

Effect of TiO_2 and $\text{Al}(\text{OH})_3$ on Sintering Behavior of $\text{UO}_2\text{-Gd}_2\text{O}_3$ Fuel Pellets

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Abstract

The sintering behavior of $\text{UO}_2\text{-Gd}_2\text{O}_3$ fuel pellets under H_2 gas has been investigated using dilatometry and XRD methods. The addition of TiO_2 or $\text{Al}(\text{OH})_3$ increased the density and grain size. A density of 95 % TD and a grain size larger than $6 \mu\text{m}$ are achieved by the addition of 0.1 wt% TiO_2 or $\text{Al}(\text{OH})_3$. It was found that the densification of $\text{UO}_2\text{-Gd}_2\text{O}_3$ pellets was suppressed in the temperature range of 1300 to 1500°C, compared to UO_2 pellets. The formation of a (U,Gd) O_2 solid solution is the main reason for the suppression of densification. The role of TiO_2 in densification and grain growth is discussed on the basis of the densification curve and ceramography.

Key Words : $\text{UO}_2\text{-Gd}_2\text{O}_3$ fuel, sintering, TiO_2 additive, dilatometry

1. Introduction

$\text{UO}_2\text{-Gd}_2\text{O}_3$ fuel has been widely used to suppress initial excess reactivity at the BOL (beginning of life) in LWRs. The fabrication method of $\text{UO}_2\text{-Gd}_2\text{O}_3$ pellets has been developed, mainly based on that of normal UO_2 fuel [1], and thus it includes mixing, pressing and sintering processes. The fabrication of $\text{UO}_2\text{-Gd}_2\text{O}_3$ pellets is more difficult than that of UO_2 pellets, since the $\text{UO}_2\text{-Gd}_2\text{O}_3$ pellet is apt to have a low density and a small grain size. Gd_2O_3 contents of 4 to 10 wt% are commonly used in a fuel pellet.

The fabrication method of $\text{UO}_2\text{-Gd}_2\text{O}_3$ pellets has been greatly studied to improve fuel properties. Davis and Potter [2] studied the sinterability of $\text{UO}_2\text{-Gd}_2\text{O}_3$ compacts in hydrogen

gas using UO_2 powders made through two different methods. Riella et al. [3] studied the effect of powder preparation method on the density and Gd homogeneity of $\text{UO}_2\text{-Gd}_2\text{O}_3$ fuel. Their results showed that coprecipitated (U,Gd) O_2 powder was better in homogeneity than any other method for mixing UO_2 and Gd_2O_3 powders.

The effect of sintering atmosphere on the property of $\text{UO}_2\text{-Gd}_2\text{O}_3$ fuel has also been studied. Ho and Radford [4] sintered $\text{UO}_2\text{-9wt\% Gd}_2\text{O}_3$ in dry, wet, and very wet hydrogen gases, and they reported that the sintered density decreased as the oxygen potential of the sintering atmosphere increased. Yuda and Une [5] studied the sintering kinetics of $\text{UO}_2\text{-(5,10)wt\% Gd}_2\text{O}_3$ pellets in a gas mixture of CO and CO_2 . They found that the sintered density decreased with increasing oxygen

potential of the sintering atmosphere, and that large pores formed in accordance with the decrease in density.

Song et al. [6] studied the sintering behavior of $\text{UO}_2\text{-Gd}_2\text{O}_3$ pellets using a simple mixing of UO_2 and Gd_2O_3 powders, and found that the density was below 92 % of the theoretical density (TD). This suggests that using a simple mixing of UO_2 and Gd_2O_3 powders is not an adequate method in the fabrication of $\text{UO}_2\text{-Gd}_2\text{O}_3$ pellets. However, Assmann et al. [7] showed that a simple mixing of UO_2 and Gd_2O_3 powders was able to be sintered up to a 95 % TD by adding aluminum oxide.

This work has been undertaken to improve the density and grain size of $\text{UO}_2\text{-Gd}_2\text{O}_3$ pellets by using sintering additives. TiO_2 and Al(OH)_3 were added separately to the simple mixing of UO_2 and Gd_2O_3 powders, and their effects on the sintering behavior were investigated.

