

Sintering of $\text{UO}_2\text{-Gd}_2\text{O}_3$ Pellets in Various Atmospheres and with Additives

Ki Won Kang, Keon Sik Kim, Kun Woo Song, Jae Ho Yang and Jong Hun Kim

Korea Atomic Energy Research Institute

150 Dukjin-dong, Yusong-gu. Taejon, Korea 305-353

Abstract

The sintering behavior of $\text{UO}_2\text{-Gd}_2\text{O}_3$ fuel pellets has been investigated to fabricate a pellet with high density and large grain size. When a simple mixture of UO_2 and Gd_2O_3 powders is used, TiO_2 and Al(OH)_3 of the additives including MgO and V_2O_3 have the most enhancing effect on density and grain size. A density of 95 % TD and a grain size of larger than 6 μm are achieved by the additions of 0.1 wt% TiO_2 and Al(OH)_3 . The TiO_2 effect is discussed on the basis of compact shrinkage and ceramography. The milled powder of UO_2 and Gd_2O_3 yields a high density of pellets, compared to a simple mixture of UO_2 and Gd_2O_3 powders without additives. As the oxygen potential of the sintering atmosphere increases, the density of $\text{UO}_2\text{-Gd}_2\text{O}_3$ pellets decreases but the grain size increases. For $\text{UO}_2\text{-(5,10)wt\% Gd}_2\text{O}_3$ pellets, a density of higher than 94 % TD and a grain size of larger than 4.5 μm are achieved with an oxygen potential of -307 kJ/mol at 1680°C.

1. Introduction

$\text{UO}_2\text{-Gd}_2\text{O}_3$ fuel has been widely used to suppress the initial excess reactivity at 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 the processes of mixing, pressing and sintering. However, 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. The Gd_2O_3 contents of 4 to 10 wt% are commonly used in a fuel pellet.

The fabrication of $\text{UO}_2\text{-Gd}_2\text{O}_3$ pellets has been continuously 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 methods on density and Gd homogeneity of $\text{UO}_2\text{-Gd}_2\text{O}_3$ fuel. Their results showed that coprecipitated $(\text{U,Gd})\text{O}_2$ powder was better in homogeneity than any other method of mixing UO_2 and Gd_2O_3 powders.

The effect of a 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_2O_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_2O_3 pellets in a gas mixture of CO and CO_2 . They found that the sintered density decreased with increasing oxygen potential of a 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 mixture of UO_2 and Gd_2O_3 powders, and found that the density of $\text{UO}_2\text{-Gd}_2\text{O}_3$ pellets decreased with increasing Gd_2O_3 content and oxygen potential. The density was below 92 % of the theoretical density (TD), which suggests that using a simple mixture 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. According to Assman et al. [7], however, a simple mixture of UO_2 and Gd_2O_3 powders was sintered up to 95 % TD powder 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 and by milling UO_2 and Gd_2O_3 powders. Sintering additives are added to the simple mixture of UO_2 and Gd_2O_3 powder, and their effects on the sintering behavior have been investigated. For the milled powder of UO_2 and Gd_2O_3 , the effect of the oxygen potential of sintering gas on the sintering behavior of $\text{UO}_2\text{-Gd}_2\text{O}_3$ pellets has been studied

2. Experimental Procedures

2.1. The sintering of a simple mixture of UO_2 and Gd_2O_3 powders with various additives

Three powders, UO_2 powder ex-AUC [8], Gd_2O_3 and an additive, were mixed in a tumbling mixer to make a uniform mixture. The Gd_2O_3 content was 6 wt %, and the additives were TiO_2 , $\text{Al}(\text{OH})_3$, MgO and V_2O_5 , of which the contents were between 0.01 and 0.2 wt %. The powder mixtures with additives were pressed into compacts and sintered at 1730°C for 4 hours in hydrogen gas.

The compacts were made of each of three powders ; UO_2 , $\text{UO}_2\text{-6wt}\%$ Gd_2O_3 and $\text{UO}_2\text{-6wt}\%$ Gd_2O_3 containing 0.1 wt% TiO_2 . The shrinkage of the compacts was

measured in an 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 (H₂) gas.

