Effect of a Gas Atmosphere on the Grain Growth of UO_2

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1. Introduction

The grain and pore structures of a ceramic pellet as a nuclear fuel is one of the most important properties, which is related to the fission gas release and the pellet/clad interaction (PCI) during a irradiation in a reactor [1]. UO_2 or MOX pellets having large grains can be obtained by a control of the sintering parameters and/or by the application of an oxidative sintering process. The pellet properties can also be modified by using sintering additives such as TiO_2, Cr_2O_3 and Nb_2O_5, and this method has been attempted by various researchers [2,3,4]. Recently, Joung et al. [5] reported that the isothermal sintering of UO_2 compacts in air was possible at a high temperature above 1803K. They confirmed that the sintered UO_2 pellet consisted of a single grain. The oxygen in the air contributes to the grain growth for this sintering process, but we need to understand the oxidation behavior and phase change of the pellet in air at a high temperature.

In this work, the sintering behavior of UO_2 was studied by using both a TGA and an alumina tube furnace to confirm the effect of air on the grain growth of the pellet in the first step of an air sintering. The densification and grain growth of the pellet for the sintering in H_2-air-H_2 were compared with those for the sintering in CO_2-air-CO_2-H_2. This study demonstrates a sintering process and its sintering conditions for the UO_2 pellets which consist of large grains or a single grain.

2. Experimental

UO_2 powder was produced by the Integrated Dry Route in BNFL co, and it had an O/U ratio of 2.15, an average particle size of 2.2 ㎛, and a specific surface area of 2.36m^2/g. The milling of UO_2 powder was accomplished by using a planetary mill (FRITSCH pulverisette 6). This prepared powder was pressed with a compaction pressure of 300MPa with a die-wall lubrication method and the compacts have green density of 5.8g/cm^3 for UO_2. Thermogravitic (Cahn, TG171) experiments to observe the O/M ratio changes during the oxidation were carried out in the H_2-air and CO_2-air at 1550℃. The TG was heated up in a H_2 or CO_2 atmosphere and the gas was changed into air at the reaction temperature. The air sintering in a tube furnace was conducted by the following four stages. Firstly, the UO_2 compact was heated up to the sintering temperatures (1530-1700℃) in CO_2. Secondly, it was soaked for a range of 0~60 min. at the set temperature in air. Thirdly, it was reduced down to 1200℃ in CO_2. Fourthly, it was soaked in H_2 at the same temperature for 2h and then cooled down to a room temperature with flowing H_2 to adjust the O/U ratio of UO_2 pellets to 2.00. For the sintering in H_2-air-H_2, UO_2 compact was heated up to the sintering temperatures of 1530℃, 1600℃ or 1700℃ in H_2 then soaked for 1h in the air. At the soaked temperature, the pellet was reduced in H_2 for 1h. To avoid a reaction between H_2 and air, N_2 gas was purged into the furnace for 1 min. The sintered density of the pellets was measured by the liquid immersion method. In order to observe the microstructures of the UO_2 pellets, thermal etching was carried out at 1450℃ for 1 hour in CO_2. The average grain size was determined using the linear intercept method.

3. Results

Thermo gravimetric (TG) curves of UO_2 samples at 1550℃ are shown in Fig. 1. Before flowing air for the CO_2-air reaction, the O/U ratio of the UO_2 sample was 2.18 and for the H_2-air reaction it was 2.00. The saturation levels (phase boundary) and oxidation gradients were similar for both the CO_2-air and H_2-air reactions.

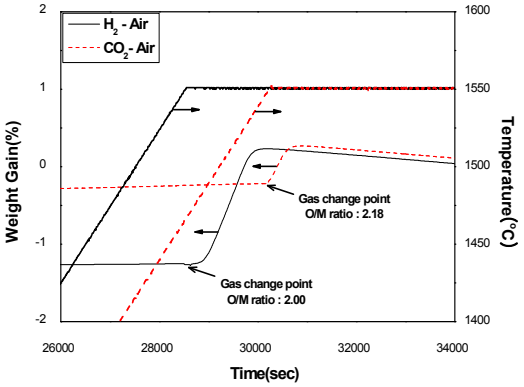

Fig. 1 TG curves of UO_2 samples reacted in the H_2-air and CO_2-air atmosphere.

