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The possible usage of ex-ADU uranium dioxide fuel pellets with low-temperature sintering

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Abstract

UO_2 fuel pellets are prepared conventionally by high- and low-temperature sintering. Both ex-ammonium uranyl carbonate (AUC) and ex-ammonium diuranate (ADU) UO_2 are used in these techniques. Larger quantities of chemicals (NH_3 and CO_2) are required for the AUC process which is a significant complication compared with the ADU process. In this work, it is aimed to search the important parameters such as theoretical density (TD) and grain size of ex-ADU UO_2 pellets which are in an oxidative atmosphere at low temperature. A density of $\approx$95% TD is obtained at 1150°C. The grain structure of the pellets sintered in an oxidative atmosphere is monomodal unlike the duplex grain structure of ex-AUC oxide, but it is in accord with ex-ammonium uranate (AU) oxide. The grain structure, distribution and size are compared with the ex-AUC and ex-AU conversion processes. It is shown that the grain structure development depends on both the powder properties and the sintering atmosphere. © 2000 Published by Elsevier Science B.V. All rights reserved.

1. Introduction

Uranium dioxide nuclear fuel pellets are sintered conventionally at about 1700°C in a hydrogen atmosphere [1–3]. This high temperature is necessary to obtain the required density of 95% theoretical density (TD). In addition, this method necessitates a high temperature, and working with hydrogen is critical and dangerous. Both ex-ammonium uranyl carbonate (AUC) and ex-ammonium diuranate (ADU) UO_2 powders are used for preparing nuclear fuel pellets. High density UO_2 pellets can also be produced using the two-step low-temperature sintering (oxidative sintering) [3–9]. In these techniques, the green compacts are first sintered at 1100°C in a CO_2 atmosphere and then reduced in a hydrogen atmosphere. In this method, ex-AUC UO_2 powder is requested. According to Dörr and Assmann [3], UO_2 powder produced by the 'AUC conversion process' and UO_2 green pellets pressed from ex-AUC powder by the direct pelletizing process are suitable, and other conversion processes are not as readily suitable for the oxidative sintering procedure as ex-AUC powder. Haas [10] has indicated that large quantities of chemicals (NH_3 and CO_2) are required for the AUC process which is a significant complication. The AUC process requires 11 operations and has the greatest gaseous waste treatment and recycle requirements. In this work, it is aimed to investigate the probability of sintering of ex-ADU UO_2 pellets at low temperatures.

Density and microstructure are the most important parameters in nuclear fuel pellets. These parameters affect the reactor performance [11,12]. The density of nuclear fuel pellets for the LWR should be in the range 94–96% TD, which is directly related with the pore structure, since density and pore structure govern the dimensional behaviour of the fuel [13]. The grain structure may affect the mechanical properties of the fuel and the kinetics of the fission product release during reactor operation [14,15].

By using ex-ADU UO_2 powder the following is investigated in the present work:

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(a) the sinterability and the maximum density of pellets sintered at low temperature (1150°C) in a CO_2 atmosphere;

(b) the grain structure of pellets sintered at 1150°C and in a CO_2 atmosphere.

It is known that the duplex grain structure, which consists of fine and coarse grains, develops in ex-AUC UO_2 which is sintered in a CO_2 atmosphere at low temperature [4,8,9,16]. The purpose of this work is to identify the feature of the grain structure of ex-ADU UO_2 sintered at low temperature (1150°C) in a CO_2 atmosphere. This work also describes the grain structure and the grain size distribution which are compared with the uniform grain structure of ex-ADU UO_2 pellets sintered at high temperature, bimodal grain structure of ex-AUC UO_2 pellets sintered at low temperature and uniform grain structure of ex-ammonium uranate (AU) UO_2 pellets (the experiment done by Song et al. [7]). Factors that influence the changes in the grain structure at low-temperature sintering will also be discussed.

2. Experimental

Uranium dioxide powder which was supplied by the Department of Nuclear Fuel Technology of Cekmece Nuclear Research and Training Centre (CNRTC) was produced by the conventional ADU conversion process. The O/U ratio was determined as 2.15 using gravimetric techniques, and the specific surface area measured by the BET method was 4.8 m^2/g. The powder purity was 99.9%.