2.2. Sintering of the milled powder of UO₂ and Gd₂O₃ under various oxygen potentials

The UO₂ powder ex-AUC and Gd₂O₃ powder were mixed with a tumbling mixer and then ball-milled for 2 hours in an alumina jar rotating at 120 rpm. The aluminum pick-up during the process of ball-milling was 30 ppm, which was much below the aluminum content to be capable of enhancing the densification of UO₂-Gd₂O₃ fuel pellets [7]. The Gd₂O₃ contents were 5 and 10 % by weight of both UO₂ and Gd₂O₃ powders.

The ball-milled powder was pressed into compacts and sintered at 1680°C for 4 hours. Four different sintering gases were used in this work; pure hydrogen and gas mixtures of hydrogen and carbon dioxide. The dew point of hydrogen gas was -30°C, and thus hydrogen had a water (H₂O) content of 5×10^{-2} % by volume. The ratios of CO₂ to H₂ gas in the gas mixtures were 0.05, 0.15, and 0.30, and the gas mixtures are symbolized by H₂-5CO₂, H₂-15CO₂, and H₂-30CO₂, respectively.

The SOLGASMIX program [9], which can calculate the free energy and equilibrium constant of reactions, was used to calculate the oxygen potentials of sintering atmospheres. The oxygen potentials of sintering gases are summarized at some temperatures in Table 1. The oxygen potential ($RT \ln p(O_2)$) increases with the ratio of CO₂ to H₂ gas. It is supposed that the oxygen potential of the pellet material changes almost in accordance with the calculated value during the heating stage of sintering and it is equivalent to the calculated value for the period of holding at a sintering temperature.

3. Results and discussion

3.1. The properties of pellets made from a simple mixture of UO₂ and Gd₂O₃ powders with various additives

Fig. 1 shows the dependence of the sintered density of UO₂-6wt% Gd₂O₃ pellets on the content of additives. The density increases significantly with the content of TiO₂ and Al(OH)₃, and thus it is increased from 91 to 95 % TD by the additions of 0.1 wt % TiO₂ and Al(OH)₃. The additions of V₂O₃ and MgO slightly increase the density compared to those of TiO₂ and Al(OH)₃.

Fig. 2(a) shows the shrinkage (densification) of the UO_2 compact and UO_2 -6wt% Gd_2O_3 compacts with and without 0.1 wt% TiO_2 , and Fig. 2(b) shows the related shrinkage rates. Fig. 2(a) 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 UO_2 -6wt% Gd_2O_3 compact is significantly suppressed in the temperature range of 1300 to 1500°C, and that of the UO_2 -6wt% Gd_2O_3 compact with TiO_2 seems to be suppressed slightly below 1300°C.

Fig. 2(b) shows that the densification rate of the UO_2 compact has a single peak at 1320°C over the whole range of temperatures, but that of the UO_2 - Gd_2O_3 compact has two peaks at 1250 and 1620°C. The densification rate of the UO_2 - Gd_2O_3 compact decreases with temperature at 1300 to 1500°C, and thus the amount of densification appears to be significantly suppressed (see Fig. 2(a)). According to Manzel and Dorr [10], the suppression of densification was related to the formation of a solid solution of $(\text{U,Gd})\text{O}_2$, and the first peak at 1250°C was mainly due to the sintering between UO_2 and UO_2 particles.

It is found from Fig. 2(b) that the densification rate of the UO_2 - Gd_2O_3 compact with TiO_2 is slower at temperatures of 1100 to 1300°C and much faster above 1400°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 with the formation of $(\text{U,Gd})\text{O}_2$, it can be deduced that the added TiO_2 causes a solid solution of $(\text{U,Gd})\text{O}_2$ to form at lower temperatures.

The densification of a compact is a process of decreasing the free energy of a compact by means of a decrease in surface energy. It is supposed that the formation of a solid solution of $(\text{U,Gd})\text{O}_2$ can also decrease the free energy of a compact by means of the increase in 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 $(\text{U,Gd})\text{O}_2$ when the formation of a solid solution is an easier way to decrease the free energy of a compact.

