

Sintering of a Mixture of UO_2 and Gd_2O_3 Powders Doped with Cr_2O_3 - SiO_2

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Abstract

Mixtures of AUC- UO_2 and Gd_2O_3 powders doped with Cr_2O_3 or Cr_2O_3 - SiO_2 were pressed and sintered at 1730℃ in hydrogen gas with various water-vapor contents. The density of UO_2 -6wt% Gd_2O_3 pellets can be increased from 91% TD to 94.5% TD in 1 vol% H_2O - H_2 gas by the addition of 0.02wt% Cr_2O_3 -(0.01~0.04) wt% SiO_2 . The magnitude of density increase is much larger in (1~3 vol%) H_2O - H_2 gases than in 0.05 vol% H_2O - H_2 gas. The densification of UO_2 - Gd_2O_3 compact is significantly delayed in the temperature range between 1300 and 1500℃, but that of compacts with Cr_2O_3 - SiO_2 is not. The role of Cr_2O_3 and SiO_2 in densification is discussed.

Key Words : UO_2 - Gd_2O_3 fuel, sintering, Cr_2O_3 , SiO_2 , oxygen potential

1. Introduction

UO_2 - Gd_2O_3 fuel is widely used as a burnable absorber in LWRs. The fabrication method of UO_2 - Gd_2O_3 pellets is quite similar to that of UO_2 fuel [1] and thus it includes the processes of mixing or milling, pressing and sintering. But UO_2 - Gd_2O_3 pellets are generally difficult to produce compared to UO_2 pellets since the UO_2 - Gd_2O_3 pellet is apt to have a low density and a small grain size. To overcome this difficulty the milling process of UO_2 and Gd_2O_3 powders is widely adopted in the fabrication of UO_2 - Gd_2O_3 pellets. The Gd_2O_3 contents of 4 to 10 wt% are commonly used.

The fabrication method of UO_2 - Gd_2O_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 UO_2 - Gd_2O_3 compacts in hydrogen gas using 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 UO_2 - Gd_2O_3 fuel and have reported that the coprecipitated (U,Gd) O_2 powder was better in homogeneity than any other methods of mixing

UO_2 and Gd_2O_3 powders.

Ho and Radford [4] sintered UO_2 -9wt% Gd_2O_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 UO_2 -(5,10)wt% Gd_2O_3 pellets in mixed gases of CO and CO_2 . They also found that the sintered density decreased with increasing oxygen potential.

Song et al. [6] have studied the sintering behavior of UO_2 - Gd_2O_3 pellets using a mixture of UO_2 and Gd_2O_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 UO_2 and Gd_2O_3 powders is not an adequate method in the fabrication of UO_2 - Gd_2O_3 pellets. However, Assman et al. [7] have reported that a mixture of UO_2 and Gd_2O_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 TiO_2 also have a beneficial effect on the densification of UO_2 - Gd_2O_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 UO_2 - Gd_2O_3 pellets by using a composite additive of Cr_2O_3 - SiO_2 . This additive was added to a mixture of UO_2 and Gd_2O_3 powders, and its effect on the sintering behavior of UO_2 - Gd_2O_3 pellets have been investigated.

2. Experimental Procedures

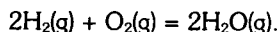
The UO_2 powder used in this work was made through the AUC (Ammonium Uranyl Carbonate) process. The UO_2 powder ex-AUC [9] has a large

particle size of about 20 μm and a round shape, so it can be more uniformly mixed with Gd_2O_3 and sintering additives than the other UO_2 powders made through ammonium diuranate and dry conversion processes. UO_2 , Gd_2O_3 and a sintering additive (Cr_2O_3 or Cr_2O_3 - SiO_2) powders were mixed with a tumbling mixer to make a uniform powder mixture in which the content of Gd_2O_3 was 6 wt%.

