

## **Sintering of a Mixture of $\text{UO}_2$ and $\text{Gd}_2\text{O}_3$ Powders Doped with $\text{Cr}_2\text{O}_3$ - $\text{SiO}_2$**

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### **Abstract**

Mixtures of AUC- $\text{UO}_2$  and  $\text{Gd}_2\text{O}_3$  powders doped with  $\text{Cr}_2\text{O}_3$  or  $\text{Cr}_2\text{O}_3$ - $\text{SiO}_2$  were pressed and sintered at 1730°C in hydrogen gas with various water-vapor contents. The density of  $\text{UO}_2$ -6wt%  $\text{Gd}_2\text{O}_3$  pellets can be increased from 91% TD to 94.5% TD in 1 vol%  $\text{H}_2\text{O}$ - $\text{H}_2$  gas by the addition of 0.02wt%  $\text{Cr}_2\text{O}_3$ -(0.01 ~ 0.04) wt%  $\text{SiO}_2$ . The magnitude of density increase is much larger in (1 ~ 3 vol%)  $\text{H}_2\text{O}$ - $\text{H}_2$  gases than in 0.05 vol%  $\text{H}_2\text{O}$ - $\text{H}_2$  gas. The densification of  $\text{UO}_2$ - $\text{Gd}_2\text{O}_3$  compact is significantly delayed in the temperature range between 1300 and 1500°C, but that of compacts with  $\text{Cr}_2\text{O}_3$ - $\text{SiO}_2$  is not. The role of  $\text{Cr}_2\text{O}_3$  and  $\text{SiO}_2$  in densification is discussed.

**Key Words** :  $\text{UO}_2$ - $\text{Gd}_2\text{O}_3$  fuel, sintering,  $\text{Cr}_2\text{O}_3$ ,  $\text{SiO}_2$ , oxygen potential

### **1. Introduction**

$\text{UO}_2$ - $\text{Gd}_2\text{O}_3$  fuel is widely used as a burnable absorber in LWRs. The fabrication method of  $\text{UO}_2$ - $\text{Gd}_2\text{O}_3$  pellets is quite similar to that of  $\text{UO}_2$  fuel [1] and thus it includes the processes of mixing or milling, pressing and sintering. But  $\text{UO}_2$ - $\text{Gd}_2\text{O}_3$  pellets are generally difficult to produce compared to  $\text{UO}_2$  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. To overcome this difficulty the milling process of  $\text{UO}_2$  and  $\text{Gd}_2\text{O}_3$  powders is widely adopted in the fabrication of  $\text{UO}_2$ - $\text{Gd}_2\text{O}_3$  pellets. The  $\text{Gd}_2\text{O}_3$  contents of 4 to 10 wt% are commonly used.

The fabrication method of  $\text{UO}_2$ - $\text{Gd}_2\text{O}_3$  pellets has been greatly studied to improve fuel properties, and the studies have included mainly the effects of powder properties, sintering atmosphere, and sintering additives. Davis and Potter [2] studied the sinterability of  $\text{UO}_2$ - $\text{Gd}_2\text{O}_3$  compacts in hydrogen gas using  $\text{UO}_2$  powders made through two different methods; AUC and ADU conversion method. Riella et al. [3] have investigated the effect of powder preparation methods on the density and Gd homogeneity of  $\text{UO}_2$ - $\text{Gd}_2\text{O}_3$  fuel and have reported that the coprecipitated (U,Gd) $\text{O}_2$  powder was better in homogeneity than any other methods of mixing

$\text{UO}_2$  and  $\text{Gd}_2\text{O}_3$  powders.

Ho and Radford [4] sintered  $\text{UO}_2$ -9wt%  $\text{Gd}_2\text{O}_3$  pellets in dry, wet, and very wet hydrogen gases, and have reported that the sintered density decreased and the grain size increased with increasing oxygen potential of sintering atmospheres. Yuda and Une [5] studied the sintering kinetics of  $\text{UO}_2$ -(5,10)wt%  $\text{Gd}_2\text{O}_3$  pellets in mixed gases of CO and  $\text{CO}_2$ . They also found that the sintered density decreased with increasing oxygen potential.

Song et al. [6] have studied the sintering behavior of  $\text{UO}_2$ - $\text{Gd}_2\text{O}_3$  pellets using a mixture of  $\text{UO}_2$  and  $\text{Gd}_2\text{O}_3$  powders and found that the density was about 92 % of theoretical density (TD), which is below the density requirement of fuel specification [1]. This suggests that using a mixture of  $\text{UO}_2$  and  $\text{Gd}_2\text{O}_3$  powders is not an adequate method in the fabrication of  $\text{UO}_2$ - $\text{Gd}_2\text{O}_3$  pellets. However, Assman et al. [7] have reported that a mixture of  $\text{UO}_2$  and  $\text{Gd}_2\text{O}_3$  powders can be sintered up to 95 % TD by adding aluminum oxide. It is recently known [8] that  $\text{Al}(\text{OH})_3$  and  $\text{TiO}_2$  also have a beneficial effect on the densification of  $\text{UO}_2$ - $\text{Gd}_2\text{O}_3$  pellets.

From the viewpoint of mass production, it is important to use sintering additives that are allowed in the fuel specification [1]. These elements are Al, Mg, Fe, Ni, Cr, and Si etc. 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 a composite additive of  $\text{Cr}_2\text{O}_3$ - $\text{SiO}_2$ . This additive was added to a mixture of  $\text{UO}_2$  and  $\text{Gd}_2\text{O}_3$  powders, and its effect on the sintering behavior of  $\text{UO}_2$ - $\text{Gd}_2\text{O}_3$  pellets have been investigated.

