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AUSTRALIAN ATOMIC ENERGY COMMISSION
RESEARCH ESTABLISHMENT

QUALITATIVE RELATIONS BETWEEN THE KINETICS OF SINTERING IN HYDROGEN AND THE OBSERVED MICRO-STRUCTURES OF URANIUM DIOXIDE

by

B. Francois; R. Delmas; R. Caillat and P. Lacombe

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Translated from the French by W. Buykx
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ABSTRACT

The microscopic study of uranium dioxide sintered in hydrogen, together with density measurements, shows on the one hand that the large scale appearance of pores trapped at the grain boundaries in the course of sintering has the effect of practically stopping densification, and on the other hand that this particular microstructure is stable over a wide range of time and temperature.

1. INTRODUCTION

In a previous publication[1] the authors have shown that certain conditions of sintering uranium dioxide in hydrogen are capable of localising the residual porosity at the grain boundaries (integranular porosity) or within the grains (intragranular porosity). In fact, with uranium trioxide produced by thermal decomposition of ammonium uranate as a starting material, increasing the specific surface area of the uranium dioxide powder prepared by reduction favors the trapping of pores at the grain boundaries. The same effect is obtained by increasing the rate of temperature rise of the compact up to the sintering temperature.

Continuing the study of these phenomena, we have concentrated on establishing the relations between the appearance and development of this intergranular porosity microstructure and the corresponding sintered densities.

2. EXPERIMENTAL CONDITIONS

The uranium dioxide powders used are prepared by a process described

previously[1] by controlled reduction of the trioxide which results from the calcination of the ammonium uranate.

In the present case, the specific surface area of the trioxide is 23 m^2/g, and that of the resulting dioxide 12 m^2/g.

Without adding any organic binder[+] the powder is compacted at 4 tonne/cm^2 into square cylinders of 10 mm diameter, with a green density of between 48.3% and 49.3% of theoretical density.

The sintering cycle, used throughout, takes place in an atmosphere of hydrogen, and has the following profile :

- from room temperature to the onset of sintering in hydrogen (800-900°C) the rate of temperature rise of 16°C/min. Temperature arrests of 30 min each occur at 320°C and 600°C, at the conclusion of which the compact has a sound structure and the UO_2 is estimated to be of strichiometric composition.
- from 800°C up to the chosen sintering temperature, the rate of temperature rise is 100°C/min.

3. RESULTS

3.1 Densification

Table 1 gives the densities obtained after a soaking time of 5 hrs at the indicated temperatures (densities expressed in % of theoretical density) as well as the porosities measured by toluene impregnation under vacuum. The impregnation time of the samples was approximately 20 min.

The curve in figure 1 gives the variation in mean density as function of sintering temperature.

[+] The die wall is however lubricated slightly with a solution of stearic acid in ether, to aid in transmitting the compressive fora to the powder, and to facilitate ejection of the compact after pressing has been completed.

TABLE I

	Sintering temperature (°C)					
	1200	1300	1400	1500	1600	1700
No. of experimental points	3	4	5	5	7	3
% theoretical density	88.9-89.5	91-91.5	93.4-94.3	93.5-94.1	91.7-92.2	91.5-91.9
% total porosity	11.1-10.5	9.3- 8.6	5.9- 5.8	6.5- 5.8	8.3- 7.8	8.4- 8.1
% open porosity	8.2- 7.9	4.5- 3.6	0.4- 0.2*	0.3- 0.25*	0.4- 0.15*	0.25-0.15*

* These values cannot be regarded as significant, due to the insensitivity of the measuring method.

3.2 Microstructures Obtained

Figures 2 and 3 show the micrographic appearance of the specimens sintered at 1400°C and 1600°C respectively. In Figure 3 the pore distribution is mainly intergranular; this corresponds to the instering temperature range beyond the maximum density represented in Figure 1. In this case there exists a peripheral zone in which the grains are smaller, and the pore distribution is more nearly intragranular.

