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Effect of AlOOH on the microstructure of UO_2 pellets

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Abstract

A mechanism of reducing the open porosity and coarsening the grain size of UO_2 by the addition of AlOOH has been investigated. X-ray diffraction experiments showed that oxygen atoms released by the dissociation of AlOOH during sintering moved into the UO_2 matrix, resulting in the transformation of UO_2 to U_4O_9 at high concentrations of AlOOH. The excess oxygen atoms raised the grain size due to the increase of uranium vacancies through Schottky equilibrium. It is suggested that the Al-containing components produced by AlOOH dissociation were located at the grain boundaries with small pores. The presence of the Al-containing components at the grain boundaries hampered the movement of pores and led to the decrease of open porosity.

1. Introduction

For the improved efficiency of nuclear power plants, an increase of burnup up to 50–60 MWD/MTU with a long-term cycle has been considered. It has been widely known [1] that UO_2 pellets with large grain size and minimum open porosity are required for the desired high burnup fuel performance. There are several methods to modify the microstructure of UO_2 pellets by adding additives and changing the sintering conditions. Many experiments have been performed to investigate the effects of oxides like TiO_2 [2], Nb_2O_5 [3,4] and MgO [5,6], which were known to increase the grain size of UO_2. However, UO_2 containing such dopants has not yet been commercially used. Unlike other additives, Al compounds [7–9] have been used as dopants in the commercial UO_2 manufacturing process. It is known that Al compounds play a role in reducing open porosity and increasing grain size. For the urania–gadolinia system used as a burnable poison in BWR and PWR reactors, Al compounds have been added in a certain amount to increase grain size. SiO_2 and TiO_2 were recently added to the Al-compound-doped UO_2 as secondary additives [10]. Unlike other secondary additives, silicate is known to modify the grain boundary characteristics by forming a glassy phase at the grain boundary, which promotes sintering. Though many studies have been carried out, the role of Al compounds in the UO_2 pellet is not clearly understood.

The objective of the present study is to investigate the effect of the AlOOH additive on UO_2 pellet characteristics and to elucidate the correlation between the AlOOH additive and the open porosity as well as the grain size of UO_2 pellets. A possible mechanism is also discussed.

2. Experimental procedure

UO_2 powders prepared by a dry conversion process were used in this study. AlOOH (concentration in the range of 0.06–0.5 wt%) was added to UO_2 powders. In order to enhance the homogeneity of UO_2 powder doped with AlOOH, mixing was carried out in two steps. Firstly, the same amount of AlOOH and UO_2 powder was mixed for 40 min, and then the mixed powders were diluted with additional UO_2 powders until the desired composition was obtained. Secondly, an additional mixing was performed for 90 min. The final amounts of AlOOH in the mixed powders were 0.06, 0.1, 0.2, and 0.5 wt%, respectively. The mixed powders were

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pressed to make green pellets having densities of 6.0 ± 0.05 g/cm^3. The green pellets containing AlOOH were sintered at various times and temperatures under pure H_2 atmosphere, such as 1700°C – 12 h, 1730°C – 8 h, 1750°C – 5 h, and 1730°C – 5 h, in order to investigate the effects of sintering conditions and additive amounts on the properties of the UO_2 pellets.

Both sintered density and open porosity were measured by the immersion method. One pellet of each composition was mounted, polished and examined ceramographically. Thermal etching in carbon dioxide atmosphere at 1250°C was performed for 90 min to reveal grain boundaries. Aluminium distribution in the pellet was analyzed using an electron probe microanalyzer (EPMA) in conjunction with scanning electron microscopy (SEM). The grain size of the pellets was determined using the linear intercept method. X-ray diffraction (XRD) measurements were carried out using monochromatic Cu K_α radiation. Additional specimens containing 2 and 5 wt% AlOOH were prepared for the XRD experiment in order to understand the influence of AlOOH on the microstructure of UO_2 pellets.

3. Results

Most dopants reduce the sintered density of the pellet. AlOOH-doped UO_2 pellets also show increasingly lower density, as shown in Fig. 1. Density was reduced by as much as 0.5% TD when 0.06 wt% AlOOH was added. Density drop with increasing AlOOH concentration can be understood by the fact that the theoretical density of AlOOH is much lower than that of UO_2. Fig. 2 shows open porosity variation as a function of AlOOH contents and densities. It is certain that the AlOOH addition decreases the open porosity of UO_2, but the degree of reduction of open porosity is not greater than expected. It is well known that the amount of open porosity is inversely proportional to the sintered density. However, the open porosity of AlOOH-doped pellets is not dependent upon density in the present work. Therefore, the addition of AlOOH appears to cause a measurable decrease in open porosity, but the

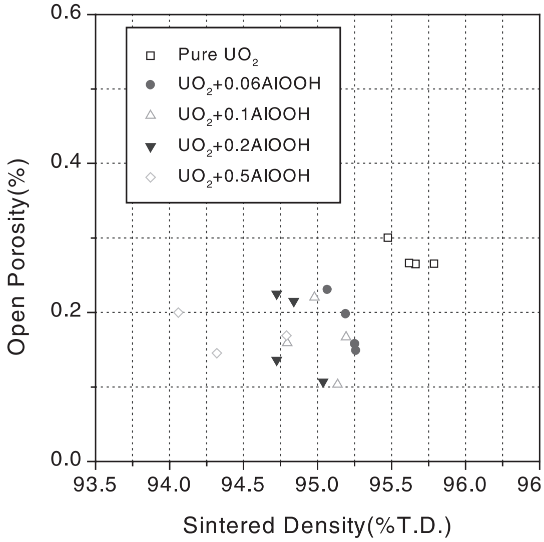

Fig. 2. Effect of AlOOH on the amount of open porosity in UO_2.

