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Effect of Various Resintering Atmospheres on Density Changes of UO_2-Gd_2O_3 Pellets

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Abstract

In order to investigate the effect of the furnace atmosphere on the resintering behavior of UO_2-Gd_2O_3 pellets, density changes of UO_2-Gd_2O_3 pellets after resintering under various atmospheres have been measured. UO_2-Gd_2O_3 pellets sintered under H_2-CO_2 mixed gas were resintered under dry H_2 and H_2-CO_2 mixed gas, respectively, at the temperature of 1700°C for 24 hrs. The experiment on UO_2 pellets were performed at the same conditions for the purpose of comparison. The resintered densities of UO_2 pellets were increased regardless of atmosphere considered in this study. Those of UO_2-Gd_2O_3 pellets were increased under H_2-CO_2 mixed gas atmosphere whereas they were decreased under dry H_2 atmosphere. This density decrease is mainly caused by the reduction of U^{5+} ions to U^{4+} under very reducing atmosphere. In addition, the expansion of UO_2-Gd_2O_3 pellet caused by increasing the number of oxygen vacancy whose size is larger than that of oxygen ion is also contributed to such density decrease.

1. Introduction

Densification behavior of UO_2 pellets is an important factor to determine the integrity of fuel rods at the beginning of reactor operation. The degree of densification during the reactor operation period can be predicted through the measurement of pellet’s density differences before and after resintering in a test lab. Assman and his colleagues [1] had found that the results of resintering tests in the lab were well consistent with the actual behavior of pellet in the reactor. In general, the resintering test is performed at 1700°C for 24 hrs in a hydrogeneous atmosphere even though its specific conditions are slightly different according to manufacturers. UO_2 has a cubic fluorite-type structure and it is relatively stable over a wide range of oxygen partial pressure but minor defects(U^{5+}, U^{6+}) can develop in a higher oxidation states [2-3]. Because of these characteristics, there are no substantial differences in the density of UO_2 pellets after resintering regardless of the atmospheres. In case of UO_2-Gd_2O_3 pellets, the structural models considered possible are more complicated. Basically, oxidation of U^{4+} to U^{5+} or U^{6+}, interstitial formation, or a combination of these defects in UO_2-Gd_2O_3 pellets occurs to compensate charge changed by the addition of Gd^{3+} ion to UO_2 matrix. The resintering atmosphere plays a key role in determining defect types. Generally, when UO_2 pellets are reheated, they become densified as a result of removing pores existed in the matrix under a hydrogeneous atmosphere. However, it is expected that UO_2-Gd_2O_3 pellets act differently because more various defects can be made depending on atmospheres. However, swelling of pellets may occur when resintering atmospheres are different from sintering atmosphere. As there is no restriction on the limit of density decrease after resintering in the current specification, more detailed information about the swelling of pellet after resinering is needed. In order to evaluate the density changes of UO_2-Gd_2O_3 pellets depending on atmosphere, their structural chemistry is to be understood. This study has been undertaken to find the relationship between density change and resintering atmosphere and to suggest a mechanism on the swelling of UO_2-Gd_2O_3 pellets after resintering.

2. Background information[4]

Since both UO_2 and Gd_2O_3 have a cubic fluorite-type structure, it is expected that UO_2-Gd_2O_3 has the same structure as UO_2. Even though there is no structural change due to the addition of Gd_2O_3 to UO_2 matrix, charge balance should be considered. The sintering atmosphere determines the charge balance that forms after charge compensation caused by the addition of Gd^{3+} to UO_2 matrix. The possible types of defect are closely related to the oxidation of U^{4+} to U^{5+} or U^{6+} or a combination of these defects. Three cases of atmosphere such as very reducing, slightly oxidizing and more oxidizing ones may be considered but the structural models only for the first two cases are proposed in this study.

A. Very reducing atmosphere

Uranium ions in the UO_2-Gd_2O_3 solid solutions will remain as a U^{4+} state under very reducing atmosphere and the charge balance is maintained by oxygen vacancies or by cation interstitials. The creation of U^{5+} ions can also be considered but they are expected to be very small under this atmosphere. Three structure models may be proposed as shown below.