In the first experiment to investigate the effects of additive concentration on sintering, The amounts of Cr_2O_3 varied from 0.015 to 0.2 wt%, and the amounts of Cr_2O_3 - SiO_2 changed from 0.025 to 0.2 wt%. The content of Cr_2O_3 in Cr_2O_3 - SiO_2 was 50 wt%. The powder mixture of UO_2 , Gd_2O_3 and Cr_2O_3 or Cr_2O_3 - SiO_2 was pressed into compacts (green pellets) at a pressure of 3 t/cm² and then sintered at 1730℃ for 4 h in three different gas atmospheres; hydrogen (H_2), 1 vol% H_2O - H_2 , and 3 vol% H_2O - H_2 . Pure hydrogen used in the experiment a dew point of -30℃ and thus contained a water vapor of 5×10^{-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, H_2 , 1 vol% H_2O - H_2 and 3 vol% H_2O - H_2 , having the H_2O -to- H_2 ratios of 5×10^{-4} , 1×10^{-2} , and 3×10^{-2} , respectively.

In the second experiment to investigate the effect of very small amounts of Cr_2O_3 - SiO_2 on sintering, both 0.02 wt% Cr_2O_3 and 0.01 ~ 0.04 wt% SiO_2 were used. The above amounts are allowable in the specification [1]. The powder mixture was pressed and sintered at 1730℃ for 4 h in four different gas atmospheres; H_2 , 0.5 vol% H_2O - H_2 , 1 vol% H_2O - H_2 , 2 vol% H_2O - H_2 , and 4 vol% H_2O - H_2 , giving the H_2O -to- H_2 ratios of 5×10^{-4} , 5×10^{-3} , 1×10^{-2} , 2×10^{-2} , and 4×10^{-2} , respectively, in that order.

The gas mixture of H_2 and H_2O generates oxygen partial pressure according to the following reaction:



The oxygen partial pressure (PO_2) is proportional to the term of $[P(H_2O)/P(H_2)]^2$, increasing with the H_2O -to- H_2 ratio. The oxygen potential defined by $RT \ln P(O_2)$ 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, ρ_{pellet} : sintered density of pellet, P_{op} : ratio of open porosity to total porosity

W_{dry} : dry weight, W_{imp} : impregnated weight, W_{sus} : suspended weight

ρ_x : density of water,

ρ_{TD} : theoretical density of pellet = $10.96 - 0.04$ (wt% of Gd_2O_3) [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_2 -6wt% Gd_2O_3 and UO_2 -6wt% Gd_2O_3 with 0.02wt% Cr_2O_3 -0.04wt% SiO_2 . The shrinkage of the compacts was measured in an

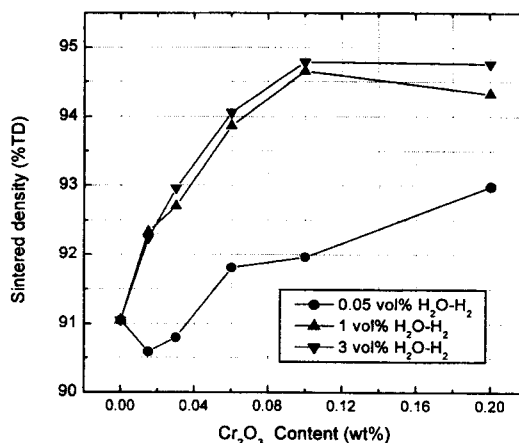


Fig. 1. Dependence of the Density of UO_2 -6wt% Gd_2O_3 Pellets on Cr_2O_3 Content for Various Sintering Atmospheres

axial direction with a LVDT transducer in a push rod type dilatometer. Compacts were heated to 1650°C with a heating rate of $5^\circ\text{C}/\text{min}$ in 1 vol% H_2O - H_2 gas.