3.3 Behaviour of Specimens with Intergranular Porosity Microstructure

It seems then that from a certain temperature upwards, the interval portion of the specimens undergoes an important change. Leaving aside for the moment the real cause of the phenomenon, some tests have been carried out in order to determine more precisely the conditions under which this internal morphology of intergranular porosity appears, and its development in the course of further thermal treatment.

3.3.1 Rate of appearance

Figure 4, representing a specimen treated for 2 minutes at 1600°C shows that the density (91.5% of theoretical density) and the distribution of pores at the grain boundaries are practically attained right at the

start of the soaking period. The peripheral zone has also been formed to a large extent.

3.3.2 Thermal stability

By way of example, a cylindrical specimen sintered for 1 hour at 1600°C according to the method described above, was subsequently treated for 50 hours at 1800°C in hydrogen.

- Before this second treatment the density was 91.9% of theoretical density. A micrographic examination on a circular section through the internal zone shows the presence of pores at the grain boundaries in the internal portion (Figure 5).
- After treatment for 50 hours at 1800°C the density of this specimen has increased to 93% of theoretical density. The micrographic appearance of an axial section of the cylinder is shown in Figure 6. Also shown is the appearance of the previous section (Fig. 5) under the legend "free surface created before treatment".

  The average grain size in the central zone and the microstructure remain virtually unchanged, even in the immediate vicinity of this section, which replaces the original peripheral zone.
- Contrasting with this behaviour, the initial peripheral zone has undergone a change : the number of pores has decreased and the average grain size has increased from 2-4 μm to approximately 15-20 μm (Figure 6). This growth is in agreement with the usually observed kinetics in the case of sintered uranium dioxide of the "intragranular" type. Furthermore, it seems possible that the developments in this zone alone can account for the increased density of the pellet as a whole during the thermal treatment.

3.3.3

The question may be asked what would be the developments in a sintered specimen of intragranular microstructure, identical with that shown in Figure 2, if it was re-treated at a higher temperature. Figure 7 shows the appearance of such a product after re-treatment for 5 hours at 1600°C in hydrogen.

The pore distribution is still of the intragranular type, the mean grain size has increased. At the same time the bulk density of the specimen has increased from 94.1% to 96.4% of theoretical density. The relative stability of the microstructure containing large pores at the grain boundaries is noted, contrasting with the possibility of micro-structural change in the intragranular type.

4. CONCLUSION

The results announced above lead to the following conclusions :

1. Under conditions which lead to the appearance of pores at the grain boundaries, the density attained by the specimen in the first few minutes of isothermal heating does not increase appreciably on further prolonged treatment.
2. In certain cases, such as described above, there exists a sintering temperature threshold above which the pores occur only at the grain boundaries. The curve representing the change in density as function of sintering temperature, for a fixed soaking time, therefore exhibits a maximum.
3. The microstructure with intergranular porosity is stable over a large range of time and temperature .

CAPTIONS TO FIGURES

Figure 1 Variation of density as function of sintering temperature.
"Fast approach" sintering cycle
Soaking time : 5 hours

Figure 2 Density : 94.1% of theoretical density
Sintered 5 hours, 1400°C, in hydrogen

Figure 3 Density : 91.9% of theoretical density
Sintered 5 hours at 1600°C, in hydrogen

Figure 4 Density : 91.5% of theoretical density
Sintered 2 minutes, 1600°C, in hydrogen

Figure 5 Density : 91.9% of theoretical density
Sintered 1 hour, 1600°C, in hydrogen

Figure 6 Density : 93.0% of theoretical density
Supplementary treatment 50 hours at 1800°C in hydrogen,
applied to the specimen shown in Figure 5
Top : free surface created before treatment
Middle : central zone
Bottom : original peripheral zone

Figure 7 Density : 96.4% of theoretical density
Supplementary treatment of 5 hours at 1600°C in hydrogen
applied to the specimen shown in Figure 2.

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