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Fabrication method for UO_2 pellets with large grains or a single grain by sintering in air

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Abstract

The effects of a powder treatment, the sintering temperature and the sintering time on the grain growth of UO_2 pellets were investigated in air to obtain UO_2 pellets with large grains. Air could be used for sintering because an oxidation path above 1803 K does not pass through a two-phase ($UO_{2+x} + U_3O_{8-z}$) region. The UO_2 pellets sintered by the CO_2–air–CO_2–H_2 process consisted of a single grain or some large grains in the order of several millimeters.

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1. Introduction

Thermal conductivity, the mobility of gas bubbles and the creep rate of UO_2 at high temperature are very important in connection with fuel temperature, swelling, fission gas release and PCMI (pellet-clad mechanical interaction) as these properties determine the fuel performance [1]. Many researchers [2–4] have been interested in the thermal properties of UO_2, but the measured values have shown some differences from each other. The differences are due to the fact that the thermal properties of UO_2 pellets at a high temperature are affected by both the grain and pore structures. So, it is necessary to fabricate single crystal specimens of UO_2 to study its thermal properties.

UO_2 pellets with large grains can be fabricated by controlling the sintering conditions or by using sintering additives such as TiO_2, Nb_2O_5 or Cr_2O_3 [5–7]. Recently, Harada [8] found that the grain size of a UO_2 pellet sintered in reducing–oxidizing (air)–reducing atmospheres for 1–2–1 h at 1773 K was larger by a factor of 3 than that of the reference pellet sintered in wet H_2 for 5 h at 2023 K (8 μm) with a 96% T.D. (theoretical density). But, the grains were not grown to a large size, in the order of several millimeters, by his sintering process.

The oxidation and sintering behaviors of UO_2 in air were studied by using both a TGA (thermogravimetric analyzer) and a sintering furnace. This study demonstrates a sintering process and its sintering conditions for UO_2 pellets which consist of large grains or a single grain.

2. Experimental

The raw powder used in this study was an IDR (Integrated Dry Route) UO_2 [9] from British Nuclear Fuels public limited Co. (BNFL), and it had an O/U ratio of 2.15, an average particle size of 2.2 μm, and a specific surface area of 2.36 m^2/g. The milling of the UO_2 powder was accomplished by using a planetary mill (FRITSCH, pulverisette-6) for 1 h. The milled UO_2 powder had a particle size of less than 0.40 μm and a specific surface area of 4.39 m^2/g. The as-received and the milled powders were pressed under a compaction pressure of 300 MPa with the die-wall lubrication. For the die-wall lubrication, zinc stearate suspended in benzene was used. It was coated on the inner surface of the die. The average density of the UO_2 compacts was around 5.8 g/cm^3 for

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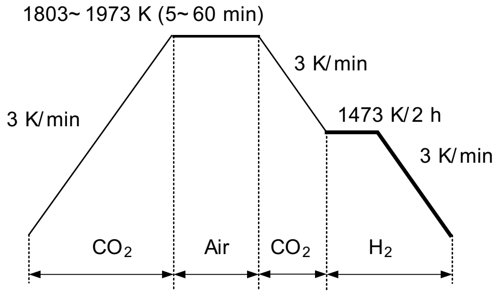

Fig. 1. Schematic diagram of the sintering methods used in this study.

the as-received powder and 6.7 g/cm^3 for the milled powder. The UO_2 compacts were heated up in CO_2 using TGA (Cahn, TG171) then the atmosphere was switched to air at a holding temperature, and the weight changes of the samples in the air were measured in the range of 1673–1823 K.

The UO_2 compacts were sintered according to the CO_2–air–CO_2–H_2 sintering process which consists of four stages as shown in Fig. 1. At the first stage, the compacts were heated up to the sintering temperatures (1803–1973 K) in CO_2. Secondly, dry air was passed through the furnace at the sintering temperatures for a given period from 5 min to 1 h. At the third stage, the sintering gas was changed to CO_2 and the temperature was simultaneously cooled down to 1473 K. Finally, the sintered pellets were reduced to stoichiometric UO_2 in hydrogen at 1473 K for 2 h and then cooled down to room temperature in the same atmosphere.