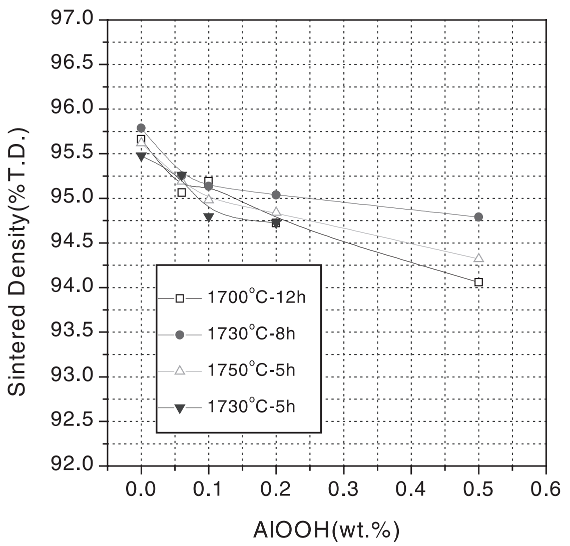

Fig. 1. Sintered density of AlOOH-doped UO_2.

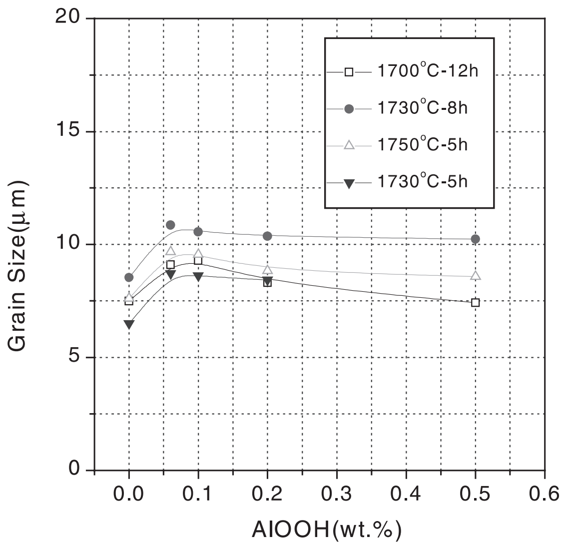

Fig. 3. Variation of grain size of UO_2 due to the addition of AlOOH.

degree of reduction is insensitive to AlOOH contents and densities. An increase of grain size is another important effect of AlOOH on the UO_2 pellet (Fig. 3). Although the coarsening of grains is not greater than expected, the grain size of the pellets increases with the addition of AlOOH. The grain growth of pellets is not dependent upon the contents of AlOOH when the AlOOH added is more than 0.06 wt%, as shown in Fig. 3.

4. Discussion

Excess oxygen atoms formed as a result of the dissociation of AlOOH during sintering may move to interstitial sites in the UO_2 matrix. The oxygen-to-uranium ratio of some areas of the pellet increases by absorption of these excess oxygen atoms. It is believed that the UO_2 crystal structure transforms to the U_4O_9 structure if sufficient oxygen atoms are supplied. Fig. 4 shows the X-ray diffraction patterns of UO_2 pellets containing AlOOH in the concentration range of 0.06–5 wt%. Quite different peaks were observed as the AlOOH content increased. The peaks of U_4O_9 are shown for UO_2 pellets doped with 0.06 wt% AlOOH and their intensity starts to increase with increasing amounts of AlOOH. Distinct peaks of U_4O_9 can be identified in the pellet with 5 wt% AlOOH. It is thought that grain growth by the addition of AlOOH is closely connected with the oxygen atoms formed from the decomposition of AlOOH. The prevailing defects in UO_2 are anti-Frenkel defects (oxygen vacancies and interstitials), but Schottky disorders (uranium vacancies and oxygen vacancies) are present simultaneously [11]. The formation of oxygen atoms leads to an increase in the concentration of uranium vacancies through Schottky equilibrium. An increase in the number of U lattice vacancies made uranium atoms diffuse more rapidly and consequently enhanced the grain growth. AlOOH played an important role in grain coarsening, but increasing concentration of AlOOH in the pellet had no enhancing effect on grain growth. A high content of AlOOH in the pellet would retard the movement of uranium atoms, rather than accelerate it. Therefore, further grain growth in UO_2, including more than 0.06 wt% AlOOH, cannot be observed, as shown in Fig. 3.