2. Experimental Procedures

Three powders, that is, UO_2 powder ex-AUC [8], Gd_2O_3 and an additive, were mixed with a tumbling mixer to make a uniform mixture. The Gd_2O_3 content was 6 wt %, and the content of either Al(OH)_3 or TiO_2 was between 0.02 and 0.2 wt %. The powder mixtures with additives (namely $\text{UO}_2/\text{Gd}_2\text{O}_3/\text{Al(OH)}_3$, $\text{UO}_2/\text{Gd}_2\text{O}_3/\text{TiO}_2$) were pressed into compacts and sintered at 1730°C for 4 hours in hydrogen gas.

The sintered density and open porosity were determined from the following correlation between dry weight, suspension weight in water, and impregnated weight of the sintered pellets :

$$\text{sintered density} = \rho_{\text{pellet}} = \frac{W_{\text{dry}}}{W_{\text{imp}} - W_{\text{sus}}} \rho_x$$

$$\text{open porosity} = P_{\text{op}} = \frac{W_{\text{imp}} - W_{\text{dry}}}{W_{\text{imp}} - W_{\text{susp}} - W_{\text{dry}} \frac{\rho_x}{\rho_{\text{TD}}}} \times 100, \%$$

where,

ρ_{pellet} : sintered density of the pellet,

P_{op} : ratio of open porosity to total porosity

W_{dry} : dry weight,

W_{imp} : impregnated weight,

W_{susp} : suspended weight

ρ_x : density of water,

ρ_{TD} : theoretical density of the pellet = $10.96 - 0.04 \cdot (\text{wt}\% \text{ of } \text{Gd}_2\text{O}_3)$ [1]

The pellets were sectioned longitudinally and polished with a diamond paste, and the microstructures were then observed. In order to observe the grain boundary, thermal etching was performed at 1250°C for 1 hr in carbon dioxide gas. The grain size was determined by a linear intercept method, in which more than 300 points were counted. The microscopic distribution of Al, Ti and Gd were analyzed by an electron probe micro analyzer (EPMA).

The compacts were made of each of the three powders ; UO_2 , $\text{UO}_2\text{-6wt}\%\text{Gd}_2\text{O}_3$ and $\text{UO}_2\text{-6wt}\%\text{Gd}_2\text{O}_3$ containing 0.1 wt% TiO_2 . The shrinkage of the compact was measured in the axial direction with an LVDT transducer in a push rod type dilatometer. The compacts were heated to 1650°C with a heating rate of 5°C/min and held for 150 minutes in hydrogen (H_2) gas.

3. Results and Discussion

Fig. 1 shows the dependence of the sintered density of $\text{UO}_2\text{-6wt}\%\text{Gd}_2\text{O}_3$ pellets on the additive content. The density increases significantly with the content of TiO_2 and Al(OH)_3 , and thus it increased from 91 to 95 % TD with the addition of 0.1 wt % TiO_2 or Al(OH)_3 .

Fig. 2(a) shows the shrinkage (densification) of the UO_2 compact and $\text{UO}_2\text{-6wt}\%\text{Gd}_2\text{O}_3$ compacts with and without 0.1 wt% TiO_2 , and Fig. 2(b) shows the related shrinkage rates. Fig. 2(a)

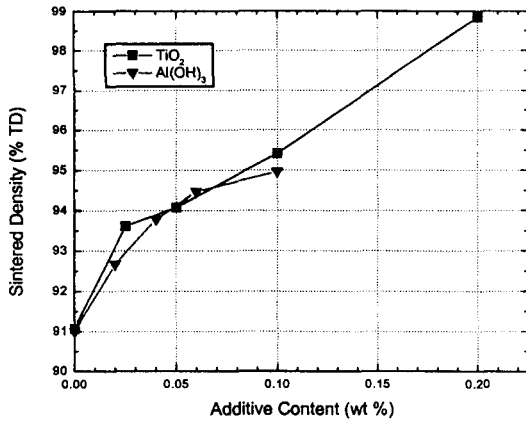


Fig. 1. Dependence of the Sintered Density of $\text{UO}_2\text{-6wt}\%\text{Gd}_2\text{O}_3$ Pellets on Additive Content