In order to increase the pressing capabilities, the powder was mixed with a 0.2% binder (zinc stearate) and compacted with lubricant under 300 MPa into cylindrical specimens of 10 mm diameter and approximately 11 mm height. The compacted powder showed a density in the range of $(50 \pm 1)\%$ of TD. The green pellets were sintered partially in a CO_2 atmosphere by heating up to 600°C, 750°C, 900°C, 1000°C, 1050°C, 1100°C and 1150°C, respectively (partial pressure $= 3.2 \times 10^{-2}$ atm, total pressure = 1 atm), and then cooled in a hydrogen atmosphere (partial pressure $= 3.1 \times 10^{-5}$ atm, total pressure = 1 atm). They were heated in an alumina tube by means of a Kanthal A wound furnace. The reduction of the sintered pellets was carried out by changing the gas flowing from CO_2 to H_2 and then holding for 0.5 h at 1100°C. The absolute density of the sintered pellets was measured on each pellet using the immersion technique according to Archimedes principle.

The second group of green pellets was sintered at 1150°C for 4 h under the control of water vapour, which was introduced in a CO_2 atmosphere and then reduced under a hydrogen atmosphere for 1 h. The sintered pellets were cut longitudinally and polished in order to check the grain size distribution. Thermal etching was carried out at 1100°C for 2 h in a CO_2 atmosphere to disclose the grain boundary.

The grain size distribution after high-temperature sintering (supplied from CNRTC and sintered at 1700°C for 4 h in a pure H_2 atmosphere, refer ex-ADU oxide) and after low-temperature sintering (at 1150°C for 4 h in a CO_2 atmosphere, ex-ADU UO_2 powder) was determined quantitatively by an image analyser. More than 1000 grains were counted for the determination of the grain size distribution. The O/U ratio of each pellet was determined by oxidation to U_3O_8 at 900°C for 2 h in air and by calculation of the original composition from the weight gain. The O/U ratio is determined as 2.01.

The process variables (sintering atmospheres, powder properties and details) of the experiments in two types A and B and the studies C [20] and D [7] are shown in Table 1.

3. Results and discussion

Fig. 1 shows a comparison of the sintering curves of the UO_2 pellets sintered at high temperature and low temperature, which refer to the work of Dörr and Assmann [3] with ex-AUC oxide and to this experimental work with ex-ADU oxide. It can be seen that the den-

Table 1
The experimental conditions of the pellets used or compared in this study

Processing variables	Type A[a]	Type B	Type C[b]	Type D[c]
Powder manufacturing	ADU	ADU	AUC	AU
Sintering atmospheres and partial pressures	H_2	CO_2 + water vapour	CO_2	CO_2
	3.1×10^{-5} bar	3.2×10^{-2} bar	–	–
Sintering temperature and time	1700°C	1150°C	1100°C	1300°C
	4 h	4 h	1/2 h	0.1 h
Heating rate	300°C/h	300°C/h	300°C/h	300°C/h

[a] These pellets were supplied from CNRTC, but they were cut longitudinally, polished, etched thermally and the grains were determined by an image analyser in this experiment.

[b] The work done by Dörr et al. [20].

[c] The work done by Song et al. [7].

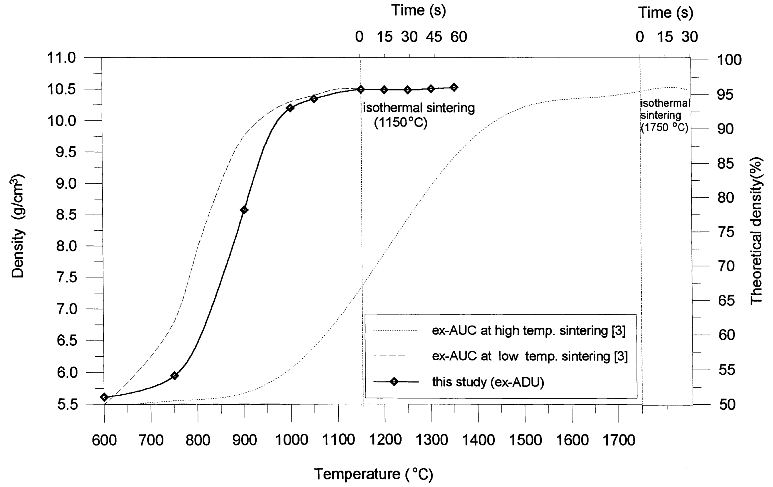

Fig. 1. Comparison of high- and low-temperature sintering with ex-AUC oxide [3] and low-temperature sintering with ex-ADU oxide.

