Rate control sintering of the uranium dioxide

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Abstract. The application of rate controlled sintering (RCS) technique for fabricating oxide fuel pellets in industrial conditions is investigated. Green pellets of UO$_2$ (with no additives) which underwent industrial-type compacting were sintered in reducing Ar – 8% H$_2$ medium using dynamic and isothermal RCS modes with exposure at 1600 °C during 8 hours. Decreasing shrinkage rate resulted in growth of sintered density for the dynamic RCS mode. Opposite to the results of earlier works [1,2], decreasing heating rate did not result in reducing sintering rate. Isothermal mode allowed sintering rate to be maintained between 0.1 – 0.15 %/min. Temperature-time modes obtained using RCS are close to the operation mode of through-type furnace used for mass production.

1. Introduction
Currently oxide nuclear fuel based on UO$_2$ is essential for atomic energy. To maintain product quality, security requirements and to improve economic indicators a continuous improvement of the technological aspects of manufacturing powders, molding powders and fuel compacts based on uranium dioxide is a relevant issue. The sintering process "raw" compacts receives considerable attention due to the strong economic performance of this process step, with a single cycle can be more than 40 hours. At this step the basic parameters of the sintered fuel pellets are formed: geometry, density, average grain size, porosity, pore distribution, etc. To obtain a ceramic fuel based on stoichiometric uranium dioxide a reducing atmosphere of hydrogen or mixtures of hydrogen and nitrogen is used as medium. Another important characteristic of the sintering medium is humidity, it’s control is urgent to obtain stable characteristics of the fuel pellets.

In papers [1-3] the authors presented the results of the analysis of the sintering process UO$_2$ pellets and (U, Gd)O$_2$ with different composition when changing the temperature mode and sintering medium. In the papers a preset constant heating rate technique is used. To get more information on the features of the fuel pellets sintering and possible effects on sintered structure the rate control sintering (RCS) method is considered useful.

The RCS method due to changes in the rate of heating is known for a long time. With it, in particular, a very fine grain structure is received, while maintaining a high density. To do this it is necessary to divide the two competing processes - pore coalescence and growth, and grain growth, which is achieved by providing a special densification rate profile [4] (figure 1).
Figure 1. Typical dependence of the sintering rate to shrinkage using RCS with denoted processes, limiting the densification rate [4].

The data on a use of the RCS method to manage the final microstructure of uranium dioxide is absent in literature. In addition, for an oxide nuclear fuel an urgent problem is to increase the grain size using a limited amount of additives that activate grain growth or its complete rejection. Thus, application of the method for uranium dioxide based pellets sintering enables not only a more effective control of structural parameters, but improve the nuclear purity of the fuel.

2. Materials and equipment

In the paper oxide nuclear fuel compacts produced in industrial conditions are investigated. UO$_2$ powder was obtained by ammonium diuranate (ADU) process. The compacts were produced by the method based on preliminary briquetting with a liquid plasticizing component and then grinding to press powder. The density of the obtained compacts was about 50% of theoretical density (TD).

To investigate the size change kinetics of compacts during of its sintering a horizontal dilatometer Netzsch DIL 402 C (Germany) is used, using its software application a constant heating rate sintering and RCS is possible. Sintering is performed in a dynamic medium of Ar-8% H$_2$ using a gas flow rate of 50 ml/min.

The microstructure of the sintered UO$_2$ pellets is investigated by the scanning electron microscope JEOL JSM-6610LV (Japan).

3. Dilatometric measurements

As part of the works on sintering of oxide fuel pellets in modes that simulate industrial production (under laboratory conditions the maximum sintering temperature is 1600 °C), a series out of experiments varying the temperature of isothermal exposures was carried out. Figure 2 shows the dilatometric curves for UO2 pellets, sintered with regular program (hereinafter referred to as the "basic" program – curve 1) and the program with a higher temperature of 4 and 5 isothermal exposures ("optimized" program – curve 2). With 4 and 5 isothermal exposures at 100 °C higher the sintering rate (i.e. the time derivative of length change) was nearly constant.

For the "basic" program sintering takes place in four steps:
   1) initial - at temperatures of 800-1000 °C;
   2) slow - at temperatures of 1000-1100 °C;
   3) accelerated - from 1100 °C and up to a maximum temperature of 1600 °C;
   4) fading - throughout the isothermal holding.