Creation of anion vacancies : $(U^{4+}_{1-x}Gd^{3+}_{x})O_{2-(x/2)}$

Perfect fluorite-type lattice: $(U^{4+}_{1-(3/4)x}Gd^{3+}_{x})O_{2}$

Creation of U^{5+} ions : $(U^{4+}_{1-x-y}U^{5+}_{y}Gd^{3+}_{x})O_{2-[(x-y)/2]}$

B. Slightly oxidizing atmosphere

The atmospheres with a more oxidizing potential than dry H_2 reducing atmosphere can be generated using such as mixed gas of H_2-CO_2 mixed gas or H_2 bubbles passing through a water bath. Under these oxidizing atmosphere, some U^{4+} ions in the UO_2-Gd_2O_3 may convert to U^{5+} to compensate for charge variation due to the addition of Gd_2O_3. Two possible structure models can be proposed as shown below.

Perfect fluorite-type lattice : $(U^{4+}_{1-2x}U^{5+}_{x}Gd^{3+}_{x})O_2$

Creation a oxygen interstitials : $(U^{4+}_{1-x-y}U^{5+}_{y}Gd^{3+}_{x})O_{2+[(y-x)/2]}$

3. Experimental procedure

3-1 Fabrication of the specimens

UO_2-Gd_2O_3 pellets were fabricated by using ex- DC UO_2 powders in H_2-CO_2 atmosphere and Gd_2O_3 of 6 wt% was added to the UO_2 matrix. More detailed manufacturing procedure is shown in Fig. 1. UO_2 pellets were also made in the same atmosphere for the purpose of comparison.

3-2 Resintering

Both UO_2 and UO_2-Gd_2O_3 pellets were reheated for 24 hrs at 1700^{o}C under dry H_2 and H_2-CO_2 atmosphere, respectively. The resintering process was repeated 4 times at the same conditions to investigate the effect of the number of heating cycles on density change. Density of each specimen was measured using a immersion method at each cycle. Diameter and weight change of each pellet were also measured.

4. Results and discussion

Density of UO_2 pellets after resintering is found to increase regardless of the atmospheres considered whereas that of UO_2-Gd_2O_3 pellet resintered under dry H_2 atmosphere is found to decrease as much as 0.75%T.D as shown in Fig. 2. Fig. 3 shows the density changes of UO_2 and UO_2-Gd_2O_3 pellets which were sintered under H_2-CO_2 and resintered under dry H_2

atmosphere. The density of UO_2 pellets is found to increase until the third cycle but there is no further density increase at the fourth cycle. The UO_2-Gd_2O_3 pellets which show density decrease at the first cycle of resintering show reverse density change since then but the density increase is so small that the resintered density can not reach the sintered density even after the fourth cycle. The density decrease of UO_2-Gd_2O_3 pellet after resintering under dry H_2 atmosphere can be explained by charge balance. As explained above, U^{5+} ions are created as a result of the addition of Gd^{3+} ions under a slightly oxidizing condition.