3. Results

Fig. 1 shows a plot of the relationships between the sintered density of UO_2 -6wt% Gd_2O_3 pellets and Cr_2O_3 content for various sintering atmospheres. The density increases with the content of Cr_2O_3 , and the increasing rate quite changes with the gas atmosphere. In 0.05 vol% H_2O - H_2 gas, the density slightly decreases in the range of 0.04 wt% Cr_2O_3 and then increases gradually up to 93 %TD at 0.2 wt% Cr_2O_3 . In 1 and 3 vol% H_2O - H_2 gas, the density increases substantially up to about 94.7 %TD in the range of 0.1 wt% Cr_2O_3 and thereafter leveled off. This result suggests that the role of Cr_2O_3 in the densification of UO_2 -6wt% Gd_2O_3 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

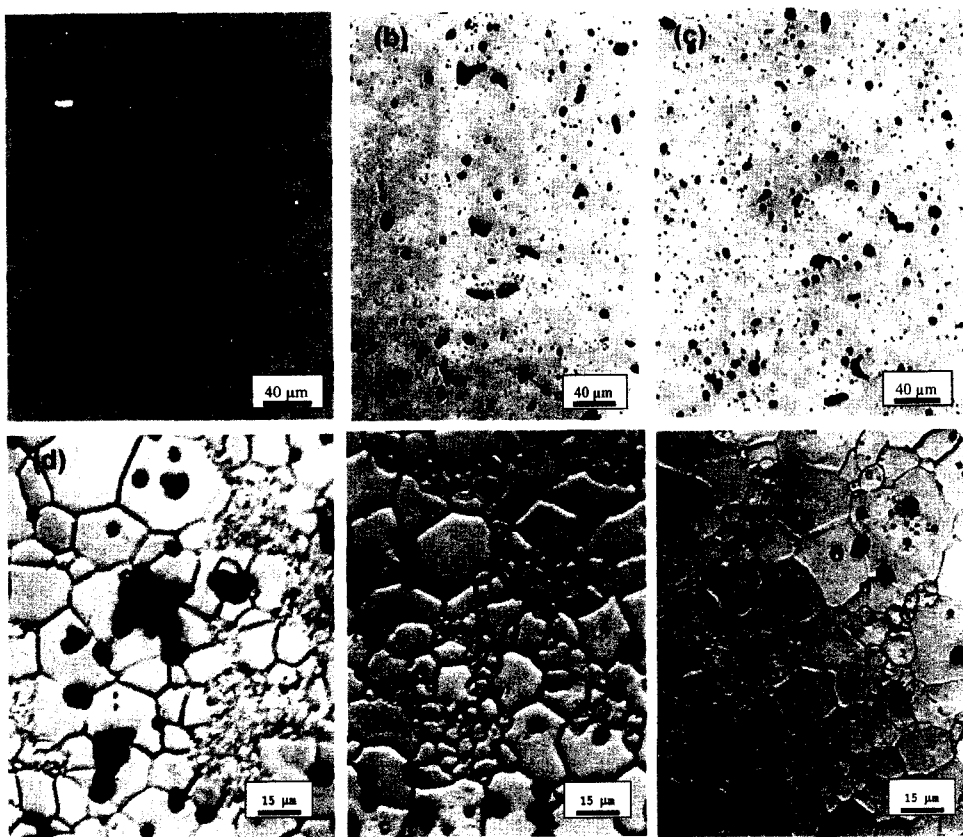


Fig. 2. Microstructures of UO_2 -6wt% Gd_2O_3 Pellets Doped with 0.2 wt% Cr_2O_3 in Various Sintering Atmospheres: Pore Structures (a) 0.05 vol% H_2O - H_2 ; (b) 1 vol% H_2O - H_2 ; (c) 3 vol% H_2O - H_2 . Grain Structures (e) 0.05 vol% H_2O - H_2 ; (f) 1 vol% H_2O - H_2 ; (g) 3 vol% H_2O - H_2

and 3 vol% H_2O - H_2 atmospheres and simultaneously of more than 0.1 wt% Cr_2O_3 .