## 2. Experimental Procedures

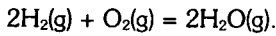
The  $\text{UO}_2$  powder used in this work was made through the AUC (Ammonium Uranyl Carbonate) process. The  $\text{UO}_2$  powder ex-AUC [9] has a large

particle size of about 20  $\mu\text{m}$  and a round shape, so it can be more uniformly mixed with  $\text{Gd}_2\text{O}_3$  and sintering additives than the other  $\text{UO}_2$  powders made through ammonium diuranate and dry conversion processes.  $\text{UO}_2$ ,  $\text{Gd}_2\text{O}_3$  and a sintering additive ( $\text{Cr}_2\text{O}_3$  or  $\text{Cr}_2\text{O}_3$ - $\text{SiO}_2$ ) powders were mixed with a tumbling mixer to make a uniform powder mixture in which the content of  $\text{Gd}_2\text{O}_3$  was 6 wt%.

In the first experiment to investigate the effects of additive concentration on sintering, The amounts of  $\text{Cr}_2\text{O}_3$  varied from 0.015 to 0.2 wt%, and the amounts of  $\text{Cr}_2\text{O}_3$ - $\text{SiO}_2$  changed from 0.025 to 0.2 wt%. The content of  $\text{Cr}_2\text{O}_3$  in  $\text{Cr}_2\text{O}_3$ - $\text{SiO}_2$  was 50 wt%. The powder mixture of  $\text{UO}_2$ ,  $\text{Gd}_2\text{O}_3$  and  $\text{Cr}_2\text{O}_3$  or  $\text{Cr}_2\text{O}_3$ - $\text{SiO}_2$  was pressed into compacts (green pellets) at a pressure of 3 t/cm<sup>2</sup> and then sintered at 1730 $\text{C}$  for 4 h in three different gas atmospheres; hydrogen ( $\text{H}_2$ ), 1 vol%  $\text{H}_2\text{O}$ - $\text{H}_2$ , and 3 vol%  $\text{H}_2\text{O}$ - $\text{H}_2$ . Pure hydrogen used in the experiment a dew point of -30 $\text{C}$  and thus contained a water vapor of  $5 \times 10^{-2}$  vol% as an impurity. To change the amount of water vapor hydrogen gas was passed through a water bath set at given temperatures, so that it was saturated with equilibrium water vapor and then flew into the sintering furnace to give three different atmospheres,  $\text{H}_2$ , 1 vol%  $\text{H}_2\text{O}$ - $\text{H}_2$  and 3 vol%  $\text{H}_2\text{O}$ - $\text{H}_2$ , having the  $\text{H}_2\text{O}$ -to- $\text{H}_2$  ratios of  $5 \times 10^{-4}$ ,  $1 \times 10^{-2}$ , and  $3 \times 10^{-2}$ , respectively.

In the second experiment to investigate the effect of very small amounts of  $\text{Cr}_2\text{O}_3$ - $\text{SiO}_2$  on sintering, both 0.02 wt%  $\text{Cr}_2\text{O}_3$  and 0.01 - 0.04 wt%  $\text{SiO}_2$  were used. The above amounts are allowable in the specification [1]. The powder mixture was pressed and sintered at 1730 $\text{C}$  for 4 h in four different gas atmospheres;  $\text{H}_2$ , 0.5 vol%  $\text{H}_2\text{O}$ - $\text{H}_2$ , 1 vol%  $\text{H}_2\text{O}$ - $\text{H}_2$ , 2 vol%  $\text{H}_2\text{O}$ - $\text{H}_2$ , and 4 vol%  $\text{H}_2\text{O}$ - $\text{H}_2$ , giving the  $\text{H}_2\text{O}$ -to- $\text{H}_2$  ratios of  $5 \times 10^{-4}$ ,  $5 \times 10^{-3}$ ,  $1 \times 10^{-2}$ ,  $2 \times 10^{-2}$ , and  $4 \times 10^{-2}$ , respectively, in that order.

The gas mixture of H<sub>2</sub> and H<sub>2</sub>O generates oxygen partial pressure according to the following reaction:



The oxygen partial pressure (P(O<sub>2</sub>)) is proportional to the term of [P(H<sub>2</sub>O)/P(H<sub>2</sub>)]<sup>2</sup>, increasing with the H<sub>2</sub>O-to-H<sub>2</sub> ratio. The oxygen potential defined by RT ln P(O<sub>2</sub>) was calculated with the Solgasmix program [10].

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

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

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

where,  $\rho_{\text{pellet}}$  : sintered density of pellet,  $P_{\text{op}}$  : ratio of open porosity to total porosity

$W_{\text{dry}}$  : dry weight,  $W_{\text{imp}}$  : impregnated weight,  $W_{\text{sus}}$  : suspended weight

$\rho_x$  : density of water,

$\rho_{\text{TD}}$  : theoretical density of pellet = 10.96-0.04 (wt% of Gd<sub>2</sub>O<sub>3</sub>) [1]

Pellets were sectioned longitudinally, polished with diamond paste, and the microstructure was then observed. In order to reveal the grain boundary, thermal etching was performed at 1250 °C for 1 h in carbon dioxide gas. The grain size was determined by the linear intercept method, in which more than 300 points were counted for each specimen. Microscopic distribution of Gd and Cr was analyzed by electron probe microanalysis (EPMA) using wave length dispersive spectroscopy.

Compacts (green pellets) were made of each of two powders ; UO<sub>2</sub>-6wt% Gd<sub>2</sub>O<sub>3</sub> and UO<sub>2</sub>-6wt% Gd<sub>2</sub>O<sub>3</sub> with 0.02wt% Cr<sub>2</sub>O<sub>3</sub>-0.04wt% SiO<sub>2</sub>. The shrinkage of the compacts was measured in an

