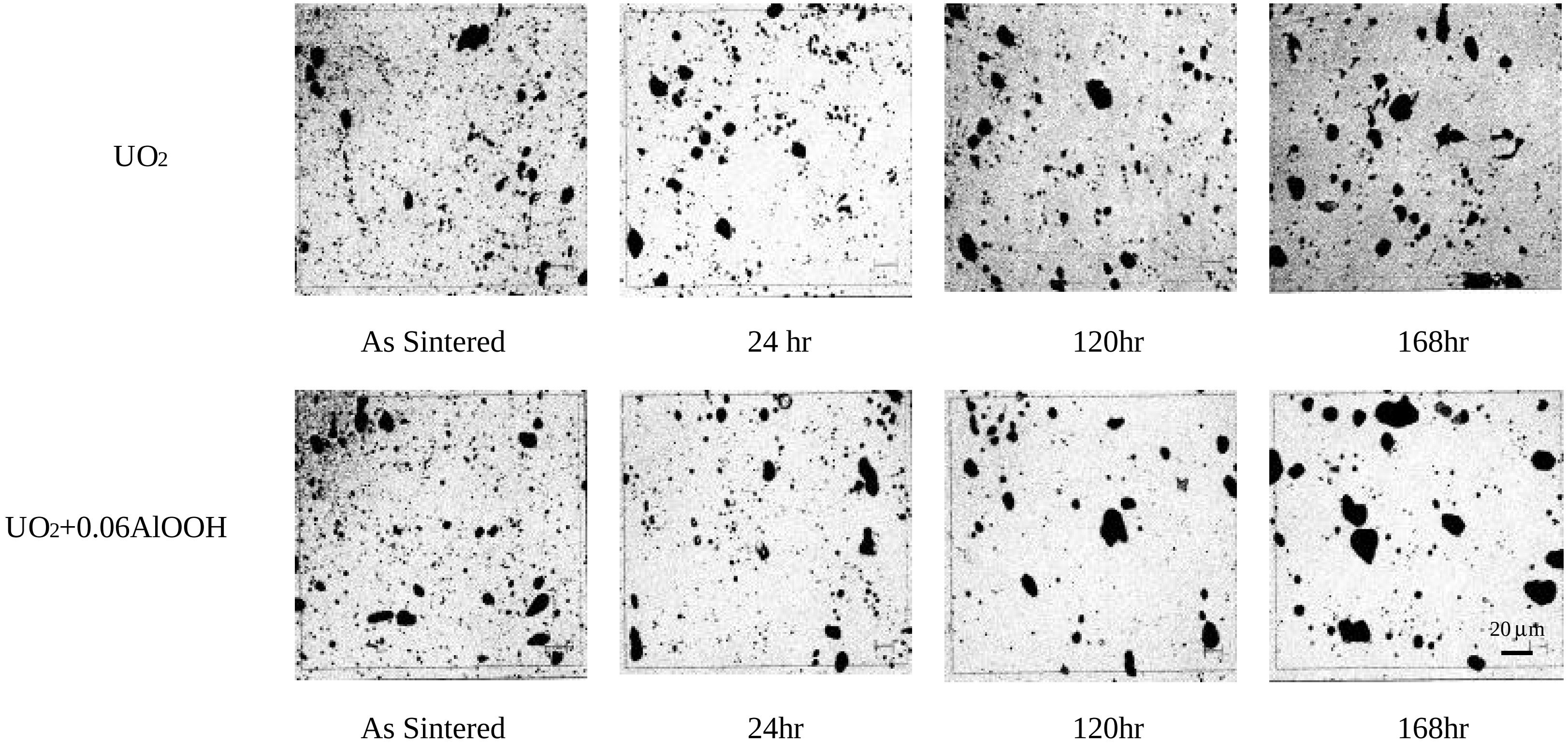

Fig. 7. Pore structure changes of pellet due to annealing

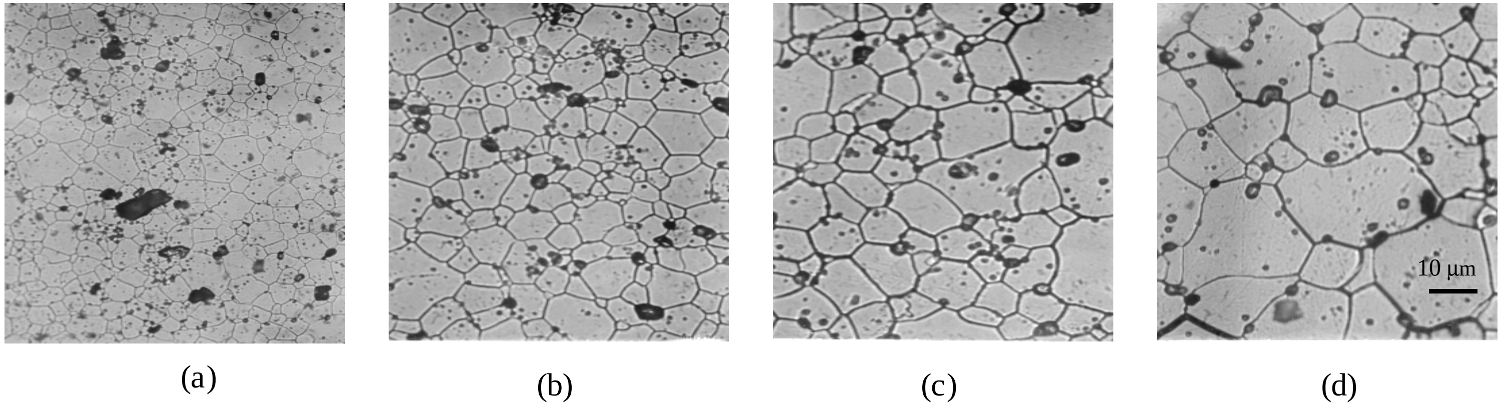

Fig. 8. Microstructure changes of 0.06AlOOH doped UO_2 pellet
(a) as sintered (b) annealed for 24hr
(c) annealed for 120hr (d) annealed for 168hr