indicates that all three compacts start to shrink at similar temperatures between 800 and 900°C, and that the compacts containing Gd_2O_3 densify to a lesser extent than the UO_2 compact as the temperature increases. The densification of the $\text{UO}_2\text{-6wt}\%\text{Gd}_2\text{O}_3$ compact is significantly suppressed in the temperature range of 1300 to 1500°C. Fig. 2(b) shows that the densification rate of the UO_2 compact has a single large peak at 1320°C over the whole temperature range, but that of the $\text{UO}_2\text{-Gd}_2\text{O}_3$ compact has two small peaks at 1250 and 1620°C. The densification rate of the $\text{UO}_2\text{-Gd}_2\text{O}_3$ compact decreases with temperature at 1300 to 1500°C, and thus the amount of densification appears to be significantly suppressed.

Fig. 3 show the X-ray diffraction maps of the partly sintered pellets obtained at intermediate temperatures during sintering. The Gd_2O_3 phase is detected at temperatures below 1200°C and disappears at 1450°C, suggesting that a $(\text{U,Gd})\text{O}_2$ solid solution forms in the temperature range of 1200 to 1450°C, where the densification of the $(\text{U,Gd})\text{O}_2$ pellet is significantly suppressed. The Gd-rich $(\text{U,Gd})\text{O}_2$ phase is detected with a weak

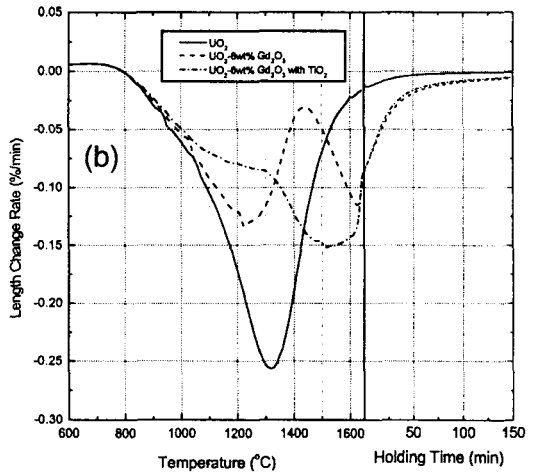
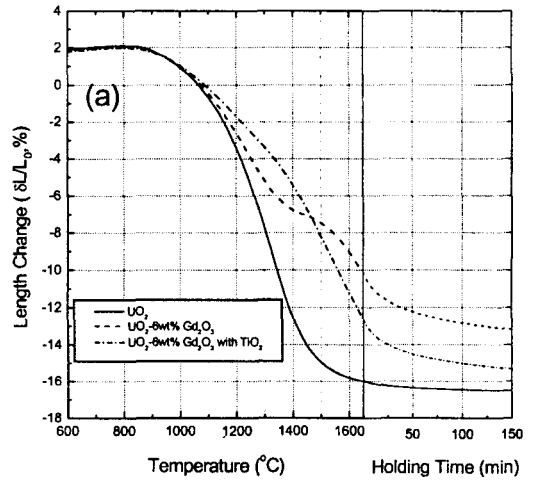


Fig. 2. Densification Behavior of UO_2 , $\text{UO}_2\text{-6wt}\%\text{Gd}_2\text{O}_3$ and $\text{UO}_2\text{-Gd}_2\text{O}_3$ with TiO_2 Compacts Under H_2 Gas
(a) Densification, (b) Densification rate

intensity at 1450°C but with a strong intensity at 1680°C. The UO_2 phase is also detected at 1680°C, thus a solid solution of $(\text{U,Gd})\text{O}_2$ is not yet fully formed. Manzel and Doerr [9] suggested that the suppression of densification was related to the formation of a solid solution of $(\text{U,Gd})\text{O}_2$, and our X-ray diffraction work leads to the same results. It can be further inferred that the first peak at 1250°C