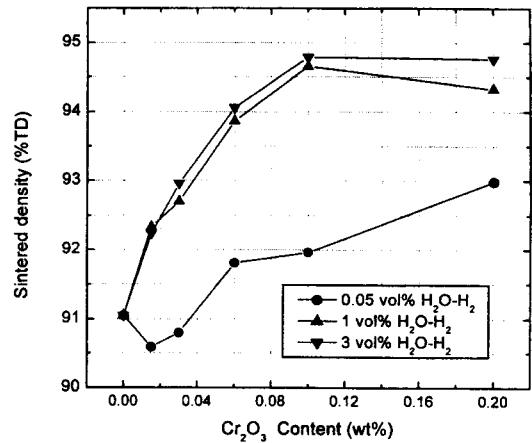
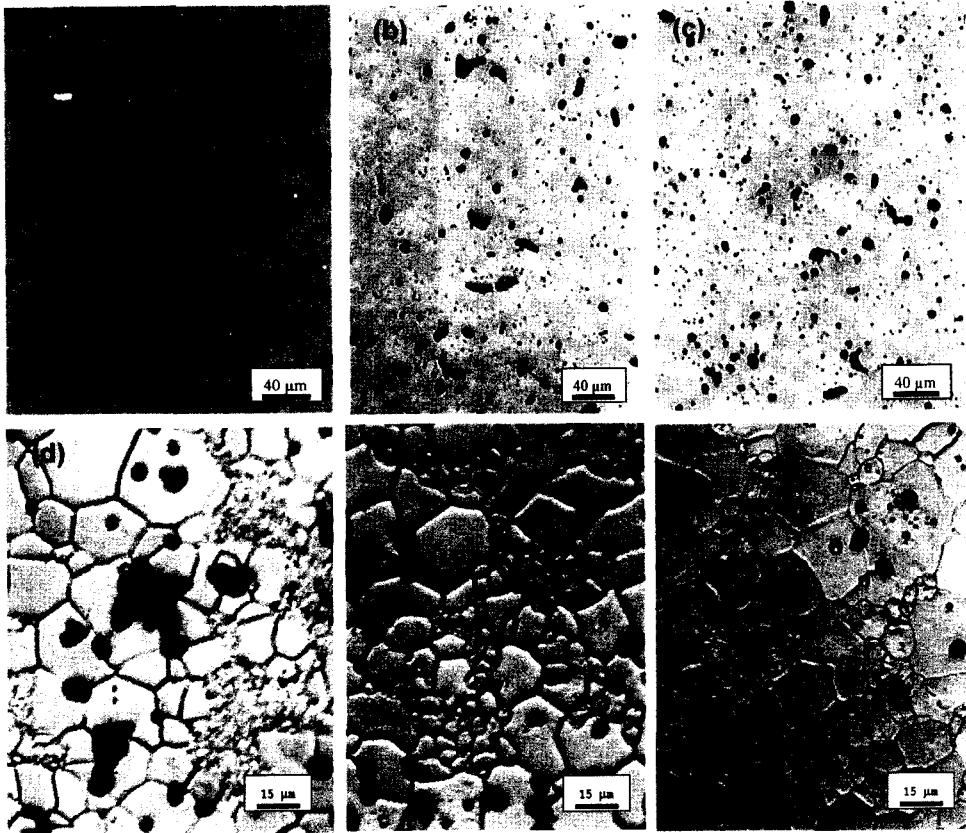


Fig. 1. Dependence of the Density of UO<sub>2</sub>-6wt%Gd<sub>2</sub>O<sub>3</sub> Pellets on Cr<sub>2</sub>O<sub>3</sub> Content for Various Sintering Atmospheres

axial direction with a LVDT transducer in a push rod type dilatometer. Compacts were heated to 1650 °C with a heating rate of 5 °C/min in 1 vol% H<sub>2</sub>O-H<sub>2</sub> gas.

### 3. Results

Fig. 1 shows a plot of the relationships between the sintered density of UO<sub>2</sub>-6wt% Gd<sub>2</sub>O<sub>3</sub> pellets and Cr<sub>2</sub>O<sub>3</sub> content for various sintering atmospheres. The density increases with the content of Cr<sub>2</sub>O<sub>3</sub>, and the increasing rate quite changes with the gas atmosphere. In 0.05 vol% H<sub>2</sub>O-H<sub>2</sub> gas, the density slightly decreases in the range of 0.04 wt% Cr<sub>2</sub>O<sub>3</sub> and then increases gradually up to 93 %TD at 0.2 wt% Cr<sub>2</sub>O<sub>3</sub>. In 1 and 3 vol% H<sub>2</sub>O-H<sub>2</sub> gas, the density increases substantially up to about 94.7 %TD in the range of 0.1 wt% Cr<sub>2</sub>O<sub>3</sub> and thereafter leveled off. This result suggests that the role of Cr<sub>2</sub>O<sub>3</sub> in the densification of UO<sub>2</sub>-6wt% Gd<sub>2</sub>O<sub>3</sub> pellets can be greatly influenced by the oxygen potential. Fig. 1 indicates that the density higher than 94.5% TD can be achieved under the sintering condition of 1

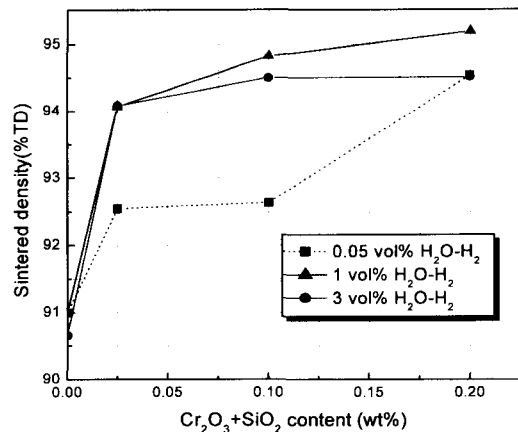


**Fig. 2. Microstructures of  $\text{UO}_2$ -6wt% $\text{Gd}_2\text{O}_3$  Pellets Doped with 0.2 wt%  $\text{Cr}_2\text{O}_3$  in Various Sintering Atmospheres: Pore Structures (a) 0.05 vol%  $\text{H}_2\text{O-H}_2$ ; (b) 1 vol%  $\text{H}_2\text{O-H}_2$ ; (c) 3 vol%  $\text{H}_2\text{O-H}_2$ . Grain Structures (e) 0.05 vol%  $\text{H}_2\text{O-H}_2$ ; (f) 1 vol%  $\text{H}_2\text{O-H}_2$ ; (g) 3 vol%  $\text{H}_2\text{O-H}_2$**