According to the work on the TiO_2 effect on the densification of UO_2 pellets [11], TiO_2 is stable from an ambient temperature to 900°C in hydrogen gas, Ti_3O_5 between 900 and 1300°C, and Ti_2O_3 above 1300°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°C but increases the shrinkage rate above 1400°C (see Fig. 2(b)), it is supposed that Ti_3O_5 may facilitate the formation of a solid solution of $(\text{U,Gd})\text{O}_2$ and Ti_2O_3 may enhance the densification. Ti_3O_5 and Ti_2O_3 are expected to be dissolved in UO_2 and/or $(\text{U,Gd})\text{O}_2$ and then to

enhance the material transport which is related with both the formation of a solid solution and the densification of a pellet.

Fig. 3 shows the variations of grain size of the UO_2 -6wt% Gd_2O_3 pellets with the content of additives. The grain size increases with each content of TiO_2 , $\text{Al}(\text{OH})_3$, V_2O_5 and MgO , and thus it becomes larger than $6 \mu\text{m}$ above a content of 0.1 wt%. The effect of TiO_2 is the largest and those of the other additives are almost the same. The UO_2 -6wt% Gd_2O_3 compacts with 0.2 wt% TiO_2 were heated to 1600°C and 1730°C , respectively, and then cooled in order to examine which temperature range is influential on grain growth. The grain sizes of the former and the latter pellets are $5 \mu\text{m}$ and $6 \mu\text{m}$, respectively. The same pellet sintered at 1730°C for 4 hours has a grain size of $10.5 \mu\text{m}$ (see Fig. 3), 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 forms 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 low melting point. Fig. 4 shows that a secondary phase containing a high Ti content is formed on the grain boundary in the UO_2 - Gd_2O_3 pellet which were doped with TiO_2 . 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 the grain growth due to TiO_2 addition is mainly ascribed to the presence of a liquid phase.

3.2. The properties of pellets made from the milled powder of UO_2 and Gd_2O_3

Fig. 5 shows the size distribution of the milled powder and the UO_2 powder ex-AUC. It is found that both powders have a monomodal distribution, and the mode of the size distribution is $17 \mu\text{m}$ for UO_2 powder and $2 \mu\text{m}$ for milled powder.

Fig. 6 shows the dependence of pellet density on the ratio of CO_2 to H_2 gas in a sintering atmosphere. The density of UO_2 pellets is around 97 % TD, independent of the gas ratio (oxygen potential). The density of UO_2 - Gd_2O_3 pellets is between 94 and 96 % TD in all the sintering atmospheres and such values of density meet the fuel specification [1]. Previous work [6] showed that the density of UO_2 - Gd_2O_3 pellets was below 92 % TD when a simple mixture of UO_2 and Gd_2O_3 powders were used. Thus the milling of UO_2 and Gd_2O_3 powders has an enhancing effect on the density of UO_2 - Gd_2O_3 pellets, probably because of the reduction of particle size.

It can be noticed from Fig. 6 that the density of UO_2 - Gd_2O_3 pellets decreases gradually with the gas ratio. A similar phenomenon was reported by other workers

[5,13]. Yuda and Une [5] found that the density of UO_2 -10wt% Gd_2O_3 pellets decreased from 93 % to 87 % TD with an oxygen potential of -200 kJ/mol and simultaneously large pores were formed. They proposed that the sintering between UO_2 and UO_2 particles rapidly progressed prior to that between UO_2 and Gd_2O_3 particles with high oxygen potentials so that large pores were formed just near the Gd_2O_3 particle by the shrinkage of UO_2 particles. Once large pores were formed, they hardly shrink and were moreover subject to growing by absorbing vacancies from small pores.

The grain sizes of UO_2 - Gd_2O_3 pellets are plotted in Fig. 7 as a function of the ratio of CO_2 to H_2 gas. The grain size increases with the gas ratio, and it is smaller for UO_2 -10wt% Gd_2O_3 than for UO_2 -5wt% Gd_2O_3 . The grain size of UO_2 -(5,10)wt% Gd_2O_3 pellets is larger than 4 μm at a CO_2 to H_2 ratio of 0.3, which yields an oxygen potential of -307 kJ/mol at 1680°C. This relationship between grain size and oxygen potential is in good agreement with other published works [5,13]. According to Une and Oguma [14], the O/M ratios of $\text{U}_{0.86}\text{Gd}_{0.14}\text{O}_{2\pm x}$ ($\sim\text{UO}_2$ -10wt% Gd_2O_3) increases with the oxygen potential. It is supposed that the O/M ratio of the UO_2 -10wt% Gd_2O_3 pellet in this work also increases increasing CO_2 to H_2 ratio. As the O/M ratio increases, the concentration of oxygen vacancies decreases, and in turn the concentration of uranium vacancies increases through the Schottky equilibrium. Eventually, the diffusion of uranium ions can be enhanced, and the increase in grain size is expected.