For the "optimized" program, the sintering process rather quickly reaches a constant rate (average 0.07%/min) until the isothermal exposure. Thus, instead of slow 2nd and 3rd stages fast one is observed at an average speed.

From Figure 3 it is evident that during sintering with the "basic" program at the 2nd step the sintering rate is less than 0.02%/min, and at the 3rd - changes along a curve with a maximum of 0.27%/min; in the case of the "optimized" program sintering rate is generally in the range of 0.05-0.10%/min and is less than 0.14%/min.
Figure 2. Dilatometric sintering curves (—) with the temperature program (····), simulating a shortened production program with a 12 min beam cycle: 1 - basic, 2 - optimized.

Figure 3. The time dependence of the sintering rate (— and ---) for temperature program (····), simulating a shortened production program with a 12 min beam cycle: 1 - basic, 2 - optimized.

The sintered microstructures analysis, that is shown in figure 4, shows that the shrinkage rate close to constant gives a more homogeneous structure and a smaller pore size.

From these results, it is seen that the fuel pellets produced with "optimized" program have pores not exceeding 2 µm in diameter and a grain size of 5-12 µm.

Figure 4. The microstructure of UO₂ pellets, sintered with program simulating a shortened production program with a 12 min beam cycle: a) basic, b) optimized.

As mentioned above, the use of RCS can significantly affect on the microstructure parameters. As for ceramic nuclear fuel grain size is important from the standpoint of performance, one of the aims is to eliminate the second sintering stage (figure 1), which suppresses the grain growth. For this purpose, a series of experiments were carried out with the preset shrinkage rates. From figure 5 it is evident, that it is difficult to receive the stable value of the shrinkage rate in the long time interval in the heating process, however, it becomes possible to local time intervals (20-40 min) with reducing the shrinkage rate to 0.05%/min.

The reason it was not possible to maintain a desired sintering rate can be seen on the curve 3, wherein the two peaks are distinctly different. With this a second one, that is more acute, most likely corresponds to the enabling of a new, more rapid sintering mechanism. Such a mechanism may be a plastic material flow. At figure 6 showing the shrinkage and shrinkage rate to temperature it can be
seen how quickly the process proceeds almost instantaneously accelerating the sintering in the range of 1325-1350 °C.

**Figure 5.** The time dependence of the sintering rate (•••) with the temperature program (⋯) using RCS in dynamic mode with preset rate of 1 – 0.1; 2 – 0.07; 3 – 0.05 % / min

When using a low shrinkage rate of 0.004% / min (figure 7) receiving a constant shrinkage rate also failed. The reason is the limitation of the method and software part in the definition of the value of the derivative at the current time, by which the temperature program is adjusted. However, at the shrinkage rate curve the two peaks corresponding, as supposed, to the two different predominant sintering mechanism, which are activated at these temperatures, are also clearly distinguished. The second peak, showing sintering acceleration finishes at 1327 °C, which is close to the previous case (figure 6).

Thus, obtaining a constant sintering rate of 0.05 or 0.07% / min by feedback method is very difficult due to the rapid sintering acceleration by enabling of new mechanisms when increasing temperature.

However, providing of dynamic mode sintering is only possible with laboratory equipment. Therefore, from the standpoint of practical implementation more preferable is use sintering programs, which are based on the formation of uniform heating segments and some isothermal exposures. Thus, the use of the RCS technique to simulate industrial production conditions is possible only in the isothermal mode.

**Figure 6.** Temperature dependence of shrinkage (—) and sintering rate (•••) using RCS in the dynamic mode at a preset rate of 0.05% / min

**Figure 7.** Time dependence of shrinkage (1) and sintering rate (2) with a temperature program (3) using RCS in the “start / stop” mode at a preset rate of 0.004 %/min

**Figure 8.** Time dependency of shrinkage (1) and sintering rate (2) when sintering with a temperature program (3) using RCS in isothermal mode at a preset rate interval 0.1-0.15 %/min
Based on the data obtained from previous experiments, limitations to the shrinkage rate were selected of 0.1-0.15% / min. To a temperature of 900 °C, the heating was conducted in the mode simulating the manufacturing sintering (see figure 2). On Figure 8 it is seen that shrinkage is linear during intensive sintering, and the shrinkage rate lies within preset limits.

The resulting temperature program comprises three isothermal exposures at high temperatures and is similar to a program simulating industrial production with higher temperature of 4 and 5th isothermal exposures (figure 9). Thus, the task of improving the profile of temperature for getting the structure with more uniform grain size distribution and fewer microcracks can be solved by maintaining shrinkage rate at a preset level.