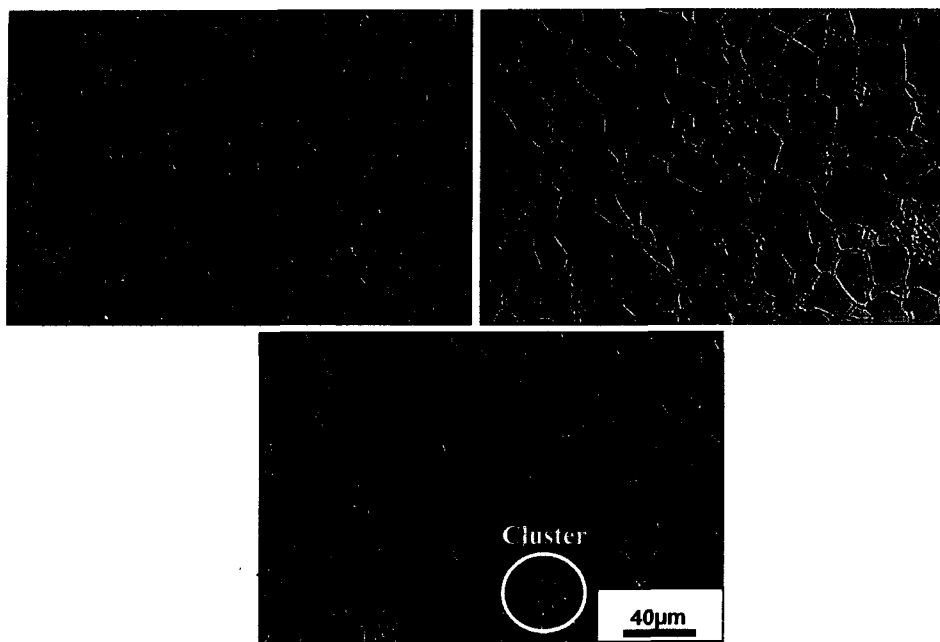
and 3 vol%  $\text{H}_2\text{O-H}_2$  atmospheres and simultaneously of more than 0.1 wt%  $\text{Cr}_2\text{O}_3$ .

Figs. 2a to 2f show the pore and grain structures of 0.2 wt%  $\text{Cr}_2\text{O}_3$ -doped pellets sintered in 0.05 vol%  $\text{H}_2\text{O-H}_2$ , 1 vol%  $\text{H}_2\text{O-H}_2$  and 3 vol%  $\text{H}_2\text{O-H}_2$  sintering atmospheres, respectively. Comparing Fig. 2a with Fig. 2b or 2c, it can be readily noticed that pore shape becomes round with the oxygen potential of sintering atmospheres. All microstructures show an irregular grain structure; some clusters of small grains in the matrix of normal grains.

Fig. 3 shows the dependence of the sintered density of  $\text{UO}_2$ -6wt%  $\text{Gd}_2\text{O}_3$  pellets on the  $\text{Cr}_2\text{O}_3$ -



**Fig. 3. Dependence of the Density of  $\text{UO}_2$ -6wt% $\text{Gd}_2\text{O}_3$  Pellets on  $\text{Cr}_2\text{O}_3$ - $\text{SiO}_2$  Content for Various Sintering Atmospheres**



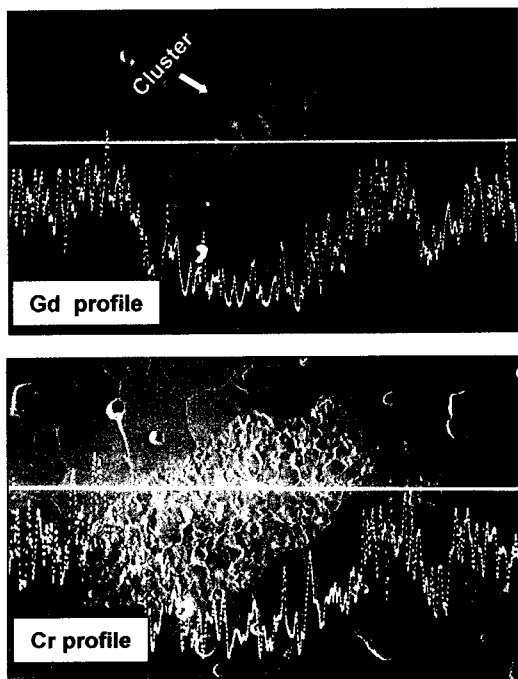
**Fig. 4. Microstructures of  $\text{UO}_2\text{-6wt}\%\text{Gd}_2\text{O}_3$  Pellets Doped with 0.1 wt%  $\text{Cr}_2\text{O}_3\text{-0.1 wt}\%\text{SiO}_2$  in Various Sintering Atmospheres: (a) 0.05 vol%  $\text{H}_2\text{O-H}_2$ ; (b) 1 vol%  $\text{H}_2\text{O-H}_2$ ; (c) 3 vol%  $\text{H}_2\text{O-H}_2$**

$\text{SiO}_2$  content in 0.05 vol%  $\text{H}_2\text{O-H}_2$ , 1 vol%  $\text{H}_2\text{O-H}_2$  and 3 vol%  $\text{H}_2\text{O-H}_2$  sintering atmospheres. The ratio of  $\text{Cr}_2\text{O}_3$  to  $\text{SiO}_2$  in the  $\text{Cr}_2\text{O}_3\text{-SiO}_2$  dopant mixture is 0.5 by weight. It can be found that the relation between the density and the  $\text{Cr}_2\text{O}_3\text{-SiO}_2$  content is somewhat similar to that between the density and the  $\text{Cr}_2\text{O}_3$  content in each atmosphere (see Fig. 1). The density increases rapidly in the range of 0.05 wt%  $\text{Cr}_2\text{O}_3\text{-SiO}_2$  in 1 and 3 vol%  $\text{H}_2\text{O-H}_2$  atmospheres, but it increases gradually in 0.05 vol%  $\text{H}_2\text{O-H}_2$  atmosphere. This result suggests that the role of  $\text{Cr}_2\text{O}_3\text{-SiO}_2$  in densification is affected by the oxygen potential in a similar way to the role of  $\text{Cr}_2\text{O}_3$ . The largest difference between Fig. 1 and Fig. 3 is found in that the addition of  $\text{Cr}_2\text{O}_3\text{-SiO}_2$  improve the density more significantly below the content of 0.025 wt% than the addition of  $\text{Cr}_2\text{O}_3$ . This result the higher density with lower amount of  $\text{Cr}_2\text{O}_3\text{-SiO}_2$  could be beneficial since the amount of

sintering additives should be as low as possible.