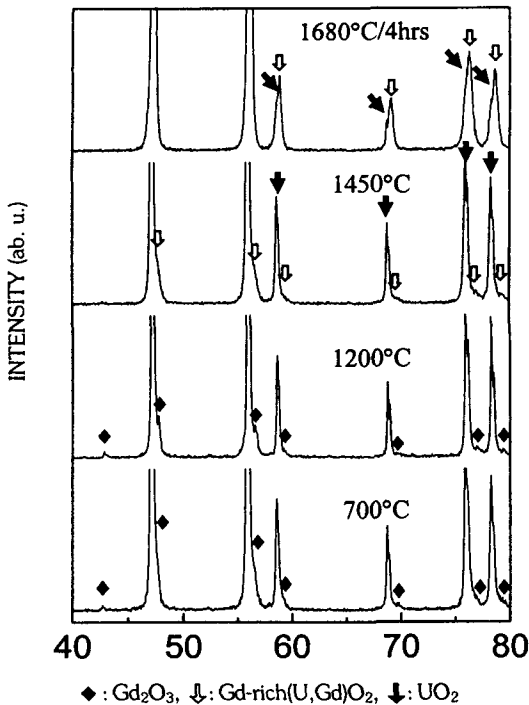


Fig. 3. X-ray Diffraction Map of Partly Sintered UO_2 - Gd_2O_3 Pellets

in Fig. 2(b) is mainly due to sintering between the UO_2 particles.

The densification of a compact is the process of decreasing the free energy of a compact by means of a decrease in surface area. It is supposed that the formation of a solid solution of $(U,Gd)O_2$ can also decrease the free energy of a compact by means of an increase in the mixing entropy of U and Gd. Thus, the densification of the UO_2 - Gd_2O_3 compact may be suppressed during the formation of a solid solution of $(U,Gd)O_2$ when the formation of a solid solution is an easier way to decrease the free energy of the compact.

It is found from Fig. 2(a) that the UO_2 -6wt% Gd_2O_3 compact with TiO_2 seems to be very slightly suppressed below $1300^\circ C$. Fig. 2(b) shows that the densification rate of the UO_2 - Gd_2O_3 compact with TiO_2 is slower at temperatures of

1100 to $1300^\circ C$, and much higher above $1400^\circ C$ than that of the compact without TiO_2 . Under the assumption that the suppression of the densification rate in the UO_2 - Gd_2O_3 pellet is related to the formation of $(U,Gd)O_2$, it can be deduced that the added TiO_2 causes a solid solution of $(U,Gd)O_2$ to form at lower temperatures.

According to the work on the thermodynamic calculation of TiO_2 [10], TiO_2 is stable from an ambient temperature to $900^\circ C$ in hydrogen gas, Ti_3O_5 between 900 and $1300^\circ C$, and Ti_2O_3 above $1300^\circ C$. Since the added TiO_2 decreases the shrinkage rate of the UO_2 - Gd_2O_3 compact in the temperature range of 1100 to $1300^\circ C$, but increases the shrinkage rate above $1400^\circ C$ (see Fig. 2(b)), it is supposed that Ti_3O_5 may facilitate the formation of a solid solution of $(U,Gd)O_2$ and Ti_2O_3 may enhance densification. Ti_3O_5 and Ti_2O_3 are expected to be dissolved in UO_2 and/or $(U,Gd)O_2$ and to then enhance material transport, which is related to both the formation of a solid solution and the densification of a pellet.

Fig. 4(a) shows the microstructure of the UO_2 -6wt% Gd_2O_3 pellet doped with 0.1 wt% $Al(OH)_3$, and Figs. 4(b) and 4(c) show the maps of aluminum and gadolinium concentrations, respectively. It can be seen from Fig. 4(b) that aluminum is uniformly scattered over the matrix and highly concentrated in the pores. Fig. 4(c) shows that gadolinium is not preferentially present in the pores. Assmann et al. [7] found that the addition of Al_2O_3 increased the density of the UO_2 - Gd_2O_3 pellets and proposed that Al_2O_3 and Gd_2O_3 might form oxide compounds which assist the densification of UO_2 - Gd_2O_3 pellets. Figs. 4(a) to 4(c) suggest, however, that both aluminum and gadolinium are not likely to combine, so an oxide compound consisting of aluminum and gadolinium might not be formed. Flipot and Delbrassinne[11] found that aluminum in the UO_2 - Dy_2O_3 system

