



Large Grain Size UO₂ Sintered Pellets Obtaining used for Burn up Extension

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ABSTRACT:

The actual tendency all over the world is to manufacture fuel bundles capable to resist high burn-up. The main factors affecting the burn-up increase are: the pellet-cladding mechanical interaction (PCMI), the oxidation and hydriding of the Zircaloy-4 sheath, the increase of internal pressure, stress corrosion cracking, Zircaloy-4 irradiation growth, fuel swelling.

A way to increase fuel burn-up is to diminish the elements internal pressure by an adequate large grain UO₂ fuel pellet structure. In the large grain size UO₂ pellets, fission gas release rate decreases and the elements internal pressure increase slowly.

One of the ways to increase pellets grain size without increasing sintering temperature and time is the addition of small quantities (< 1% wt M/U) of sintering additives. By the addition of certain dopants in the UO₂ powder (TiO₂, Nb₂O₅, Cr₂O₃, CaO, V₂O₅) the grain size, the porosity and the mean free diffusion path are increased, whereas the grain boundary area is reduced.

At the Institute for Nuclear Research (ICN) - Pitesti a project for obtaining large grains size UO₂ pellets using dopants was developed. Two UO₂ non-free flowing powders, manufactured by ADU and IDR routes, were mixed with dopants (TiO₂, Nb₂O₅, Cr₂O₃), content of metals being 0.05-1 % wt M/U. The green pellets obtained by pressing UO₂ powders were directly sintered (4 hours at 1700°C) in a sintering furnace.

The physical, mechanical and microstructural properties of UO₂ sintered pellets with large grain size are studied, as compared to the undoped ones.

The diagrams presented the dependency of the main sintered pellet characteristics (pore radius distribution, pores volume, density, grains size) as function of the dopant nature and concentration, UO₂ sinterable powder nature and sintering temperature. Other sintered pellets characteristics (electrical conductivity, Seebeck coefficient, high temperature molar heat capacity and thermomechanical properties) are important to study.

The beneficial effects resulted from theoretical and practical projects are presented.

KEY WORDS: advanced fuel, burn up, UO₂, dopants, Nb₂O₅, Cr₂O₃, TiO₂, green pellets, radial expansion, sintered pellets, radial contraction, grain size, pores volume.

INTRODUCTION

A main concern all over the world is to increase fuel burn up for reducing nuclear electricity costs and the high active level waste (spent fuel) amount. Very good results were obtained in the disentanglement of the factors affecting the burn-up increase and the theoretical and practical (experimental results) solutions proposed to diminish adverse effects.

Table 1 there is presented a few factors affecting the burn-up increase and the solutions.

Table 1. Factors affecting burn up increase

Factor	Solutions
Increase of internal temperature	<ul style="list-style-type: none"> - reducing of elements diameter [1] - pellets with central hall [2] - duplex pellets [3] - graphite discs between pellets [4-5]
increase of internal pressure	<ul style="list-style-type: none"> - large grain size pellets [6-8] - controlled closed porosity
pellet-cladding mechanical interaction (PCMI)	<ul style="list-style-type: none"> - pellet length/diameter < 1 [9] - pellet geometry modifying [10]
stress corrosion cracking	<ul style="list-style-type: none"> - Zy-4 sheath covered with pure Zr [11]
oxidation and hydriding of the Zircaloy-4 sheath	<ul style="list-style-type: none"> - new microstructure for Zy-4 [12] - new Zr alloys (ZIRLO- Nb1%, Sn1% and Fe 0.1%) [13]

A way to increase fuel burn-up is to diminish the elements internal pressure by adequate UO₂ fuel pellet structure (large grain or controlled closed porosity). In the large grain size UO₂ pellets, fission gas release rate decreases and the elements internal pressure increases slowly. Similarly, in the UO₂ sintered pellet with controlled closed porosity the fission gas accommodation is better and the elements internal pressure increase slowly.

One of the ways to increase pellets grain size without increasing sintering temperature and time is the addition of small quantities (< 1% wt M/U) of sintering additives (aliovalent metal or rare earth oxide).

By the addition of certain dopants in the UO₂ powder (TiO₂, Nb₂O₅, Cr₂O₃, CaO, V₂O₅) the grain size, porosity and the mean free diffusion path are increased, whereas the grain boundary area is reduced [14] - [16].

For the production of niobia doped UO₂ fuel the “direct pelletizing process” which has been developed in relation with the AUC powder technology can be applied without any change beside the admixture of niobia to the UO₂ powder.

In a master mix UO₂ and Nb₂O₅ powders are added and homogenized. The blended powder is directly pressed without the addition of a lubricant. The green pellets are sintered in the sintering furnace. Under the same sintering conditions, the density of the pellets can be adjusted by U₃O₈ addition, UO₂ - Nb₂O₅ pellets with densities between 9.9 - 10.75 g/cm³ and grain size between 2 - 50 μm being obtained [17].