Figs. 4a-4c show the microstructures of  $\text{UO}_2\text{-6wt}\%\text{Gd}_2\text{O}_3$  pellets with 0.1wt%  $\text{Cr}_2\text{O}_3\text{-0.1wt}\%\text{SiO}_2$  in 0.05 vol%  $\text{H}_2\text{O-H}_2$ , 1 vol%  $\text{H}_2\text{O-H}_2$  and 3 vol%  $\text{H}_2\text{O-H}_2$  atmospheres, respectively. All microstructures show some clusters of very small grains in the matrix of normal grains as the microstructures shown in Figs. 2a-2c. However, the overall area of clusters tends to be smaller in Fig. 4 than in Fig. 2, suggesting that  $\text{Cr}_2\text{O}_3\text{-SiO}_2$  can produce more uniform grains than  $\text{Cr}_2\text{O}_3$ .

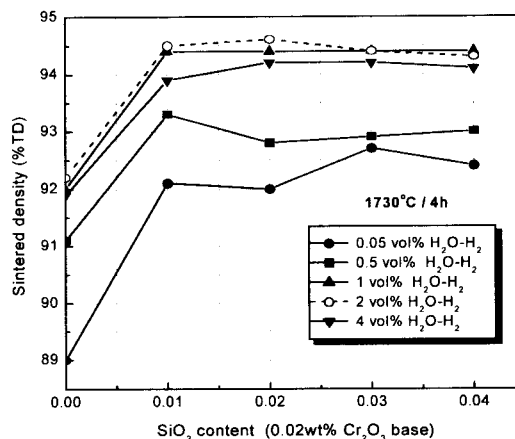
Gd and Cr concentrations in a cluster of small grains of sintered pellet of Fig. 4a were analyzed by EPMA, and the results are shown in Figs. 5a and 5b. The Gd and Cr concentrations in the cluster are quite low compared to those in surrounding matrix, so the cluster is a Gd-poor (U-rich) and Cr-poor region. It is supposed that an inhomogeneity in Gd and Cr concentrations could affect grain growth, leading to an irregular grain



**Fig. 5. SEM Micrographs Showing Gd and Cr Concentration Profiles Across a Cluster in a Matrix: (a) Gd Profile; (b) Cr Profile (The profile is obtained along the white straight line.)**

structure.

The effect of very small amounts of  $\text{Cr}_2\text{O}_3\text{-SiO}_2$  on the density is shown in Fig. 6 for various sintering atmospheres. The amounts of  $\text{Cr}_2\text{O}_3\text{-SiO}_2$  are in the range of 0.02 wt%  $\text{Cr}_2\text{O}_3$ -(0.01~0.04wt%)  $\text{SiO}_2$ . The density is substantially increased by the addition of 0.01 wt%  $\text{SiO}_2$  and levels off with further amounts of  $\text{SiO}_2$ . This relationship between the density and the  $\text{Cr}_2\text{O}_3\text{-SiO}_2$  content is quite similar in all atmospheres. However, the  $\text{H}_2\text{O}$  content in  $\text{H}_2$  gas has a large effect on the density; The density tends to increase with the  $\text{H}_2\text{O}$  content, with the maximum density being accomplished for 1 and 2 vol%  $\text{H}_2\text{O}$  contents. Fig. 6 indicates that the powder mixture of  $\text{UO}_2\text{-6wt% Gd}_2\text{O}_3$  can be sintered up to 94.5 %TD in 1 and 2 vol%  $\text{H}_2\text{O-H}_2$  atmospheres by



**Fig. 6. Relations Between the Density of  $\text{UO}_2\text{-6wt%Gd}_2\text{O}_3$  Pellets and the  $\text{SiO}_2$  Component of  $\text{Cr}_2\text{O}_3\text{-SiO}_2$  for Various Sintering Atmospheres**

adding  $\text{Cr}_2\text{O}_3\text{-SiO}_2$  with permissible amounts, i.e., 0.02wt%  $\text{Cr}_2\text{O}_3$ -(0.01~0.04)wt%  $\text{SiO}_2$ .

Figs. 7a and 7b show the microstructures of pellets with 0.02 wt%  $\text{Cr}_2\text{O}_3$ -0.04wt%  $\text{SiO}_2$  in 0.05 vol%  $\text{H}_2\text{O-H}_2$  and 2 vol%  $\text{H}_2\text{O-H}_2$  sintering atmospheres, respectively. It is found that metallic Cr precipitates are formed in 0.05 vol%  $\text{H}_2\text{O-H}_2$  gas, suggesting that  $\text{Cr}_2\text{O}_3$  is reduced to Cr in 0.05 vol%  $\text{H}_2\text{O-H}_2$  atmosphere.