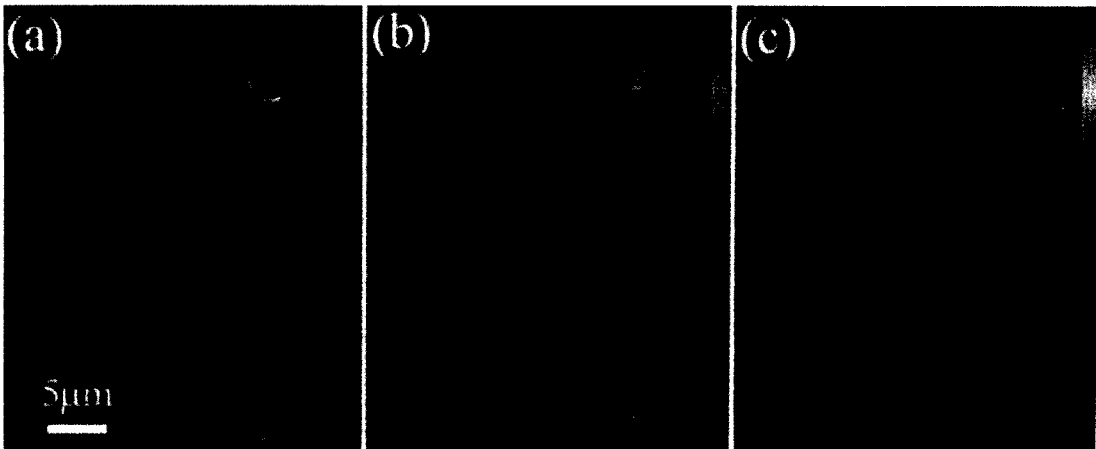


Fig. 4. SEM Micrographs Showing Al and Gd Distribution in the $\text{UO}_2\text{-Gd}_2\text{O}_3$ Pellet Doped with $\text{Al}(\text{OH})_3$
 (a) pore structure, (b) area mapping of aluminum concentration,
 (c) area mapping of gadolinium concentration

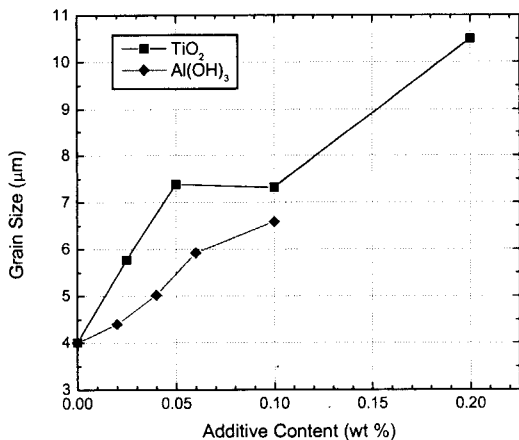


Fig. 5. Dependence of the Grain Size of $\text{UO}_2\text{-6wt}\%$ Gd_2O_3 Pellets on Additive Content

enhanced greatly the diffusion rate of dysprosium into UO_2 . Aluminum in the $\text{UO}_2\text{-Gd}_2\text{O}_3$ system may have almost the same effect and thus enhance the formation of $(\text{U,Gd})\text{O}_2$ solid solution. Accordingly, added aluminum may cause a solid solution of $(\text{U,Gd})\text{O}_2$ to form at lower temperature and in shorter time. As discussed earlier, the densification of $\text{UO}_2\text{-Gd}_2\text{O}_3$ pellets was suppressed during the formation of $(\text{U,Gd})\text{O}_2$.

Therefore, aluminum may relieve the densification suppression related to the formation of $(\text{U,Gd})\text{O}_2$ and it enhance the overall densification of $\text{UO}_2\text{-Gd}_2\text{O}_3$ pellets.