The density of the sintered pellets was measured by the water immersion method. The average grain size was determined by using the linear intercept method. X-ray diffraction was performed on the UO_2 pellets by using a Cu Kα radiation in order to determine whether they had a single grain or not.

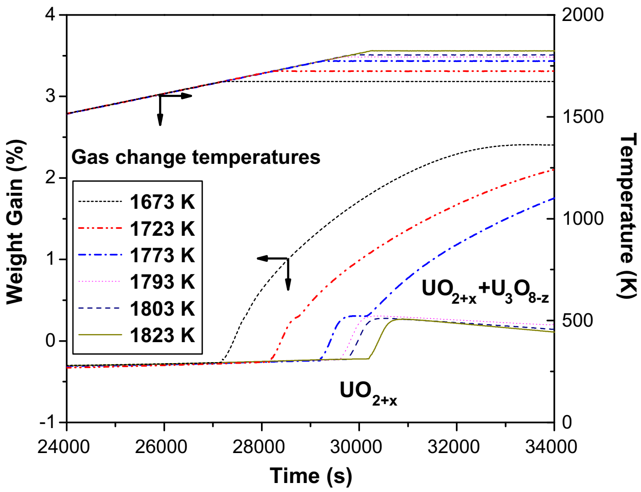

Fig. 2. TG profiles of the UO_2 samples with flowing air at each temperature.

3. Results and discussion

TGA curves of the UO_2 samples profiled for the gas change from CO_2 to air at temperatures of 1673–1823 K

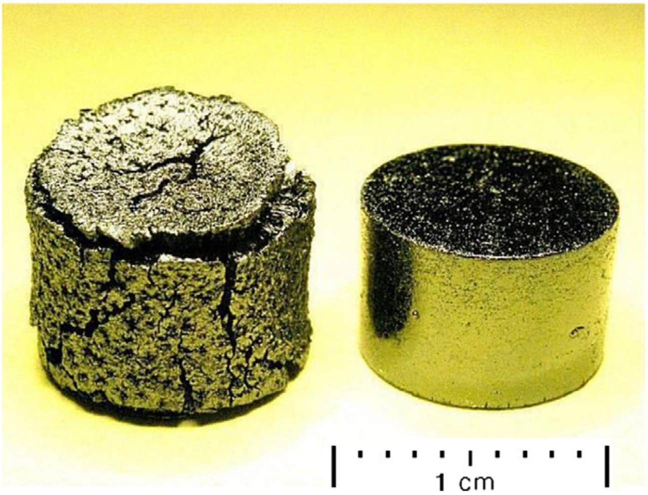

Fig. 3. The appearances of the UO_2 samples soaked for 4 h in air at 1773 K (left) and 1803 K (right).