Figs. 2a to 2f show the pore and grain structures of 0.2 wt% Cr_2O_3 -doped pellets sintered in 0.05 vol% H_2O - H_2 , 1 vol% H_2O - H_2 and 3 vol% H_2O - 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 UO_2 -6wt% Gd_2O_3 pellets on the Cr_2O_3 -

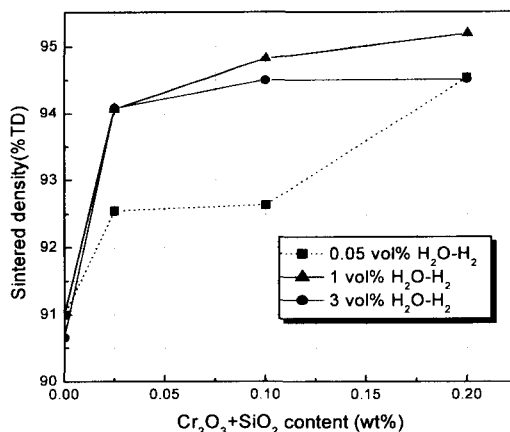


Fig. 3. Dependence of the Density of UO_2 -6wt% Gd_2O_3 Pellets on Cr_2O_3 - SiO_2 Content for Various Sintering Atmospheres

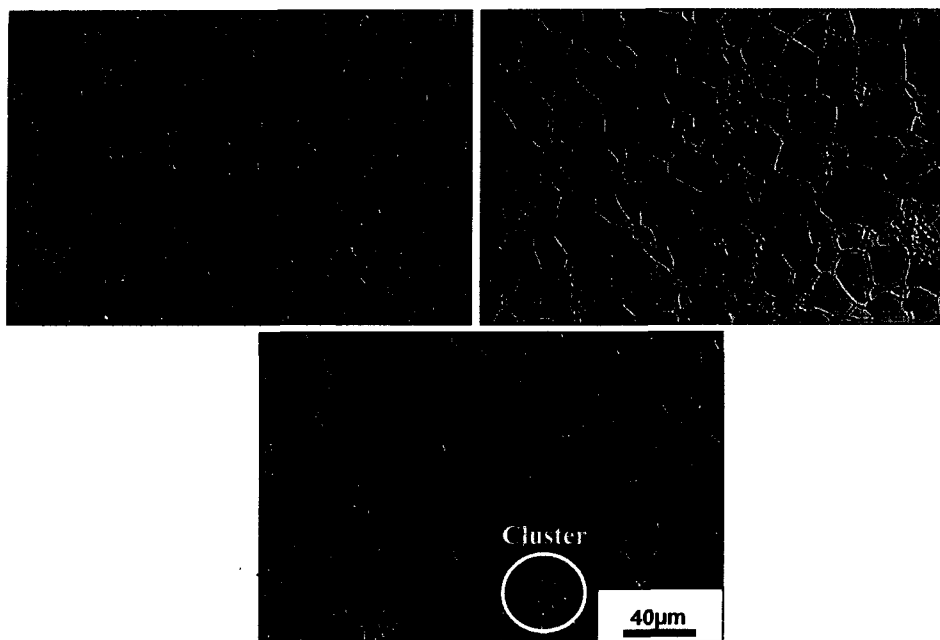


Fig. 4. Microstructures of $\text{UO}_2\text{-6wt\%Gd}_2\text{O}_3$ Pellets Doped with 0.1 wt% $\text{Cr}_2\text{O}_3\text{-0.1 wt\% SiO}_2$ in Various Sintering Atmospheres: (a) 0.05 vol% $\text{H}_2\text{O-H}_2$; (b) 1 vol% $\text{H}_2\text{O-H}_2$; (c) 3 vol% $\text{H}_2\text{O-H}_2$

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 Cr_2O_3 to 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 Cr_2O_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 Cr_2O_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 Cr_2O_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 $\text{UO}_2\text{-6wt\% Gd}_2\text{O}_3$ pellets with 0.1wt% $\text{Cr}_2\text{O}_3\text{-0.1wt\% SiO}_2$ 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 Cr_2O_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