Fig. 5 shows the variations of grain size of the $\text{UO}_2\text{-6wt}\%$ Gd_2O_3 pellets with the additive content. The grain size increases with TiO_2 or $\text{Al}(\text{OH})_3$ content and it thus becomes larger than $6 \mu\text{m}$ above $0.1 \text{ wt}\%$. The $\text{UO}_2\text{-6wt}\%$ Gd_2O_3 compacts with $0.2 \text{ wt}\%$ TiO_2 were heated to 1600°C and 1730°C and then cooled, without a period of holding time, in order to examine which temperature range is influential on grain growth. The grain sizes are 5 and $6 \mu\text{m}$, respectively, but the pellet sintered at 1730°C for 4 hours has a grain size of $10.5 \mu\text{m}$, so that it is reasonable to suppose that the added TiO_2 has an enhancing effect on grain growth mainly for the period of holding at 1730°C .

It has been known that UO_2 and TiO_2 form a new eutectic phase with a melting point of 1600°C to 1620°C [12], and thus it can be deduced that TiO_2 and $(\text{U,Gd})\text{O}_2$ may form a eutectic phase with a lower melting point. Fig. 6 shows that a secondary phase with a high Ti content is formed

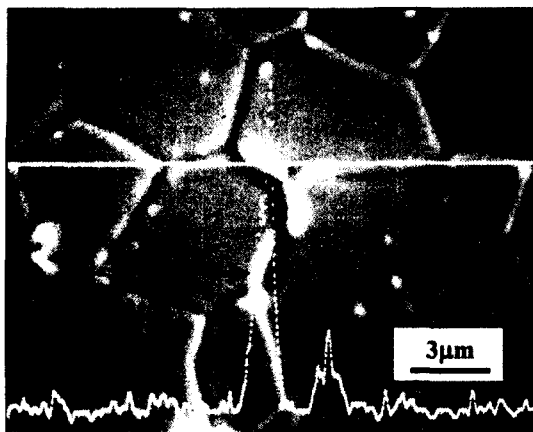


Fig. 6. SEM Micrograph Showing a Secondary Phase with a High Ti Content in the $\text{UO}_2\text{-Gd}_2\text{O}_3$ Pellet Doped with TiO_2

on the grain boundary in the $\text{UO}_2\text{-Gd}_2\text{O}_3$ pellet. This new phase might be melted at the sintering temperature, and material transport could be significantly enhanced through the liquid phase. It is supposed that grain growth due to TiO_2 addition is mainly ascribed to the presence of a liquid phase.

4. Conclusions

- (1) The density and grain size of $\text{UO}_2\text{-6wt}\% \text{Gd}_2\text{O}_3$ pellets increased by the addition of TiO_2 or $\text{Al}(\text{OH})_3$, and thus a density of 95 % TD and a grain size larger than 6 μm were achieved by the addition of 0.1 wt % TiO_2 or $\text{Al}(\text{OH})_3$.
- (2) The $\text{UO}_2\text{-Gd}_2\text{O}_3$ compact shrinks and densifies to a lesser extent than the UO_2 compact, and particularly the shrinkage of the $\text{UO}_2\text{-Gd}_2\text{O}_3$ compact is significantly suppressed in the temperature range of 1300 and 1500°C. X-ray diffraction results suggest that the suppression of densification is ascribed to the formation of $(\text{U,Gd})\text{O}_2$.
- (3) The addition of TiO_2 slightly suppresses the shrinkage of the $\text{UO}_2\text{-Gd}_2\text{O}_3$ compact in the

temperature range of 1100 and 1300°C and enhances above 1400°C. It is expected that TiO_2 is dissolved in UO_2 and/or $(\text{U,Gd})\text{O}_2$ and then enhances material transport, which is related to both the formation of a solid solution and pellet densification.

- (4) The added TiO_2 and a $(\text{U,Gd})\text{O}_2$ solid solution form a secondary phase on the grain boundary. This new phase might be a liquid phase during sintering, and the material transport needed for the grain growth in $\text{UO}_2\text{-Gd}_2\text{O}_3$ pellets may be promoted through the secondary phase. Aluminum was found to be highly concentrated in the pores, and this may enhance pore shrinkage and densification.

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