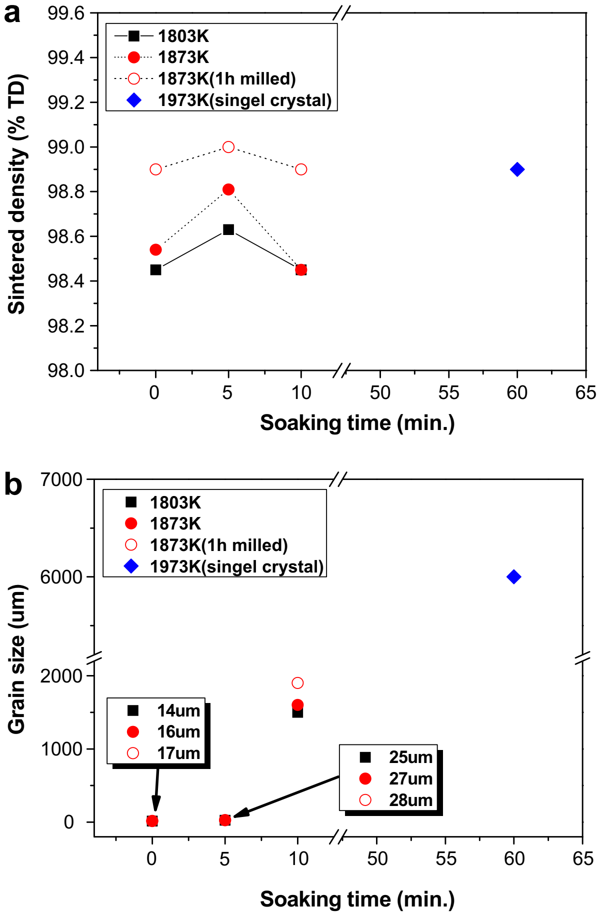

Fig. 4. Variation of (a) the sintered density and (b) the grain size of the UO_2 pellets depending on the sintering temperature and soaking time in air.

are given in Fig. 2. A breakpoint appeared on the oxidation curve at 1723 K. The oxidation reaction was retarded at a higher temperature than 1773 K and a step appeared in the curve. Above 1793 K, the step was formed, but the sample weight was not increased after that. It means that a phase change from UO_{2+x} to U_3O_{8-z} is not progressed above 1793 K and the sample maintains its geometrical integrity during a sintering in air. When comparing these experimental results with the O–U phase diagram [10], the oxidation path below 1793 K passes through a two-phase region ($UO_{2+x} + U_3O_{8-z}$) and reaches the U_3O_{8-z} + gas region. The path directly reaches the UO_{2+x} + gas region above 1803 K, therefore, the sample weight is linearly decreased with a soaking time.

Fig. 3 shows the appearance of two UO_2 pellets sintered in air at 1773 and 1803 K, respectively. The pellet sintered at 1773 K is swollen and cracked, which could be attributed to a volume change by the phase transition of UO_{2+x} (fluorite) to U_3O_{8-z} (orthorhombic). But, the other pellet sintered at 1803 K maintains its integrity because the sintering path passed through the UO_{2+x} to UO_{2+x} + gas region. Harada [8] reported that air can be used in a sintering process above 1773 K because the oxygen partial pressure of air at this temperature is an equilibrium value with the phase boundary between UO_{2+x} and $UO_{2+x} + U_3O_{8-z}$. Taylor [10] indicated that the evaluated thermal stability limit of U_3O_8 is 1878 K in air. A volatilization as shown in Fig. 2 could be a disturbance of the sintering process in air, even though the pellet maintains its integrity by evading the sintering path through the $UO_{2+x} + U_3O_{8-z}$ region.

Fig. 4 shows the variations of the density and grain size of the UO_2 pellets which were heated up to 1803 or 1873 K in CO_2, sintered for a second to 10 min in air, then reduced at 1473 K in H_2. The pellets have a grain size from 14 to 17 μm and a density higher than 98.5% T.D. The density reached 99% T.D. by a milling treatment of the raw UO_2 powder as shown in Fig. 4(a). The grain size of the sintered pellets was mainly affected by the soaking time in air as shown in Fig. 4(b). The grain size was bigger than 25 μm for a soaking time of 5 min at 1803 K and 1.5 mm for 10 min at the same temperature. Fig. 4(b) shows that a powder treatment also affected a grain growth. The pellet prepared with a milled powder had a larger grain size than that for the as-received powder.