Fig. 8a shows the shrinkage (densification) of  $\text{UO}_2\text{-6wt% Gd}_2\text{O}_3$  compacts with and without 0.02 wt%  $\text{Cr}_2\text{O}_3$ -0.04wt%  $\text{SiO}_2$ , and Fig. 8(b) shows the shrinkage rate derived from Fig. 8a. Fig. 8a indicates that two compacts start to shrink at similar temperatures between 800 and 900°C, and that the compact containing the additive densifies to a larger extent than the compact without the additive as the temperature increases. The densification of the  $\text{UO}_2\text{-6wt% Gd}_2\text{O}_3$  compact is significantly delayed in the temperatures between 1300 and 1500°C and then start again above 1500°C. It is known that the delay of densification is associated with the formation of  $(\text{U,Gd})\text{O}_2$  solid solution [11], and

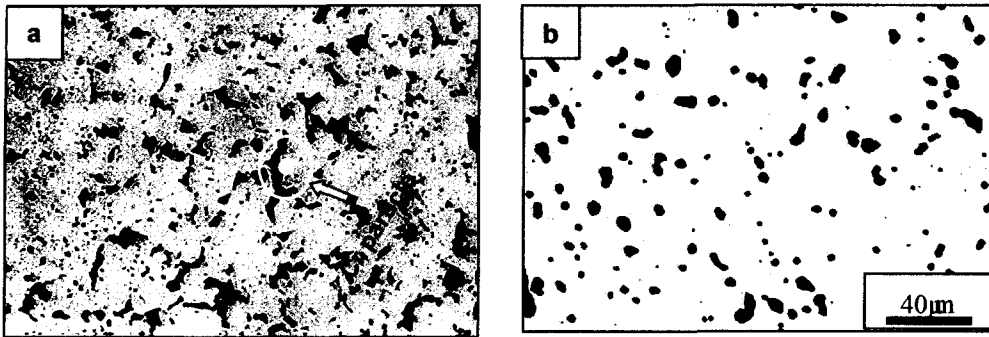


Fig. 7. Microstructures of  $\text{UO}_2\text{-6wt\%Gd}_2\text{O}_3$  Pellets Doped with  $0.02\text{wt\% Cr}_2\text{O}_3\text{-0.04wt\% SiO}_2$  in Various Sintering Atmospheres: (a)  $0.05 \text{ vol\% H}_2\text{O-H}_2$ ; (b)  $2 \text{ vol\% H}_2\text{O-H}_2$

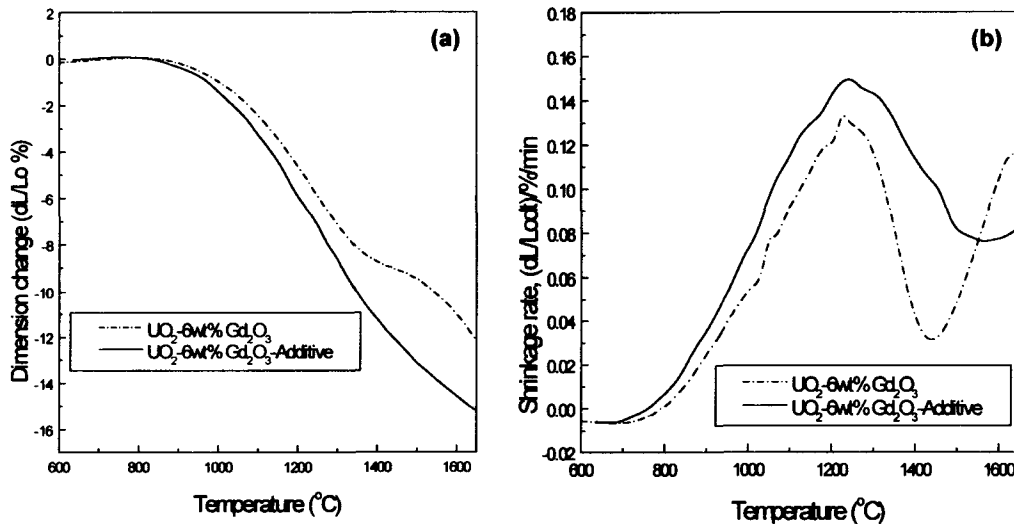


Fig. 8. Densification Behaviors of  $\text{UO}_2\text{-Gd}_2\text{O}_3$  and  $\text{UO}_2\text{-Gd}_2\text{O}_3$  with  $\text{Cr}_2\text{O}_3\text{-SiO}_2$  Compacts in  $1 \text{ vol\% H}_2\text{O-H}_2$  Atmosphere: (a) Densification; (b) Densification Rate

especially it can be attributed to the formation of Kirkendall pores as a result of the directional diffusion of Gd ions during the formation of  $(\text{U,Gd})\text{O}_2$  [12]. The densification of  $\text{UO}_2\text{-6wt\% Gd}_2\text{O}_3$  pellets with  $\text{Cr}_2\text{O}_3\text{-SiO}_2$  is not significantly delayed, and this absence of the delay of densification might apparently be one of the reasons the  $\text{Cr}_2\text{O}_3\text{-SiO}_2$  makes  $\text{UO}_2\text{-6wt\% Gd}_2\text{O}_3$  compacts be sintered up to higher density. Fig. 8b shows that the densification rate of the  $\text{UO}_2\text{-}$

$\text{Gd}_2\text{O}_3$  compact exhibits two maxima at 1250 and 1650°C and a minimum at 1400°C. The densification rate of the  $\text{UO}_2\text{-Gd}_2\text{O}_3$  compact with the additive exhibits a somewhat broad maximum at 1250°C and a plateau.

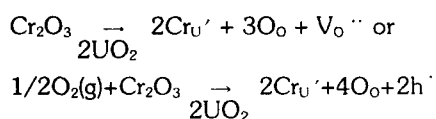
#### 4. Discussion

For the specification for fuel pellets [1] it is required that the permissible concentrations of Cr

and Si are both 250  $\mu\text{g/gU}$ . Thus the allowable amounts of  $Cr_2O_3$  and  $SiO_2$  are about 0.03wt%  $Cr_2O_3$  and 0.045wt%  $SiO_2$  with respect to  $UO_2$ . Generally, it is desirable that the amount of sintering additive is within the impurity limit specified by the fuel specification. It can be noticed from Fig. 1 that the density can be enhanced only to 93 %TD by the addition of 0.03wt%  $Cr_2O_3$ . Pellets with such a low density cannot be used since the fuel specification requires the density to be between 93.5~95.5 %TD. However, the addition of  $Cr_2O_3$ - $SiO_2$  within the permissible amount can increase the density up to 94~94.5 %TD (see Figs. 3 and 6), and this density range meets the fuel specification.