4. Conclusions

(1) When a simple mixture of UO_2 and Gd_2O_3 powders is used, the density and grain size of UO_2 -6wt% Gd_2O_3 pellets increase by the additions of TiO_2 , $\text{Al}(\text{OH})_3$, MgO , and V_2O_5 . The effect of TiO_2 and $\text{Al}(\text{OH})_3$ on the density appears to be the largest, and the effect of TiO_2 on the grain size is most significant. The density of 95 % TD and a grain size of larger than 6 μm are achieved by the addition of 0.1 wt % TiO_2 and $\text{Al}(\text{OH})_3$.

(2) The UO_2 - Gd_2O_3 compact shrinks (densifies) to a lesser extent than the UO_2 compact, and particularly the shrinkage of the UO_2 - Gd_2O_3 compact is significantly suppressed in the temperature range between 1300 and 1500°C. The addition of TiO_2 suppresses the shrinkage of the UO_2 - Gd_2O_3 compact in the temperature range between 1100 and 1300°C and enhances above 1400°C. It is supposed that the added TiO_2 may cause a solid solution of $(\text{U,Gd})\text{O}_2$ to form at lower temperatures. The added TiO_2 and a $(\text{U,Gd})\text{O}_2$ solid solution form a secondary phase which may be a liquid phase during

sintering, and the material transport needed for grain growth in $\text{UO}_2\text{-Gd}_2\text{O}_3$ pellets may be promoted through the secondary phase.

(3) Compared to a simple mixture of UO_2 and Gd_2O_3 powders without additives, the milled powder of UO_2 and Gd_2O_3 enhances the sintered density. As the oxygen potential increases, the density of $\text{UO}_2\text{-Gd}_2\text{O}_3$ pellets decreases but the grain size increases. In an oxygen potential of -307 kJ/mol at 1680°C , the $\text{UO}_2\text{-(5,10)wt\% Gd}_2\text{O}_3$ pellets have a density of 94 % TD and a grain size larger than $4.5 \mu\text{m}$.

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Table 1. The calculated oxygen potentials of sintering gases.

Temperature (°C)	H_2 gas	H_2 -5 CO_2 gas	H_2 -15 CO_2 gas	H_2 -30 CO_2 gas
	($\text{H}_2\text{O}/\text{H}_2=5\times 10^{-4}$)	($\text{CO}_2/\text{H}_2=0.05$)	($\text{CO}_2/\text{H}_2=0.15$)	($\text{CO}_2/\text{H}_2=0.30$)
	kI/mol	kI/mol	kI/mol	kI/mol
800	-511	-429	-410	-398
1200	-516	-403	-375	-356
1500	-520	-383	-349	-325
1680	-522	-371	-333	-307

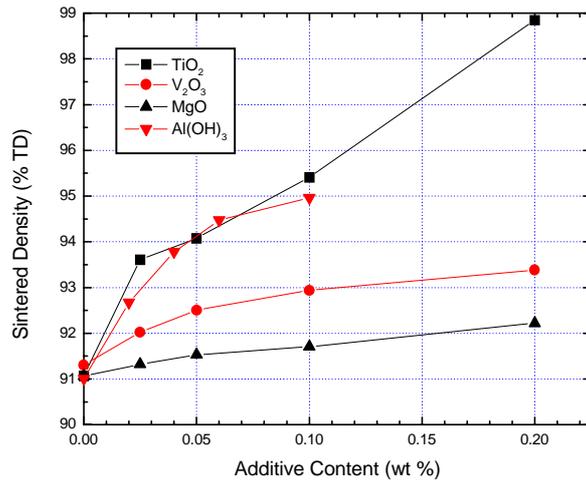


Fig. 1. Dependence of the sintered density of UO₂-6wt% Gd₂O₃ pellets on additive content.