Microstructures of the UO_2 pellets sintered by the CO_2–air–CO_2–H_2 process were observed with the soaking time in air as shown in Fig. 5. The pellet sintered at 1803 K for just a second in CO_2 consisted of fine grains with an average size of 14 μm as shown in Fig. 5(a). When the pellet was sintered for 5 min in air, the grains were grown to an average size of 25 μm as shown in Fig. 5(b). The microstructure of the pellet soaked for 6 min in air consisted of some large grains surrounded by many fine grains as shown in Fig. 5(c). This pellet shows a duplex grain structure, the so-called rocks-in-sand structure [1,11,12], in which the grain size is about 30 μm for the normal grains but about 500 μm for the abnormal ones. There are several small grains and micro pores within the large grain, as viewed in the cross section. Fig. 5(d) shows that most of the small grains had disappeared by an abnormal grain growth [13]

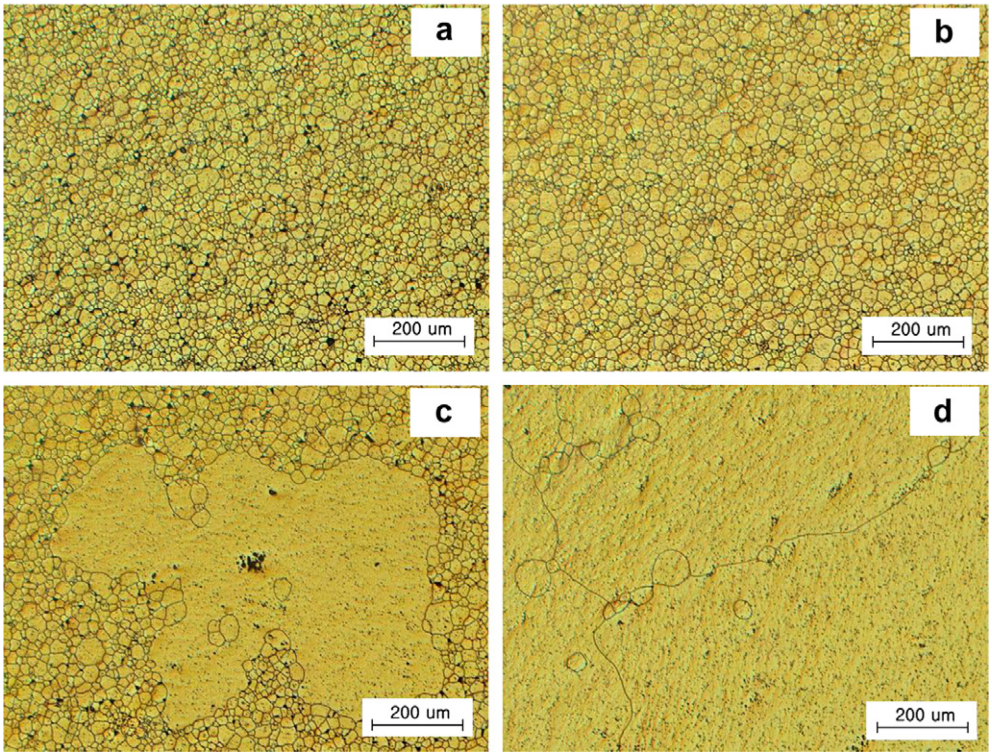

Fig. 5. Microstructures of the UO_2 pellets sintered at 1803 K; (a) for a second in CO_2, (b) for 5 min in air, (c) for 6 min in air, and (d) for 8 min in air.

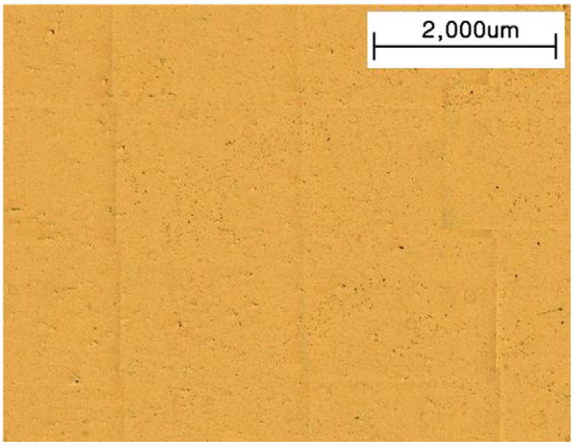

Fig. 6. The microstructure of a single grain UO_2 pellet sintered at 1973 K for 1 h in air.