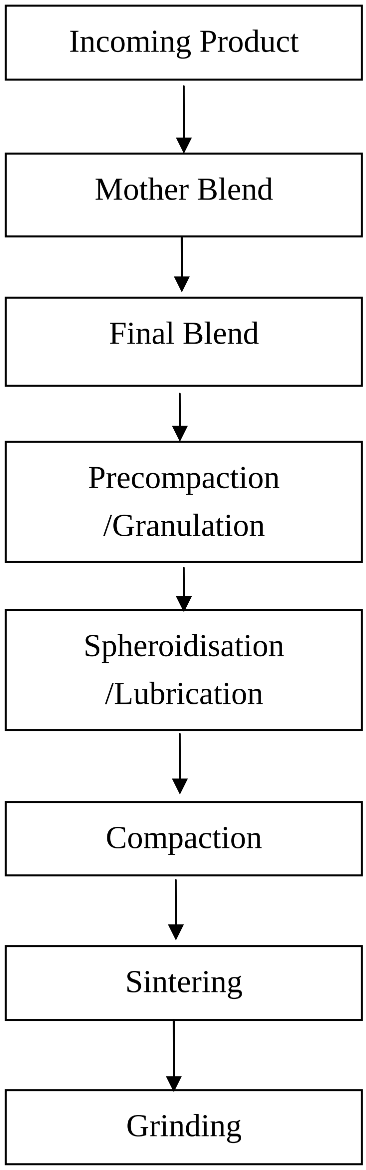

Fig. 1 Manufacturing procedure of UO_2-Gd_2O_3

In that case, the number of oxygen ions at the interstitial sites may remain constant or increase depending on the oxygen potential of sintering atmosphere. The structure formed at the sintered condition does not change if the same atmosphere is provided during resintering, but if the atmosphere is changed, especially, to more reducing conditions, some charge variations will occur. The U^{5+} ion created is likely to reduce to U^{4+} in a dry H_2 atmosphere. The reduction of U^{5+} ion to U^{4+} ion will lead to increase oxygen vacancy, which will eventually decrease the number of oxygen ions. Even if some of U^{5+} ions remain, oxygen ion should be removed to keep charge neutrality.

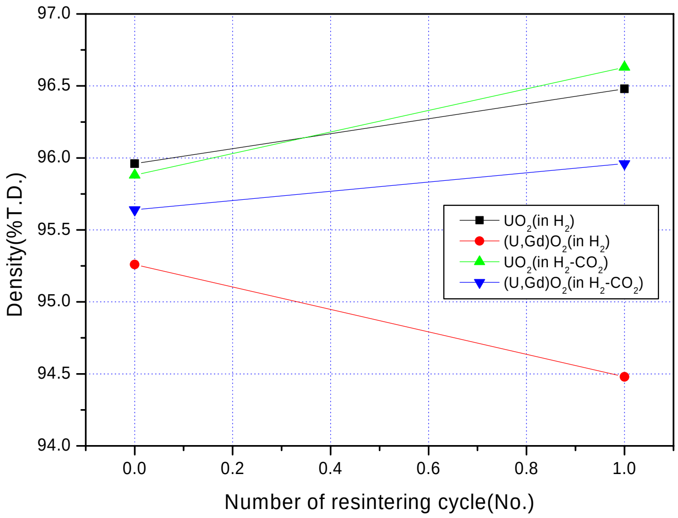

Fig. 2 Variation of density depending on resintering atmosphere

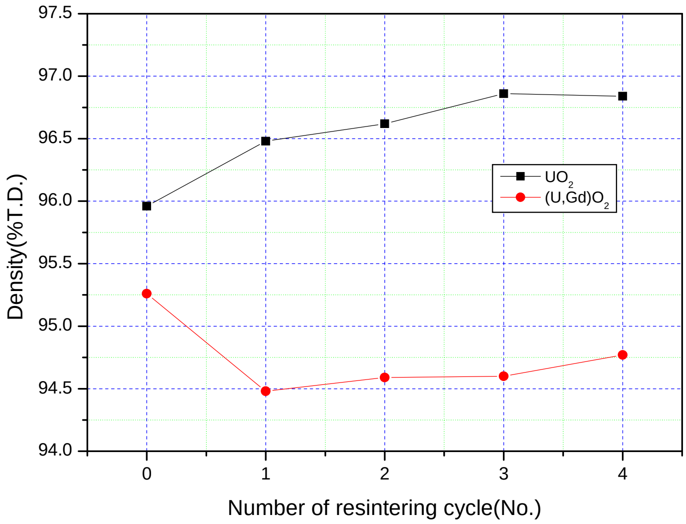

Fig. 3 Variation of density as a function of resintering cycle

(Sintered in H_2-CO_2/Resintered in H_2)

It is expected that the loss of oxygen ions in the matrix results in the loss of pellet weight. Fig. 4 shows the results of pellet weight measurement at each cycle of resintering and it can be clearly seen that quite a large amount of weight loss occurs in the UO_2-Gd_2O_3 pellet compared to UO_2 pellets after the first cycle of resintering.