sification of ex-AUC oxide begins at 800°C for high-temperature sintering and at 600°C for low-temperature sintering. For ex-ADU oxide, the densification begins at about 650°C. The temperature of the densification start is lower in ex-ADU than in ex-AUC for low-temperature sintering conditions. The curve for ex-ADU oxide shows a small deviation compared with ex-AUC oxide sintered in an oxidative atmosphere. In order to increase the capability of the oxide pressing, a lubricant and a binder were added and this caused a delay in the sintering process. The final density for ex-ADU oxide was obtained at about 1150°C. Thus, sintering temperatures $\leqslant 1200°C$ can be easily met. At this temperature, 95% TD is obtained. Table 2 shows the densities of pure ex-ADU UO_2 pellets annealed at low temperatures under the inert gas and oxidative atmosphere investigations by various authors (e.g., [4,6,17–19]). Fuhrman et al. [17] used ex-ADU UO_2 powder for sintering in a nitrogen atmosphere at 1200°C and 1300°C using a two-stage sintering process and obtained 92–98% TD. Song et al. [6] showed that the oxidizing sintering process consisting of a two-step process of sintering in CO/CO_2 and CO_2/H_2 at 1300°C leads to 96–97% TD UO_2 pellets. Han et al. [4] indicated by using a $(CO_2/CO)/H_2$ atmosphere in two-step sintering at 1200°C that it is possible to obtain UO_2 pellets with 93% TD. Harada [18] used the three-step sintering process in order to obtain a large grain pellet from UO_2 powder converted by conventional ADU. His study demonstrated that the grain size of UO_2 pellets sintered in reducing–oxidizing (air)–reducing atmospheres for 1–2–1 h at 1500°C was by a factor of 3 larger than that of the reference pellets sintered in wet H_2 for 5 h at 1750°C (8 μm) with 96% TD fuel pellets. Aybers et al. [19] showed that in a CO_2/H_2 sintering atmosphere and at 1150°C fuel pellets with 93% TD can be obtained. The experiment revealed 95% TD UO_2 pellets at 1150°C using ex-ADU UO_2 powder sintered in controlled water vapour in a CO_2/H_2

Table 2
Sintering condition, sintering temperature, maximum obtained density and grain size of the UO_2 powders made by the conventional ADU process

Authors	Sintering conditions (sintering atmosphere/ reducing atmosphere)	Sintering temperature (°C)	Sintering time (min)	Maximum reachable density (% TD)	Grain size (μm)
Fuhrman et al. [17]	N_2/H_2	1200–1300	60	92–98	12–17
Han et al. [4]	$(CO_2/CO)/H_2$	1200	210	93	≈7
Aybers et al. [19]	CO_2/H_2	1150	–	93	–
Song et al. [6]	CO_2/CO_2	1300	300	≈96–97	≈6
Song et al. [6]	CO_2/H_2	1300	300	≈97–98	7–8
Harada [18]	(H_2/N_2)/air/(H_2/N_2) (Three step sintering)	1500	60–120–60	≈96	≈24
This study (partial pressure) (total pressure)	(water vapour + CO_2)/H_2 (3.2×10^{-2} bar)/(3.1×10^{-5} bar) (1 bar/1 bar)	1150	240	≈95	≈7

atmosphere. This temperature is quite low, compared with the investigations referred to in Table 2. It is clear that the water vapour introduced in a CO_2 atmosphere increases the sintering rate and the density.

Fig. 2 compares the distribution percentage of grain sizes of pellets A and B referred to in Table 1. For high-temperature sintering, the distribution is monomodal with a peak at 19 μm in diameter and for low-temperature sintering it is also monomodal with a peak at 7 μm. Although the original powder properties of these two pellets were the same, the grain sizes were quite different. This difference seems to be related to the sintering temperature and the sintering atmosphere. Figs. 3(a)–(d) show the microstructures of specimens A, B, C and D, respectively, referred to in Table 1. The grains in Fig. 3(a) have a regular shape, 19 μm size, and the grain boundaries are straight. Small and coarse grains coexist in Fig. 3(b) which shows the microstructure of the pellets derived from ADU, sintered in a CO_2 atmosphere at 1150°C. The most frequent grain size is about 7 μm and the grain sizes are in the range 3–20 μm. It cannot be said that the duplex grain structure develops, because the amount of small grains is much more comparable to coarse grains. The small grains have a regular shape, while the coarse grains do not have a definite shape and their grain boundaries are not straight. Compared with Fig. 3(a), it seems that the temperature and the sintering atmosphere have crucial effects on grain size, grain type and grain shape although the original powders are the same. Fig. 3(c) shows that coarse grains and clusters of fine grains exist together, which means that the duplex grain structure develops (refer to the study of Dörr et al. [20]). Compared with Fig. 3(b), the differences in grain structure, shape and distribution originate from the powder characteristics (O/U ratio, agglomeration, etc.). These differences do not result from the temperature and the sintering atmospheres, because the sintering temperatures and atmospheres are nearly the same (1100°C in CO_2 and 1150°C in CO_2 for ex-AUC and ex-ADU, respectively). Fig. 3(d) shows the experimental result of grain structure of ex-AU UO_2 pellets sintered at 1300°C in CO_2 which has been done by Song et al. [7]. They obtained uniform grain structure with 6 μm size developing under the condition of a CO_2 atmosphere and powder from the AU process. Compared with Fig. 3(b), it can be seen that the grain shapes show differences but the most frequent grain size ranges are 7 μm in this experiment and 6 μm in the work of Song et al. [7]. The grain shape differences may originate from the powder properties, because CO_2 was used as the sintering atmosphere in both these studies. As a result, from Fig. 3(a)–(d) it is clear that the powder properties play a very important role on grain structure and grain type, and the sintering atmosphere has no big effect on the grain size and grain structure.

