Evolution of pore size distribution during sintering of oxide nuclear fuel

V G Baranov, Y N Devyatko, A V Tenishev, V V Mikhalchik and O V Khomyakov
National Research Nuclear University MEPhI (Moscow Engineering Physics Institute)
Kashirskoe shosse 31, Moscow, 115409, Russia
E-mail: homaykov_o_v@rambler.ru

Abstract. Uranium dioxide pellets were sintered at various temperature routes and atmospheres with different oxygen content. Statistically calculated pore size distribution of the sintered pellets and distribution function was obtained. It is shown that the average pore size is almost unchanged at intermediate stage of sintering while the total number of pores reduced.

1. Introduction
Nowadays uranium dioxide is the main fuel for commercial reactors. Due to the high melting temperature of uranium dioxide (3120 °C), the most effective way to obtain fuel pellets is high temperature sintering (at temperatures 1700-1750 °C). Industrial manufacturing of uranium dioxide has several features that can be affected on the final properties. At powder stage UO₂ is obtained with hyperstoichiometry composition (O/U > 2). Then powder was compacted by pressing at 200-250 MPa to a green density ρ₀ = 10.96 g/cm³. Sintering is carried out in reducing atmosphere to obtain fuel with stoichiometric composition. At this work sintering of uranium dioxide pellets was conducted in Ar+8%H₂ atmosphere with small additives of oxygen.

The sintering process is the most difficult to describe, and many aspects are very poorly studied. Also this fact is applies to pore formation. Green compact of uranium dioxide has a very complex inner surface. Structure of the green pellets consist of individual powder particles (or microcrystallites with typical size is about 200-300 nm) and large agglomerates of this ones (Figure 1).

![Figure 1](image-url) Structure of UO₂ green pellet.

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During sintering the powder particles are combined and grain boundaries are formed. The inner structure is restructured. Very important that the process of grain growth and dissolution process are occurred simultaneously but these processes unrelated to each other directly.

The main characteristic of sintering process is a sample shrinkage during which occurs dissolution of pores inside the compact. The relative change of the total pores volume is connected with changing of pellet volume. Therefore we need to know law of pores evolution which will allow to describe the sintering process and kinetics of this one.

Most of the papers [1-7] devoted to the theoretical description of sintering process is very often don't take into account the pore size distribution, only average pore size. All authors suppose that characteristic size of all pores are the same. In such approximation the law of change of average size isolated pore is \( \Delta <R>/<R> = g(t, T) \), where \(<R>\) – the average pore size, \( t \) – time, \( T \) – temperature, \( g \) – function of time and temperature. This type of formula corresponds with formula of linear sample dimension:

\[
\Delta L/L = N \cdot \Delta <R>/<R> = N \cdot g(t, T),
\]

where \( L \) – linear dimension of the sintered samples, \( N (= \text{Const}) \) – amount of pores in the pellet. This is equivalent to the choice of the pore distribution in the form of Dirac delta-function \( f(R, t) = N \cdot \delta(R-<R>) \) centered at a point which is equal to the average pore size. Actually, the pore distribution of pellets is not narrow and during sintering it occurs both reducing size of pores and their total amount (\( N \neq \text{Const} \)). Moreover, the average pore size does not coincide with a maximum of size distribution. Hence, the Dirac delta function is a very rough approximation for the pore size distribution function. The kinetics of nuclear fuel sintering and the value of its densification depend on many factors: oxygen potential, the annealing temperature, heating rate [8]. Evolution process of the pore size distribution function may depend on same factors.

The purpose of this work is an experimental investigation evolution of pore size distribution function during the oxide nuclear fuel pellets sintering.