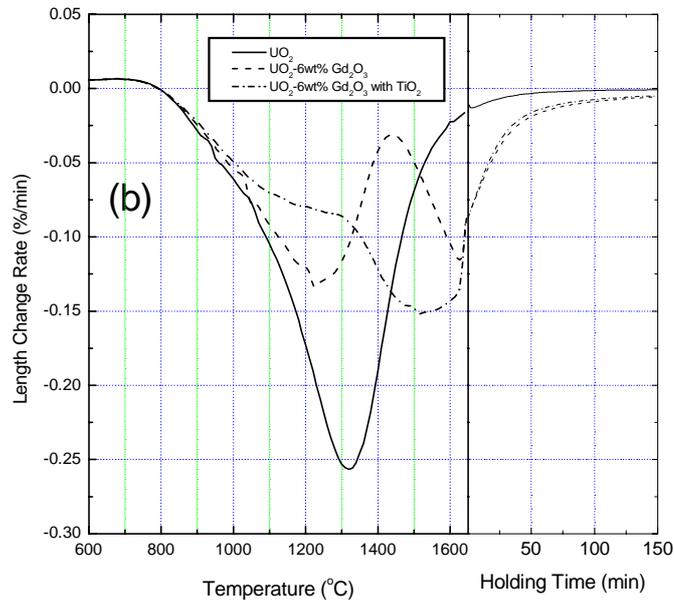
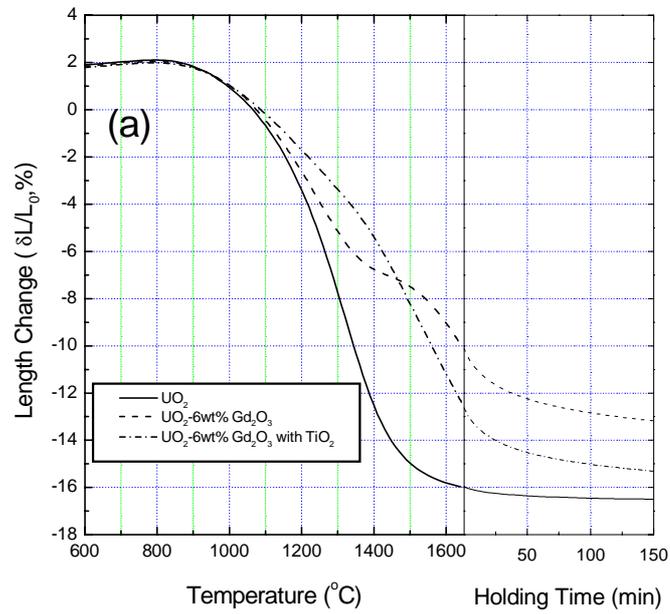


Fig. 2. Densification behavior of UO₂, UO₂-Gd₂O₃ and UO₂-Gd₂O₃ with TiO₂ compacts under H₂ gas (a) Densification, (b) Densification rate.

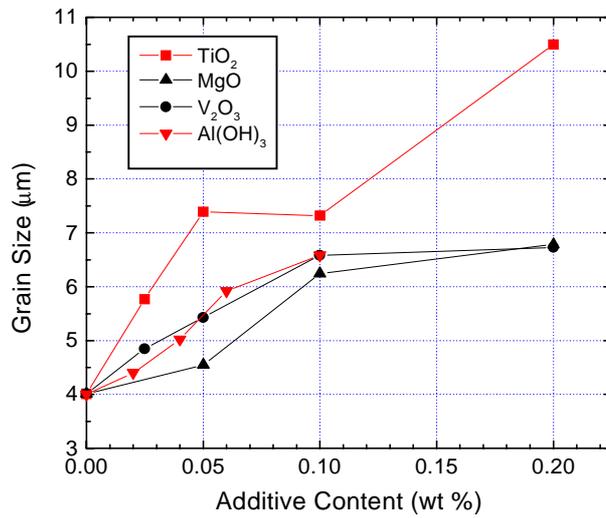


Fig. 3. Dependence of the grain size of UO_2 -6wt% Gd_2O_3 pellets on additive content.