UO_2 pellets are densified by sintering due to pore annihilation. The pores in contact with the surface are called open pores. Because pores present in the interior of the pellets become open pores by the diffusion process, open pores may be reduced by blocking the movement of interior pores. Fig. 5 is an SEM photograph of a UO_2 pellet with 2 wt% AlOOH, showing that a dark spot indicates small pores trapped at the grain boundary. Chemical analysis of the dark spot was performed using EPMA as shown in Fig. 6. In this picture, it can be seen that the Al concentration at the dark spot is higher compared to that in other areas. These small spots may be the Al-containing components, that is, AlOOH dissociation remnant. From XRD results, as shown in Fig. 4, it is confirmed that they are not Al_2O_3 because no Al_2O_3 peaks are present. Therefore, the AlOOH dissociated remnant residing at the grain boundary may hamper the movement of pores, resulting in reduction of the open pores.

The degree of open porosity decrement is not related to the content of AlOOH. There is little variation in open porosity content with increasing AlOOH content. It is well known that sintered density plays a decisive role in determining the amount of open porosity of pellets. Open porosity is drastically reduced if sintered density exceeds 94% TD, and its value reaches nearly zero when the sintered density of the pellets is above 97% TD. In this experiment, the density of all the tested pellets was higher than 94% TD, so that the open porosity content was not so high. Therefore, the observed effect of AlOOH on reducing open porosity is quite small for the samples studied in the present work. The decrease in the open porosity due to the addition of

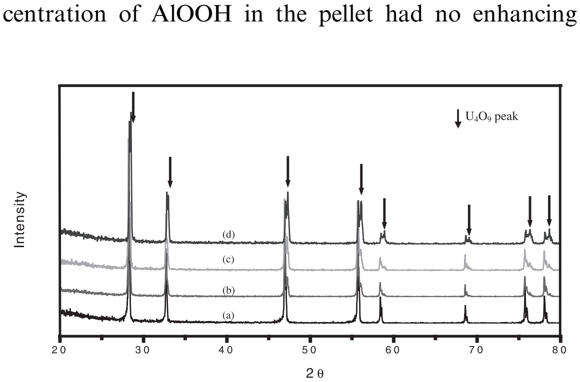

Fig. 4. X-ray diffraction patterns of AlOOH-doped UO_2. (a) pure UO_2, (b) 0.06 wt% AlOOH, (c) 2 wt% AlOOH, (d) 5 wt% AlOOH.

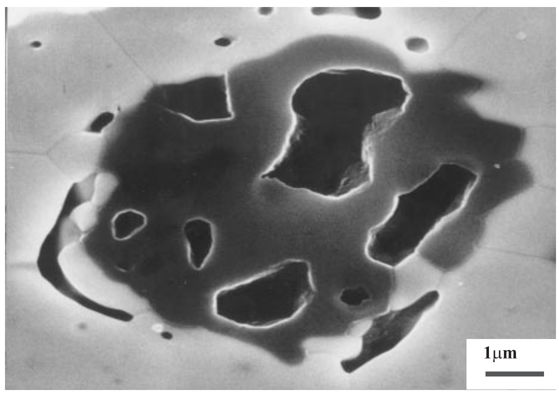

Fig. 5. SEM photograph of AlOOH-doped UO_2 showing trapped pores at the grain boundary.

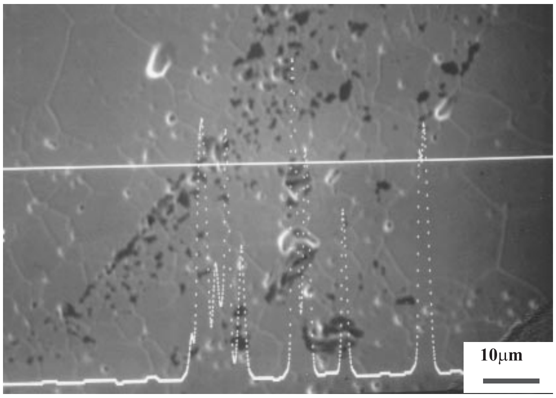

Fig. 6. Line profile of Al concentrations in a UO_2 pellet containing 0.5 wt% AlOOH.

AlOOH is almost the same with increasing AlOOH concentration because there may be a minimum open porosity in the pellets. From the above results, it may be concluded that only a small amount of AlOOH is required to improve the properties of UO_2 pellets having density more than 95% TD.

5. Conclusion

The addition of AlOOH to UO_2 coarsened the grain size and reduced the open porosity of the pellets. It is suggested that oxygen atoms formed by the dissociation of AlOOH play an important role in increasing the grain size of the UO_2 pellets due to the increase of uranium vacancies through Schottky equilibrium. The movement of pores was apparently retarded by the AlOOH dissociation products at the grain boundaries, resulting in a decrease of open porosity. The existence of residual pores in the pellets caused by AlOOH dissociation may be partly ascribed to the reduced sintered density of the pellets.

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