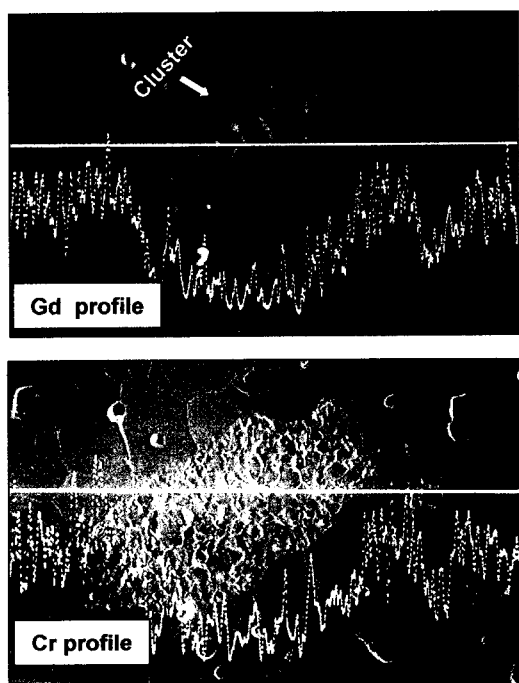


Fig. 5. SEM Micrographs Showing Gd and Cr Concentration Profiles Across a Cluster in a Matrix: (a) Gd Profile; (b) Cr Profile (The profile is obtained along the white straight line.)

structure.

The effect of very small amounts of Cr_2O_3 - SiO_2 on the density is shown in Fig. 6 for various sintering atmospheres. The amounts of Cr_2O_3 - SiO_2 are in the range of 0.02 wt% Cr_2O_3 -(0~0.04wt%) SiO_2 . The density is substantially increased by the addition of 0.01 wt% SiO_2 and levels off with further amounts of SiO_2 . This relationship between the density and the Cr_2O_3 - SiO_2 content is quite similar in all atmospheres. However, the H_2O content in H_2 gas has a large effect on the density; The density tends to increase with the H_2O content, with the maximum density being accomplished for 1 and 2 vol% H_2O contents. Fig. 6 indicates that the powder mixture of UO_2 -6wt% Gd_2O_3 can be sintered up to 94.5 %TD in 1 and 2 vol% H_2O - H_2 atmospheres by

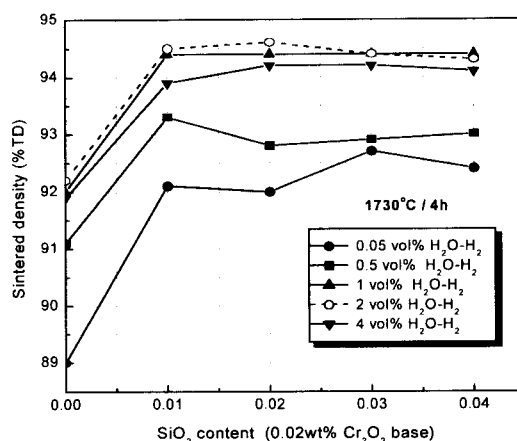


Fig. 6. Relations Between the Density of UO_2 -6wt% Gd_2O_3 Pellets and the SiO_2 Component of Cr_2O_3 - SiO_2 for Various Sintering Atmospheres

adding Cr_2O_3 - SiO_2 with permissible amounts, i.e., 0.02wt% Cr_2O_3 -(0.01~0.04)wt% SiO_2 .

Figs. 7a and 7b show the microstructures of pellets with 0.02 wt% Cr_2O_3 -0.04wt% SiO_2 in 0.05 vol% H_2O - H_2 and 2 vol% H_2O - H_2 sintering atmospheres, respectively. It is found that metallic Cr precipitates are formed in 0.05 vol% H_2O - H_2 gas, suggesting that Cr_2O_3 is reduced to Cr in 0.05 vol% H_2O - H_2 atmosphere.

Fig. 8a shows the shrinkage (densification) of UO_2 -6wt% Gd_2O_3 compacts with and without 0.02 wt% Cr_2O_3 -0.04wt% 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 UO_2 -6wt% Gd_2O_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 (U,Gd) O_2 solid solution [11], and