2. Calculation of pore size distribution function

To identify the porosity of uranium dioxide the samples were cut and polished with diamond paste. 2D pore size distribution function was calculated by means of Scanning Electron Microscope images. Images with different magnifications covered different areas on the section (such as 100, 500 and 1000 \( \mu m^2 \)). Image areas were chosen such a manner that pores of a certain size were clearly visible on the image. The total area of the pores then calculated on the images. The obtained data were presented in two columns: the areas of pores and quantity of pores with given areas. This array was based on the calculation of 2D - porosity: \( S_i : P_i = N_i/S_i \) \((N_i – \text{amount of pores}, S_i – \text{the total image area}, i – \text{group of pores with area } S_i)\). Usually there are the same dimensions of the pore areas on the different images \((i = k)\). To account these "crossing" areas we used the following algorithm. If two images with different areas \( S^{(1)} \) and \( S^{(2)} \) had groups of pores with equal size, formula of the porosity \( P_k \) will:

\[
P_k = (N^{(1)} + N^{(2)})/(S^{(1)} + S^{(2)}),
\]

where \( N^{(1)} \) and \( N^{(2)} \) – the amount of pores with the same areas on the images with different magnification.

Thus, we can calculate 2D discrete porosity over the entire range of pore size. The average area of the pores, average equivalent pore diameter and average porosity calculated based on discrete 2D - porosity by formulas:

\[
\langle S \rangle = \sum_i S_i P_i / \sum_i P_i; \quad \langle D \rangle = \frac{4}{\pi} \sum_i \sqrt{S_i} P_i / \sum_i P_i ; \quad P = \langle S \rangle \sum_i P_i .
\]

The most obvious form of pore size distribution is histogram. Where ordinate is the amount of pores in interval of pores diameters \([D_k, D_{k+1}]\) relative to the total amount of pores. Abscissa is the equivalent pore diameter.

\[
\Delta N/N = \sum_{i=k}^{k+m} P_i / \sum_i P_i.
\]
3. Pore size distribution during sintering with different heating rate

Samples of uranium dioxide were sintered with next temperature route: heating (with different heating rates 4, 6 and 8 K/min), then annealing at 1600 °C during 465 min. Temperature sintering route are shown in Figure 2. There are sintering processes of samples: duration of sintering is decreased with decreasing of heating rate. Table 1 shows the initial and final density of samples sintered with different heating rate. The densities of samples in Table 1 were determined both by means of hydrostatic weighing in water and by means of direct calculation using measured weight and volume of sample. From table 1 it is followed that the final densities of sintered pellets of uranium dioxide are equal within inaccuracy of measurements.

![Figure 2. Sintering routes of uranium dioxide samples and their sintering curves.](image)

![Figure 3. 2D pores size distributions of samples sintered at 1600 °C with different heating rates.](image)

On the figure 3 it is shown 2D pore size distribution function of samples sintered with heating rates 4, 6 and 8 K/min at annealing temperature 1600 °C. On the same figure are shown average porosity of pellet, average areas of pores and their average diameter. It can be seen that change of heating rate does not cause change of pore diameter. Average characteristics of the pore ensemble determined only by the duration and temperature of isothermal annealing. 2D histograms of pores size distributions have the same form.

Final density of samples calculated using 2D pore size distribution and measured density by usual methods are shown in the Table 1. The average density of pellets calculated by pore size distribution function is close to measured density within the deviation 1%. This coincidence within the empirical error indicates on good accuracy of the method of distribution functions in comparison with other methods of determining the density of the samples.

| Heating rate (K/min) | Initial density | Final density |
|----------------------|-----------------|---------------|
|                      | volume measurement (% TD) | volume measurement (%TD) | hydrostatic weighing in water (%TD) | pore size distribution (%TD) |
| 4                    | 49.5            | 94.2          | 94.7          | 93.9          |
| 6                    | 49.6            | 94.2          | 94.7          | 93.8          |
| 8                    | 49.5            | 93.2          | 94.8          | 93.2          |
4. Pore size distribution during sintering at different annealing temperatures

Series of long-term isothermal annealing of UO$_2$ pellets carried out at temperatures 1300 °C, 1400 °C for 40 hours and at temperature 1500 °C during 8 hours. Sintering at 1500 °C is less because sintering curve have reached the plateau. The sintering curves of these samples are shown on figure 4. It is seen that greatest density is achieved by tablet sintered at highest sintering temperature. The densities of sintered pellets obtained by dilatometer measurements are represented in table 2.