The addition of  $Cr_2O_3$  and  $Cr_2O_3$ - $SiO_2$  enhanced significantly the sintered density of  $UO_2$ -6wt%  $Gd_2O_3$  pellets. It was also found that the additives acted in different ways depending on the oxygen potential of sintering atmospheres. According to the phase diagram of  $Cr_2O_3$ - $SiO_2$  system [13], cristobalite ( $SiO_2$ ) and chromic oxide exist together below 1723  $^{\circ}\text{C}$ , and chromic oxide and a liquid phase exist together above 1723  $^{\circ}\text{C}$ . From the viewpoint of sintering, it is reasonable to suppose that  $Cr_2O_3$  and  $SiO_2$  operate independently below 1723  $^{\circ}\text{C}$  and liquid phase sintering might occur above 1723  $^{\circ}\text{C}$ .

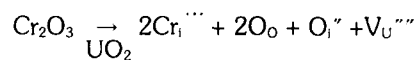
$Cr_2O_3$  might be dissolved in  $UO_2$  during sintering, and the dissolution of  $Cr_2O_3$  occurs through the entrance of Cr ion into  $UO_2$  structure in either substitutional or interstitial way. The substitutional entrance of Cr ion can be expressed as the following reactions:



where the positive hole ( $h^{\cdot}$ ) can oxidize adjacent uranium ions from  $U^{4+}$  to  $U^{5+}$ . The first reaction

indicates that oxygen vacancies are formed and thus oxygen vacancy concentration increases when Cr ions enter substitutionally in  $UO_2$ . Through Schottky equilibrium, an increase in oxygen vacancy concentration leads to a decrease in uranium vacancy concentration. Consequently, the uranium diffusion coefficient might decrease, being not consistent with the experimental results that the addition of  $Cr_2O_3$  enhances densification of  $UO_2$ - $Gd_2O_3$  pellets. The second reaction indicates the formation of  $U^{5+}$  ions, and it has been known that  $U^{5+}$  ions diffuse more slowly than  $U^{4+}$  ions [14]. Accordingly, an increase in U diffusion could not be expected.

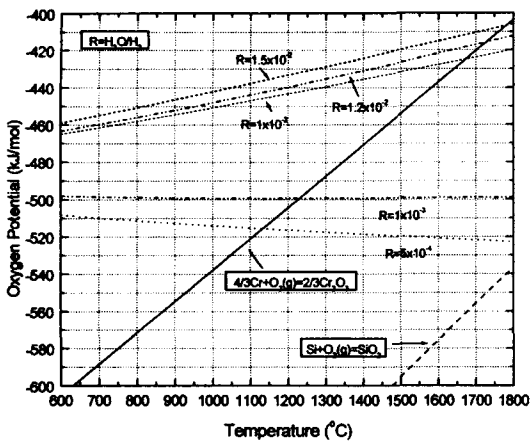
The interstitial entrance of Cr ions can be expressed as the following reaction:



If Cr ions enter interstitially in  $UO_2$ , oxygen interstitials and uranium vacancies might be formed. Thus uranium diffusion is accelerated by an increase in uranium vacancy concentration. This increase in uranium diffusion is in good agreement with the rise in sintered density (see Figs. 1, 3, and 6). An oxygen sublattice in the  $UO_2$  lattice is cubic, and the centers of oxygen sublattices are half-filled with uranium ions. The size of a central hole in oxygen octahedron is calculated to be 1.13  $\text{\AA}$  and the size of  $Cr^{3+}$  ion is about 0.8  $\text{\AA}$  [15], so the  $UO_2$  structure might have enough room to accommodate interstitial Cr ions.

Fig. 9 shows the oxygen potentials of chromic oxide, silicon oxide and sintering atmospheres as a function of temperature.  $SiO_2$  cannot be reduced to Si under any sintering atmosphere, but  $Cr_2O_3$  can be reduced to Cr under more reducing atmospheres. For example, in 0.05 vol%  $H_2O$ - $H_2$  gas  $Cr_2O_3$  is stable below 1140  $^{\circ}\text{C}$  and Cr is stable above 1140  $^{\circ}\text{C}$ . In 1 vol%  $H_2O$ - $H_2$  atmosphere





**Fig. 9. Oxygen Potentials of Chromic Oxide, Silicon Oxide and Sintering Atmospheres as a Function of Temperature**

$\text{Cr}_2\text{O}_3$  is stable below about 1670 °C, and in 1.5 vol%  $\text{H}_2\text{O}-\text{H}_2$  atmosphere  $\text{Cr}_2\text{O}_3$  is stable below 1800 °C. It was found that metallic Cr was formed in 0.05 vol%  $\text{H}_2\text{O}-\text{H}_2$  atmosphere (see Fig. 7a), and this finding is in good agreement with the thermodynamic expectation. In this atmosphere  $\text{Cr}_2\text{O}_3$  was reduced to Cr before all of the  $\text{Cr}_2\text{O}_3$  was dissolved in  $\text{UO}_2$ . However,  $\text{Cr}_2\text{O}_3$  can be dissolved without reduction during temperature rise in 1.5 vol%  $\text{H}_2\text{O}-\text{H}_2$  atmosphere. This difference suggests that the effect of  $\text{Cr}_2\text{O}_3$  on the sintered density might change with the oxygen potential. Actually, the addition of  $\text{Cr}_2\text{O}_3$  improved the density slightly in 0.05 vol%  $\text{H}_2\text{O}-\text{H}_2$  atmosphere but significantly in 1 and 3 vol%  $\text{H}_2\text{O}-\text{H}_2$  atmospheres (see Fig. 1). On the other hand,  $\text{SiO}_2$  remains unchanged in any sintering atmosphere (see Fig. 9), and thus the effect of  $\text{SiO}_2$  on the density might not be influenced by the oxygen potential. The resulting effect of  $\text{Cr}_2\text{O}_3$ - $\text{SiO}_2$  on the density is dependent on the oxygen potential in Figs. 3 and 6 can be understood by considering that the oxygen potential dependence

might be derived not from  $\text{SiO}_2$  but from  $\text{Cr}_2\text{O}_3$ .