The duplex grain structure develops only in type C, but not in types A, B and D of sintered UO_2. Assmann et al. [1] have published a study in which they showed that the bimodal grain structure with coarse grains ($\leqslant 20$ μm) in a coherent network of fine grains ($\leqslant 5$μm) offers advantages such as plasticity, as typical of fine grain structure and reduction of the fission product sweep out in the volume of the coarse grains. Assmann and Stehle [11] stated that the average grain size of UO_2 nuclear fuel pellets should be between 5 and 25 μm. The grain size result (3–20 μm) of this experiment is, in accord with both of these ideas, in the range 5–25 μm and the grains $\leqslant 20$ μm.

Assmann et al. [1] reported that the duplex grain structure consisting of coarse (30 μm) and fine (3 μm) grains developed during sintering of UO_2 in a CO_2 atmosphere (refer ex-AUC oxide), but uniform grain

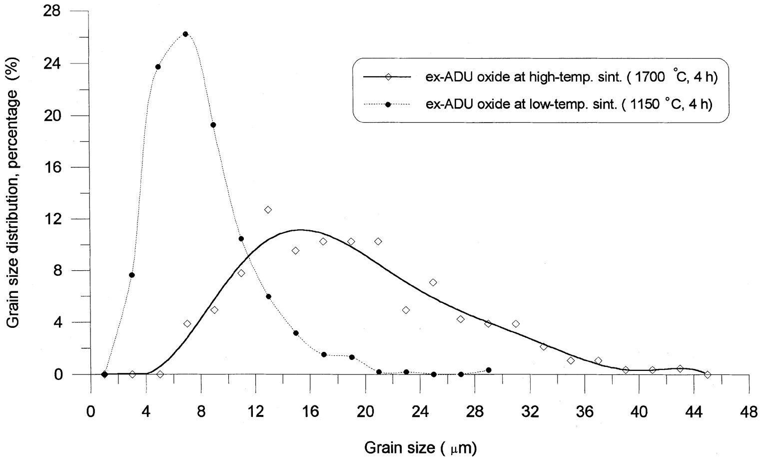

Fig. 2. Grain size distribution of the pellets sintered at high and low temperatures (refer ex-ADU oxide).