![Figure 4. Sintered curves of UO$_2$ samples](image)

![Figure 5. 2D pore size distribution of UO$_2$ samples sintered at different temperatures](image)

2D pore size distribution functions of sintered samples with different sintering temperatures are shown on figure 5. On the same figure are shown average porosity of pellet, average areas of pores and their average diameter. The figure 5 shows that the average characteristics of the distribution - the middle area and pore diameter are constant during sintering. Maximum of pore size distribution function as seen from figure 5 practically does not change while sintering temperature increased.

| Annealing temperature (°C) | Final density based on pore size distribution (%TD) | Final density based on volume measurement (%TD) |
|----------------------------|--------------------------------------------------|-----------------------------------------------|
| 1300                       | 82.4                                             | 85.4                                          |
| 1400                       | 92.6                                             | 89                                            |
| 1500                       | 94.7                                             | 88.9                                          |

Table 2. Final parameters of samples

The total amount of pores with all sizes is reduced by increasing the sintering temperature. Only small pores dissolved completely. Thus, as a result of long annealing, function of pore size distribution is narrowed, and the amount of pore size is reduced.

5. Pore size distribution during sintering in atmospheres with different oxygen content

It is known that the beginning of the sintering temperature depends on oxygen content of atmosphere in a furnace. Sintering in atmospheres with extremely low oxygen partial pressure is shifted the beginning of the sintering to the higher temperatures. Moreover, the deviation from stoichiometric composition of UO$_2$ + $x$ depends on oxygen content in atmosphere. The sintered curves of UO$_2$ samples annealed during 40 h (sample №1) and for 20 h (the other samples) at 1300 °C are shown on figure 6. Samples with conventional numbers № 2, 3 and 4 contained 180 ppm Al (OH)$_3$ and sample № 1 was
made without alloying additions. Figure 6 shows the value of oxygen potential in the atmosphere for each sample. For each value of the oxygen potential is conform deviation (x) from the stoichiometric composition. So, sintering of green pellet of uranium dioxide in atmosphere with $\Delta G_{O_2} = -440$, -395, -365 kJ/mol will result hyperstoichiometric composition of $UO_{2+x}$ and deviation from stoichiometry: $x = 0.0000$, 0.0002 and 0.0007 respectively [8].

Figure 6 shows that the alloying pellet sintered more efficiently in atmosphere with the highest oxygen potential. Final densities of the sintered samples in Figure 6 are presented in Table 3. Difference of the final density for the samples № 1 and 2 is associated with their difference in green density.

![Figure 6. Sintering curves of unalloyed and alloyed uranium dioxide samples sintered at 1300 °C in atmospheres with different oxygen potential](image)

![Figure 7. Pore size distribution in UO$_2$ samples sintered at 1300 °C in atmospheres with different oxygen potential](image)

Figure 7 shows the pore size distribution function of sintered samples. It can be seen that the greatest density is achieved through the complete dissolution of submicron pores with diameters $D < 0.3 \, \mu m$. Even a slight increase in the partial pressure of oxygen increases the rate of dissolution of the pores. Note that the average pore area and its equivalent diameter are practically independent of the sintering atmosphere.

| №  | Oxygen potential (kJ / mole) | Final density |
|----|-----------------------------|--------------|
|    |                             | hydrostatic weighing (%TD) | volume measurement (%TD) | based on pore size distribution (%TD) |
| 1  | -440                        | 91.1         | 88.7          | 92.9          |
| 2  | -440                        | 90.5         | 87.2          | 89.8          |
| 3  | -395                        | 91.8         | 89.9          | 87.1          |
| 4  | -365                        | 92.5         | 90.1          | 88.4          |
6. Conclusions
Analysis of all obtained distributions functions of sintered UO$_2$ showed that the characteristic pore size is about $0.1 < D < 2 \mu m$. During sintering average pore diameter and their average area was almost unchanged. It is found that the pore size distribution of the sintered UO$_2$ pellets wasn’t depended on heating rate but it is determined by sintering temperature and duration of sintering process and also by oxygen potential of atmosphere. During the heating, pore size distribution function reduced. This is due to complete dissolution of submicron pores (characteristic dimensions less than 0.3 micron). The total quantity of pore size decreased. It is shown that the $\delta$-function approximation of size distribution function is incorrect. Dissolution kinetics of isolated pore does not coincide with densification kinetics of fuel pellet.

Thus, it is necessary to take into account the evolution of the pore ensemble for the correct description of the sintering process.

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