In contrast to the densification of the  $\text{UO}_2$ - $\text{Gd}_2\text{O}_3$  compact, that of the compact with  $\text{Cr}_2\text{O}_3$ - $\text{SiO}_2$  was almost not delayed in the temperatures between 1300 and 1500 °C (see Fig. 8). It has been known that the densification prior to the delay is the result of  $\text{UO}_2$ - $\text{UO}_2$  particle sintering [11,12]. Song et al. [12] have proposed that new pores are produced in the original places of  $\text{Gd}_2\text{O}_3$  particles during the formation of  $(\text{U,Gd})\text{O}_2$  as a result of the directional diffusion of Gd ions into  $\text{UO}_2$  because the solubility of  $\text{Gd}_2\text{O}_3$  in  $\text{UO}_2$  is much higher than the reverse solubility. The formation of these new pores might give rise to the de-densification (swelling) of compact, but sintering between  $\text{UO}_2$  and  $\text{UO}_2$  particles still progresses in compacts. Thus these two factors determine the overall densification of compact. If the swelling due to the new pores is not small compared to the sintering between  $\text{UO}_2$  and  $\text{UO}_2$  particles, the overall densification of compact will be delayed with the amount of the swelling. This is the case of  $\text{UO}_2$ - $\text{Gd}_2\text{O}_3$  compacts. However, if the swelling is much smaller than the sintering between  $\text{UO}_2$  and  $\text{UO}_2$  particles, the overall densification of compact will progress without such noticeable delay as that of the compact with  $\text{Cr}_2\text{O}_3$ - $\text{SiO}_2$ . Consequently, it is supposed that  $\text{Cr}_2\text{O}_3$ - $\text{SiO}_2$  enhances sintering between  $\text{UO}_2$  and  $\text{UO}_2$  particles in the temperatures between 1300 and 1500 °C, in which the role of  $\text{Cr}_2\text{O}_3$  in  $\text{Cr}_2\text{O}_3$ - $\text{SiO}_2$  might be much larger than that of  $\text{SiO}_2$  since  $\text{SiO}_2$  might be most the effective in a liquid phase above 1723 °C.

Fig. 6 showed that the density is greatly enhanced even at 0.01 wt%  $\text{SiO}_2$  and then remains nearly constant with higher  $\text{SiO}_2$  contents. This large increase in density might be due to the presence of a liquid phase of  $\text{SiO}_2$  above 1723 °C. The liquid phase can accelerate uranium diffusion through it.

## 5. Conclusions

Mixtures of AUC- $\text{UO}_2$  and  $\text{Gd}_2\text{O}_3$  powders with  $\text{Cr}_2\text{O}_3$  or  $\text{Cr}_2\text{O}_3\text{-SiO}_2$  were pressed and sintered at 1730 °C in hydrogen gas containing various water-vapor contents. The following conclusions can be drawn:

(1) The density of  $\text{UO}_2\text{-6wt}\%$   $\text{Gd}_2\text{O}_3$  pellets can be increased by the addition of  $\text{Cr}_2\text{O}_3$  or  $\text{Cr}_2\text{O}_3\text{-SiO}_2$ . The magnitude of this increase is much larger in (1 ~4 vol%)  $\text{H}_2\text{O-H}_2$  atmospheres than in dry hydrogen atmosphere (0.05 vol%  $\text{H}_2\text{O-H}_2$ ). This difference might be attributed to the fact that  $\text{Cr}_2\text{O}_3$  is reduced to metallic Cr above 1140 °C during a temperature rise in 0.05 vol%  $\text{H}_2\text{O-H}_2$  atmosphere.  $\text{Cr}_2\text{O}_3\text{-SiO}_2$  is found to be more effective in densification than  $\text{Cr}_2\text{O}_3$  when the total amounts of the two additives are the same. The density is increased from 91 %TD to 94.5 %TD in 1 vol%  $\text{H}_2\text{O-H}_2$  atmosphere by the addition of 0.02wt%  $\text{Cr}_2\text{O}_3\text{-(0.01 ~0.04 wt}\%$   $\text{SiO}_2$ , which is permissible in the fuel specification.

(2) It is found that the grain structure of  $\text{UO}_2\text{-6wt}\%$   $\text{Gd}_2\text{O}_3$  pellets with additives is irregular; some clusters of 1 ~2  $\mu\text{m}$  sized grains in the matrix of about 8  $\mu\text{m}$  sized grains. The cluster was poor in Gd and Cr but rich in U, compared to the surrounding matrix.

(3) Cr ions might enter the  $\text{UO}_2$  structure in an interstitial way, thereby producing an increase in uranium vacancy concentration and in uranium diffusion coefficient. However,  $\text{SiO}_2$  might enhance densification through liquid phase sintering.

(4) The densification of  $\text{UO}_2\text{-Gd}_2\text{O}_3$  compact is significantly delayed in the temperatures between 1300 and 1500 °C, but that of the compact with  $\text{Cr}_2\text{O}_3\text{-SiO}_2$  is not. In this temperature range sintering between  $\text{UO}_2$  and  $\text{UO}_2$  particles might be significantly enhanced by the  $\text{Cr}_2\text{O}_3$  component of  $\text{Cr}_2\text{O}_3\text{-SiO}_2$  and thus becomes a predominant

portion of the overall densification of the compact with  $\text{Cr}_2\text{O}_3\text{-SiO}_2$ . Another portion, the swelling or pore formation due to the  $(\text{U,Gd})\text{O}_2$  formation, little influences the overall densification.

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