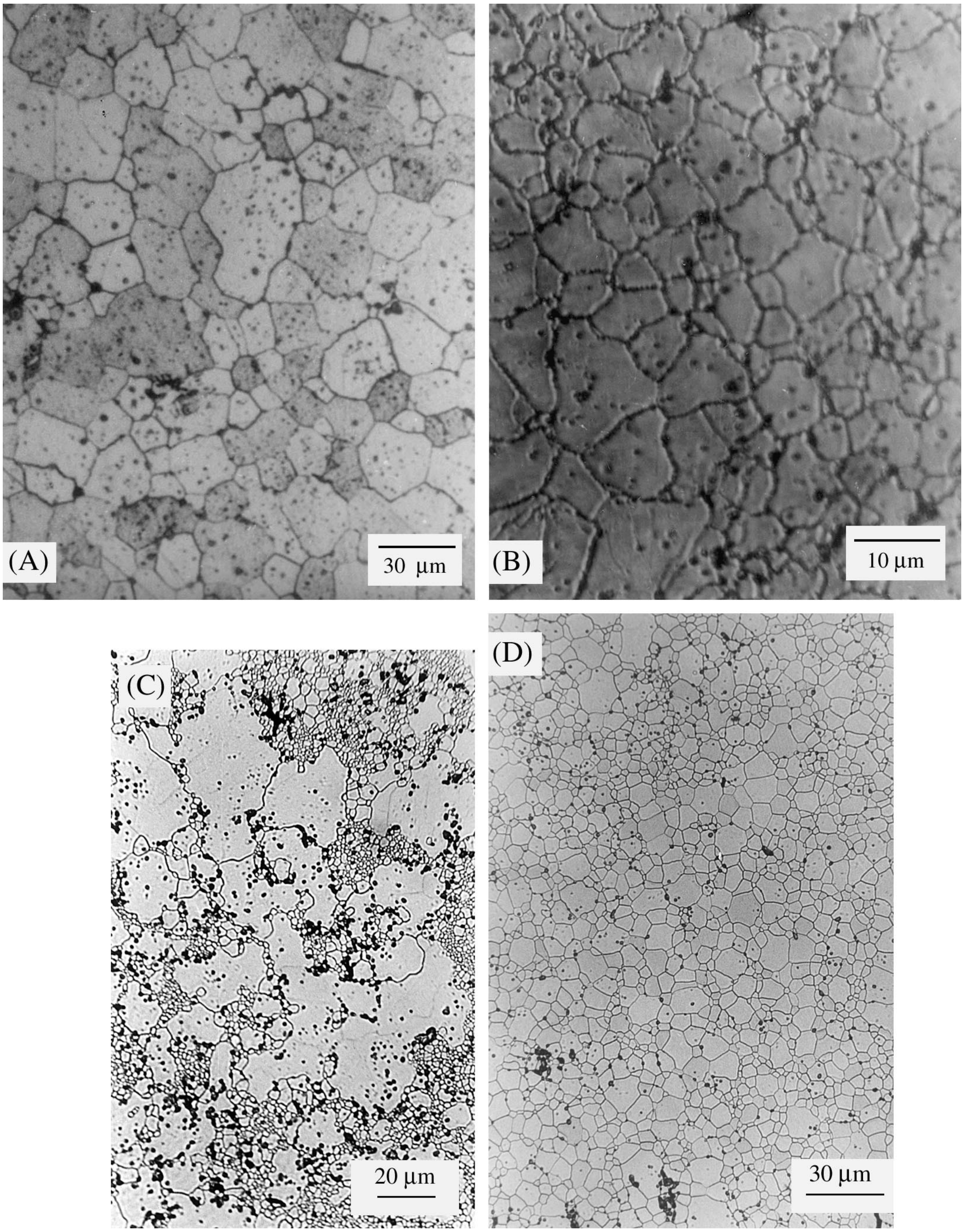

Fig. 3. Grain structures of sintered UO_2 under the conditions (a) of powder extracted from the ADU process and sintered at 1700°C in a H_2 atmosphere, (b) of powder extracted from the ADU process and sintered at 1150°C in a CO_2 atmosphere, (c) of powder extracted from the AUC process and sintered at 1100°C in a CO_2 atmosphere [20] and (d) of powder extracted from the AU process and sintered at 1300°C in a CO_2 atmosphere [7].

structure developed in a H_2 atmosphere. They obtained the duplex grain structure in a CO_2 atmosphere using powders from the AUC process. But Song et al. [7] stated that uniform grain structure was also obtained by using a CO_2 atmosphere at low-temperature sintering with ex-AU oxide. According to Song et al., the difference between the grain structures unlikely originates from the difference in the initial O/U ratio between these types of oxide powders. The development of the duplex grain structure seems to be affected by the properties of the powder or powder compact.

In this work, a uniform grain structure was obtained which is in accord with the results of the work by Song et al. [7]. In order to conclude that ex-ADU oxide with low-temperature sintering is convenient or is an alternative technique to ex-AUC with low-temperature sintering and high-temperature sintering, the pore structure should be known. Ayaz and Bilge [21] compared the pore size distribution and the pore structure of these pellets with the pellets sintered at high temperature.

4. Conclusion

The following can be concluded by using ex-AUC derived UO_2 powders with low-temperature sintering at 1150°C:

1. In the case of UO_2 powders made by the conventional ADU process, the density and grain size of the UO_2 pellets sintered in a wet CO_2 atmosphere at 1150°C for 4 h using the two-stage process, are 95% TD and 7 μm, respectively.
2. It is shown by this work that the phenomenon of Song et al. [7] is proved: 'The development of the grain structure does not depend on the sintering atmosphere, it depends on the powder properties'.
3. High-temperature sintering needs a long sintering time, so this technique is not economical, and during the production of ex-AUC powder larger quantities of chemical requirements are a significant complication compared with the ex-ADU conversion process. So it can be said that ex-ADU powder is convenient for low-temperature sintering.

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