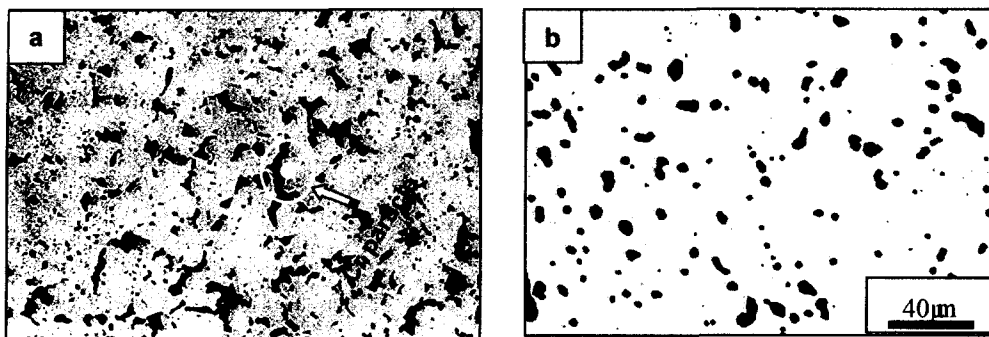


Fig. 7. Microstructures of $\text{UO}_2\text{-6wt\%Gd}_2\text{O}_3$ Pellets Doped with $0.02\text{wt\% Cr}_2\text{O}_3\text{-}0.04\text{wt\% SiO}_2$ in Various Sintering Atmospheres: (a) $0.05 \text{ vol\% H}_2\text{O-H}_2$; (b) $2 \text{ vol\% H}_2\text{O-H}_2$

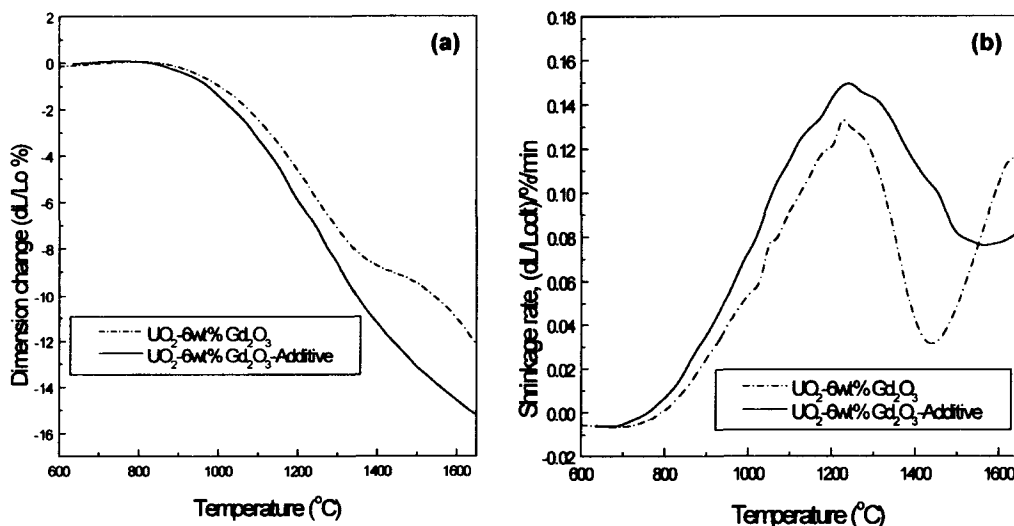


Fig. 8. Densification Behaviors of $\text{UO}_2\text{-Gd}_2\text{O}_3$ and $\text{UO}_2\text{-Gd}_2\text{O}_3$ with $\text{Cr}_2\text{O}_3\text{-SiO}_2$ Compacts in $1 \text{ vol\% H}_2\text{O-H}_2$ Atmosphere: (a) Densification; (b) Densification Rate

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 $\text{UO}_2\text{-}$

Gd_2O_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.

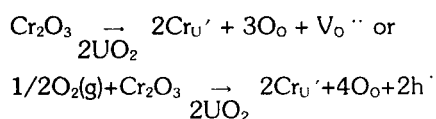
4. Discussion

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°C , and chromic oxide and a liquid phase exist together above 1723°C . From the viewpoint of sintering, it is reasonable to suppose that Cr_2O_3 and SiO_2 operate independently below 1723°C and liquid phase sintering might occur above 1723°C .