The sintered density of the resulting samples was measured by hydrostatic weighing. Accuracy of the method ± 0.03 g/cm$^3$. The results are shown in Table 1. It is seen that the density values were similar within the measurement accuracy for all temperature programs.

4. Sample structure
Sintered samples microstructure were analyzed by scanning electron microscope.

General view of the microstructure of sintered samples were compared on ×400 magnification. The sample sintered with the “optimized” program has less regions of increased porosity than pellets obtained with RCS and smaller in size, except the pellet sintered under isothermal conditions (figure 10). For this one only small regions with high porosity can be seen. The presence of such regions in all the pellets is due to the lower temperature of the final exposure, compared with the industrial production sintering conditions.

| №  | RCS sintering mode               | Shrinkage rate threshold value (%/min) | Density (g/cm$^3$) |
|----|----------------------------------|----------------------------------------|-------------------|
| 1  | No ("basic" program, see figure 2) | No                                     | 10.42             |
| 2  | No ("optimized" program, see figure 2) | No                                     | 10.40             |
| 3  | Start/stop                        | 0.004                                  | 10.43             |
| 4  | Dynamic                           | 0.1 (control factor 25)                | 10.20             |
| 5  | Dynamic                           | 0.07 (control factor 25)               | 10.42             |
| 6  | Dynamic                           | 0.05 (control factor 40)               | 10.49             |
| 7  | Isothermal                        | 0.1 – 0.15                             | 10.39             |

As a result of the hydrostatic weighing, the sample sintered in dynamic mode at a rate of 0.05%/min has the highest density. But on its microstructure porous portions is seen that are larger and more prominent (figure 11). That fact is due to the large grain size for this sample and the presence of larger pores (15 µm) in the sample that sintered in the isothermal mode.
When comparing the microstructures of samples sintered with RCS in dynamic mode at different preset sintering rates a greater number of porous regions and larger pores were found for the shrinkage rate of 0.07 %/min, then that for 0.05 %/min. Microstructure of the sample sintered at 0.1 %/min, does not satisfy the preset requirements. In the central portion of the pellet connected porosity larger than 100 µm is observed. The reason may be a temperature program with fast reaching of a large shrinkage rate, as well as the pressing defect. These dilatometric data for dynamic conditions are consistent with the density measurements: the decrease in the sintering rate increases the density of the samples.

On high magnification images, in which the grain structure is visible, the following features are identified: a sample sintered in isothermal RCS mode has smallest average grain size of less than 3 µm, for other RCS samples that value is about 5 µm. This is due to a high shrinkage rate in the isothermal mode. The most uniform grain size is obtained for the sample with “optimized” program and RCS in isothermal mode. In the dynamic mode, a decrease in the shrinkage rate caused a slight increase in grain size.

Thus, maintaining shrinkage rate at a constant level more uniform grain size can be obtained. If the temperature profile of the shrinkage rate is a curve with maximum larger grain size is available, but the grain size distribution becomes less uniform.

5. Conclusion
Dilatometric study of the sintering process in three programs was carried out: simulation of the temperature profile of the industrial band oven; optimized temperature profile, providing nearly constant shrinkage rate; heating programs, providing a controlled rate of shrinkage. Different modes of RCS were used: start / stop, dynamic and isothermal. With the isothermal mode it was possible to get a close to constant sintering rate (0.1-0.15% / min) and most uniform grain size distribution. Sintering with a dynamic mode at different preset shrinkage rates shows that the total shrinkage increases with decreasing the sintering rate. In the dynamic mode, a constant shrinkage rate was not available. The probable cause is a sharp acceleration of sintering in the temperature range of 1320-1350 °C. Temperature profiles obtained with RCS in the dynamic mode (at the rate of 0.05% / min) and isothermal mode are close to the profile of the “optimized” industrial production program.

The microstructure of sintered samples was analyzed. In general, the samples have similar microstructures and have similar average grain size. For samples sintered in a dynamic mode a decrease in the shrinkage rate caused a slight increase in the grain size. In the isothermal mode a more uniform microstructure, but with a smaller grains is observed. Sintering temperature profile for optimized program provides reduction in the number of large pores in the sintered pellet.

The use of RCS can be used to control the final structure of oxide nuclear fuel pellets and the creation of optimal temperature conditions for band ovens used in industry.
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