The density and grain size of the UO_2 pellets sintered by the H_2-air-H_2 process are compared with those for the CO_2-H_2 sintering process in Table. 1. Sintered density at 1530℃ in H_2-air-H_2 is a little lower than that of the other pellets. The grain size was continuously increased with the sintering temperature, but an abnormal grain growth did not appear in the H_2-air-H_2 process. For the CO_2-air-CO_2-H_2 sintering process, abnormal grain growth was observed in the pellet when a sintering time in air was longer than 5min.

Table 1. Properties of the UO_2 pellets sintered in H_2-Air-H_2 and CO_2-air-CO_2-H_2.

Gas Step conditions	Sintering		Sintered density (%T.D.)	Grain size (um)
	Temp. (℃)	Time (min.)		
H_2-Air-H_2	1530	10	97.1	5
	1600	60	99.1	72
	1700	60	99.0	123
CO_2-Air-CO_2-H_2	1530	10	98.2	1500

The microstructure of the pellet sintered for 6 min in air at 1530℃ with CO_2-air-CO_2-H_2 process is shown in Fig. 2. It shows a duplex grain structure, which consists of some large grains surrounded by many fine grains.

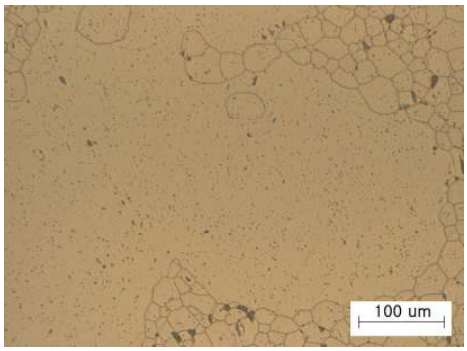

Fig. 2 Microstructures of UO_2 pellet sintered for 6min. with CO_2-air-CO_2-H_2 process.

The microstructures of the UO_2 pellets sintered for 60min. in air at (a) 1530℃, (b) 1600℃ and (c) 1700℃ in the H_2-air-H_2 process and for 10min. in air at (a) 1530℃ in the CO_2-air-CO_2-H_2 process air air shown in Fig. 3. The grain size was very fine when the pellet was sintered at 1530℃ in H_2-air-H_2, but an order of millimeters for the CO_2-air-CO_2-H_2 process at the same sintering temperature.

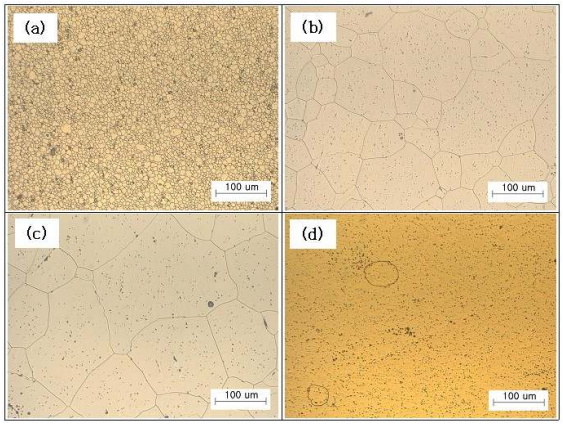

Fig. 3 Microstructures of UO_2 pellets sintered at (a) 1530℃, (b) 1600℃ and (c) 1700℃ in H_2-air-H_2 and at (a) 1530℃ in CO_2-air-CO_2-H_2.

From this result, the difference of the grain growth in H_2-air-H_2 and in CO_2-air-CO_2-H_2 seems to have originated from the O/U ratio just before flowing the air at the sintering temperature. The grain growth in the CO_2-air-CO_2-H_2 process was accelerated by the abnormal growth caused by the hyperstoichiometric O/U ratio of the pellet at the initial sintering step.

4. Conclusion

The sintering behavior of UO_2 samples was studied using a thermergravity analyzer and a tube furnace at sintering temperatures from 1530℃ to 1700℃ in air. The following conclusions were obtained from this study:

1. The saturation levels and oxidation gradients of the samples oxidized in CO_2-air and in H_2-air are similar.
2. The sintered density in H_2-air-H_2 and in CO_2-air-CO_2-H_2 is over 97%. An abnormal grain growth was observed in the CO_2-air-CO_2-H_2 process.
3. The difference in the grain growth between the H_2-air-H_2 and CO_2-air-CO_2-H_2 process originated from the hyperstoichiometric O/U ratio of a sample just before a sintering in air for the latter process.

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