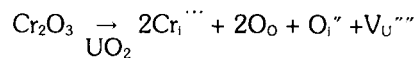
Cr_2O_3 might be dissolved in UO_2 during sintering, and the dissolution of Cr_2O_3 occurs through the entrance of Cr ion into UO_2 structure in either substitutional or interstitial way. The substitutional entrance of Cr ion can be expressed as the following reactions:



where the positive hole (h^+) 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 \AA and the size of Cr^{3+} ion is about 0.8 \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°C and Cr is stable above 1140°C . In 1 vol% H_2O - H_2 atmosphere

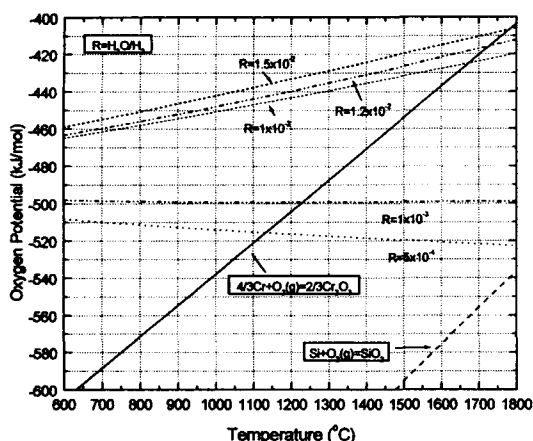


Fig. 9. Oxygen Potentials of Chromic Oxide, Silicon Oxide and Sintering Atmospheres as a Function of Temperature

Cr_2O_3 is stable below about 1670 °C, and in 1.5 vol% $\text{H}_2\text{O}-\text{H}_2$ atmosphere Cr_2O_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 Cr_2O_3 was reduced to Cr before all of the Cr_2O_3 was dissolved in UO_2 . However, Cr_2O_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 Cr_2O_3 on the sintered density might change with the oxygen potential. Actually, the addition of Cr_2O_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, SiO_2 remains unchanged in any sintering atmosphere (see Fig. 9), and thus the effect of SiO_2 on the density might not be influenced by the oxygen potential. The resulting effect of Cr_2O_3 - 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 SiO_2 but from Cr_2O_3 .

In contrast to the densification of the UO_2 - Gd_2O_3 compact, that of the compact with Cr_2O_3 - 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 UO_2 - UO_2 particle sintering [11,12]. Song et al. [12] have proposed that new pores are produced in the original places of Gd_2O_3 particles during the formation of $(\text{U,Gd})\text{O}_2$ as a result of the directional diffusion of Gd ions into UO_2 because the solubility of Gd_2O_3 in 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 UO_2 and 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 UO_2 and UO_2 particles, the overall densification of compact will be delayed with the amount of the swelling. This is the case of UO_2 - Gd_2O_3 compacts. However, if the swelling is much smaller than the sintering between UO_2 and UO_2 particles, the overall densification of compact will progress without such noticeable delay as that of the compact with Cr_2O_3 - SiO_2 . Consequently, it is supposed that Cr_2O_3 - SiO_2 enhances sintering between UO_2 and UO_2 particles in the temperatures between 1300 and 1500 °C, in which the role of Cr_2O_3 in Cr_2O_3 - SiO_2 might be much larger than that of SiO_2 since 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% SiO_2 and then remains nearly constant with higher SiO_2 contents. This large increase in density might be due to the presence of a liquid phase of SiO_2 above 1723 °C. The liquid phase can accelerate uranium diffusion through it.

5. Conclusions

Mixtures of AUC- UO_2 and Gd_2O_3 powders with Cr_2O_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 $\text{UO}_2\text{-6wt\% Gd}_2\text{O}_3$ pellets can be increased by the addition of Cr_2O_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 Cr_2O_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 Cr_2O_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% $\text{Cr}_2\text{O}_3\text{-(0.01 ~ 0.04) wt\% SiO}_2$, which is permissible in the fuel specification.

(2) It is found that the grain structure of $\text{UO}_2\text{-6wt\% Gd}_2\text{O}_3$ pellets with additives is irregular; some clusters of 1 ~ 2 μm sized grains in the matrix of about 8 μm 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 UO_2 structure in an interstitial way, thereby producing an increase in uranium vacancy concentration and in uranium diffusion coefficient. However, 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 UO_2 and UO_2 particles might be significantly enhanced by the Cr_2O_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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