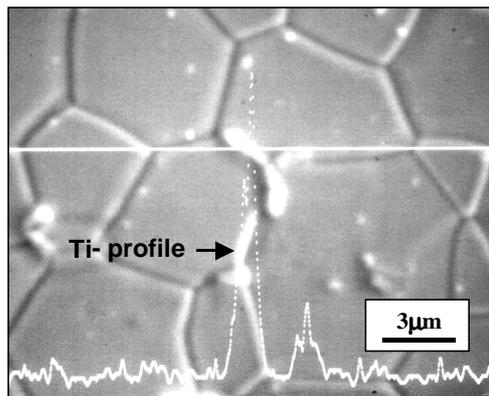


Fig. 4. SEM micrograph showing a secondary phase with a high Ti content in the UO_2 - Gd_2O_3 pellet doped with TiO_2 .

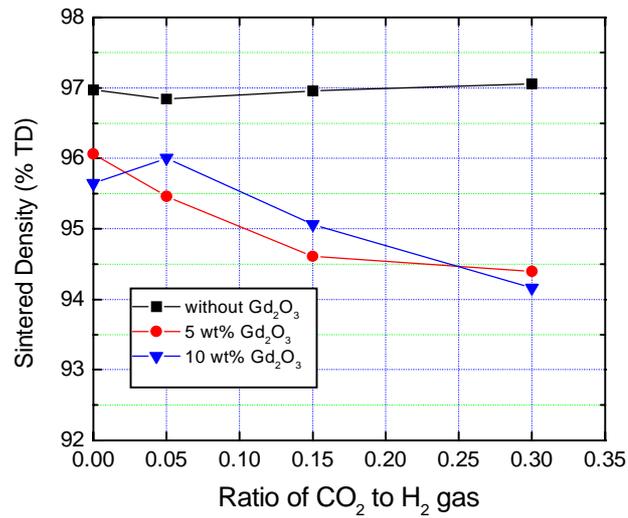
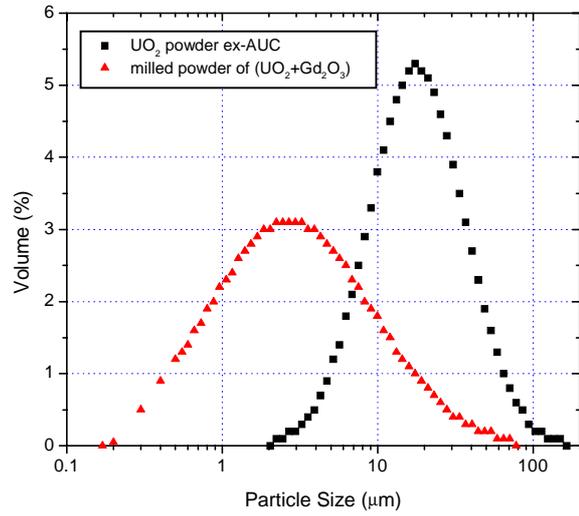


Fig. 6. Variations of the sintered density of UO₂-Gd₂O₃ pellets with the ratio of CO₂ to H₂ gas.

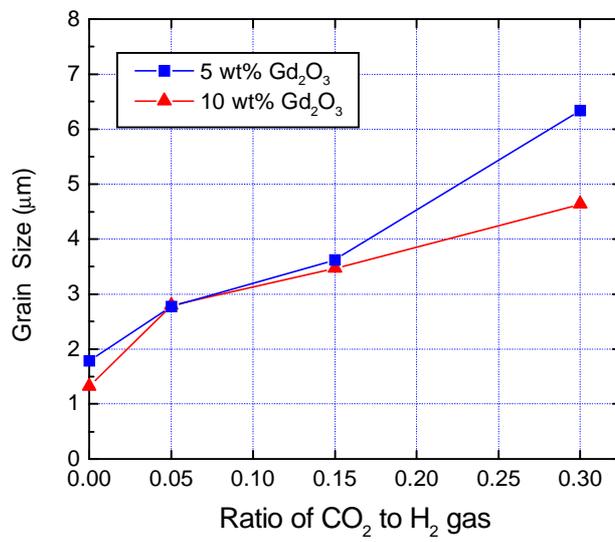


Fig. 7. Variations of the grain size of UO₂-Gd₂O₃ pellets with the ratio of CO₂ to H₂ gas.