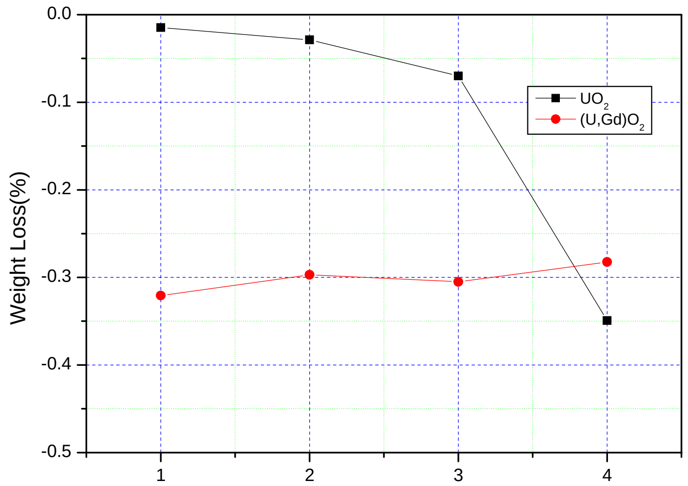

Fig. 4 Variation of weight loss as a function of resintering cycle

There is no further weight loss due to resintering after the first cycle. It is because chemical balance changes are stabilized due to dry H_2 atmosphere. A large amount of weight loss observed in the UO_2 pellet after the fourth cycle is considered to be caused by mishandling of the specimens.

Pores existed in the matrix will be removed by heating, which results in the shrinkage of pellets. As expected, the diameter of UO_2 pellet decreases with increasing resintering cycles. On the contrary, pellet diameter increase is observed in the UO_2-Gd_2O_3 pellets until the third cycle. The swelling of UO_2-Gd_2O_3 pellets which occurs until the third cycle of resintering is considered to be closely related to the formation of oxygen vacancies created as a result of charge compensation due to the change of atmosphere. According to Ohmichi et al.[5], the lattice parameter of UO_2-Gd_2O_3 pellets increases with increasing oxygen vacancies because the size of the oxygen vacancy is larger than that of the oxygen ion. These lattice expansions may be led to diameter increase shown in Fig. 5. If the pore removal by heating becomes more dominant than the lattice expansion, densification of pellets will occur. Therefore, the density decrease observed in this study on the UO_2-Gd_2O_3 pellets may be caused by the combination of weight loss and expansion of diameter.

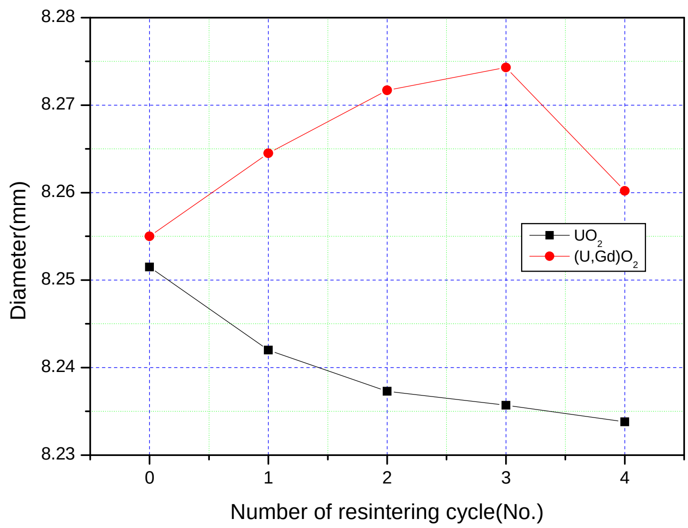

Fig. 5 Variation of diameter as a function of the number of resintering cycle

4. Conclusions

Density decrease is observed when UO_2-Gd_2O_3 pellet sintered under H_2-CO_2 atmosphere is resintered under dry H_2 atmosphere. However, no further density decrease is observed even after the extended resintering cycle. The variation of density due to change of atmosphere is closely related to the chemical balance. In general, U^{5+} ions are created under slightly oxidizing atmosphere to compensate charge changes occurred by the addition of Gd^{3+} ion. The creation of U^{5+} ions increases the concentration of oxygen ions. If atmosphere is changed from slightly oxidizing to dry hydrogen, U^{5+} ion created will be reduced to U^{4+} ion and the concentration of oxygen vacancies increases as a result of charge compensation. After all, the loss of oxygen ions in the matrix occurs during this process, which brings the weight loss of pellets observed in this study. In addition to the weight loss, diameter of UO_2-Gd_2O_3 pellets increases due to the formation of oxygen vacancies whose size is larger than that of oxygen ion. Owing to the expansion and the weight loss of pellets, density of UO_2-Gd_2O_3 pellets resintered under dry H_2 atmosphere decreases.

Acknowledgement

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