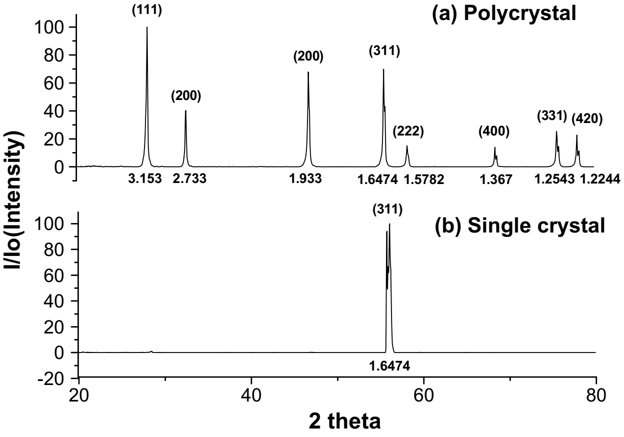

Fig. 7. XRD patterns of (a) polycrystalline and (b) a single crystalline UO_2 pellet sintered in air.

during an additional soaking time of 2 min when compared with that of Fig. 5(c).

The UO_2 pellet with a single grain was fabricated as follows: milling of the raw powder, pressing of the milled powder into compacts and a sintering of the compacts by the CO_2–air–CO_2–H_2 process with a soaking time of 1 h at 1973 K in air. Sintered pellet had a density of 99% T.D. and a grain size of about 6 mm, and it consisted of a single grain through out the whole cross section as shown in Fig. 6.

XRD peaks of the UO_2 pellet with a single crystalline or polycrystalline are shown in Fig. 7. Fig. 7(a) shows a typical XRD peak for the polycrystalline UO_2 with a FCC structure and Fig. 7(b) shows only one peak for a single crystalline UO_2.

4. Conclusions

1. A sintering of UO_2 compacts in air was possible above 1803 K because the oxidation path of the pellets does not pass through the two-phase region including UO_{2+x} and U_3O_{8-z} during the sintering process.
2. In the CO_2–air–CO_2–H_2 sintering process, the grains grow to a large size in the order of several millimeters by an abnormal grain growth.
3. A UO_2 pellet consisting of a single grain was fabricated by an application of a CO_2–air–CO_2–H_2 sintering with a soaking time of 1 h at 1973 K in air.

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References

[1] H. Assmann, W. Dorr, M. Peehs, J. Am. Ceram. Soc. 67 (1984) 631.
[2] J.K. Fink, J. Nucl. Mater. 279 (2000) 1.
[3] D.R. Olander, P.V. Uffelen, J. Nucl. Mater. 288 (2001) 137.
[4] K. Une, M. Hirai, K. Nogita, T. Hosokawa, Y. Suzawa, S. Shimizu, Y. Etoh, J. Nucl. Mater. 278 (2000) 54.
[5] K.W. Song, K.S. Kim, K.W. Kang, Y.M. Kim, J.H. Yang, Y.H. Jung, J. Kor. Nucl. Soc. 31 (1999) 455.
[6] H.S. Yoo, H.S. Kim, J. Kor. Nucl. Soc. 29 (1997) 196.
[7] L. Bourgeois, Ph. Dehaudt, C. Lemanignan, A. Hammous, J. Nucl. Mater. 297 (2001) 313.
[8] Y. Harada, J. Nucl. Mater. 245 (1997) 217.
[9] S.G. Brandberg, Nucl. Technol. 18 (1973) 177.
[10] P. Taylor, J. Nucl. Mater. 344 (2005) 206.
[11] H. Assmann, W. Dorr, M. Peehs, J. Nucl. Mater. 140 (1986) 1.
[12] K.W. Song, W.K. Choo, J. Nucl. Mater. 203 (1993) 122.
[13] M. Hillert, Acta Metall. 13 (1965) 227.