Other methods to obtain uranium dioxide pellets with large grain sizes:

- heating sintered pellet of uranium dioxide at temperatures higher than 1700°C in hydrogen stream containing silicate vapors, resulted from the aluminum silicate decomposition. The grain size values can be increased to more than 50μm [18].
- production of sintered uranium dioxide pellets by the addition of sintering agent (10 - 55wt% MgO and 90 - 45wt%SiO₂) or precursor thereof in the composition ranging from 0.1 - 0.8wt% of a sinterable mixture. The resulting mixture is turned into a compact. The sintering process is performed at a temperature where the sintering agent forms a liquid phase to produce a sintered product. The precursor is thermally decomposed below the sintering temperature [19].
- obtaining of sintered UO₂ nuclear fuel pellets, with the average grain size ranging from about 30μm to about 80μm by the addition of magnesium aluminosilicate in uranium dioxide powder. The pores volume is ranging between 2 and 10% [20].
- addition of Cr₂O₃ or Al₂O₃ and of small quantities of SiO₂ into the uranium dioxide powder.

At the Institute for Nuclear Research (ICN) - Pitesti a technology for obtaining large grains size UO₂ pellets using dopants was developed.

EXPERIMENTAL WORKS

In the UO₂ non-free flowing powders, manufactured by ADU (P1) and IDR (P2) routes, was added Nb₂O₅, Cr₂O₃ and TiO₂, content of metals being 0.05-1 % wt M/U. The blends were homogenized in a Y - con master mix. The blended powders were compacted by bilateral pressing at 270MPa. The green pellets were directly sintered under Hydrogen atmosphere (4 hours at 1700°C) in standard sintering furnace. Supplementary, green pellets doped with Nb₂O₅ were sintered at 1600°C, the rest of parameters being the same.

The green pellets density was determined geometrically. The radial expansion was calculated by formula:

$$Re (\%) = (\varphi_2 - \varphi_1) * 100 / \varphi_1 \quad (1)$$

where φ_1 is the internal diameter of mould and φ_2 is the green pellet diameter..

The sintered pellets density was determined by immersion method. The radial contraction was calculated by formula:

$$Rc (\%) = (\varphi_2 - \varphi_3) * 100 / \varphi_2 \quad (2)$$

where φ_2 is the green pellet diameter and φ_3 is the sintered pellet diameter

The sintered pellets were cut on an axial plan, polished a chemical attacked to distinguish grain boundary. The grain size was determined by linear interception method (Heyn).

The total pores volume was calculated by formula:

$$V_t(\%) = (\rho - \rho_d) * 100 / \rho \quad (3)$$

where $V_t(\%)$ is the total pores volume percent evaluated, ρ being UO₂ theoretical density and ρ_d is UO₂ density determined by immersion for each pellets.

GREEN PELLETS CHARACTERISTICS

The powders used in this project were manufactured by two different routes: P1-ADU and P2-IDR. Some characteristics of powders are presented in Table 2.

Table 2. Powders characteristics

Lot	Agglomerates distribution (%)							Bulk density g/cm ³	Pores volume cm ³ /g
	>2	2-0.9	0.9-0.63	0.63-0.315	0.315-0.1	0.1-0.04	< 0.04		
P1	0.2	2	4	11.5	14	16	52.3	1.03	0.13
P2	0	0.1	1	23	42.8	20.8	12.3	1.79	0.066

The green pellets obtained from doped UO₂ powders by bilateral pressing were characterized by geometrical density. The behavior of green pellets at ejection from mould was followed by radial expansion values obtained. For each powder type and dopant concentration, ten pellets were manufactured.

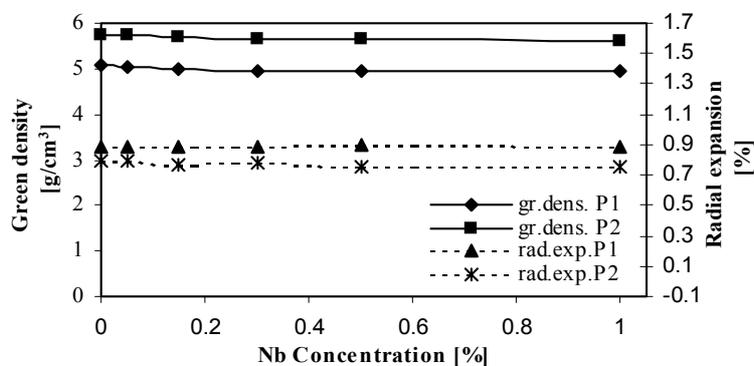


Figure 1. Green pellets density and radial expansion versus Nb concentration

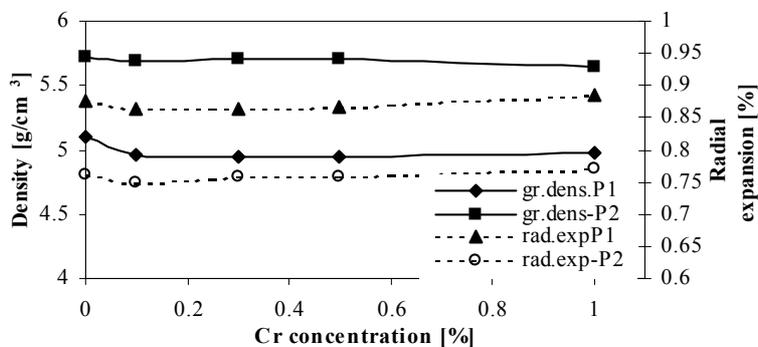


Figure 2. Green pellets density and radial expansion dependence on Cr concentration

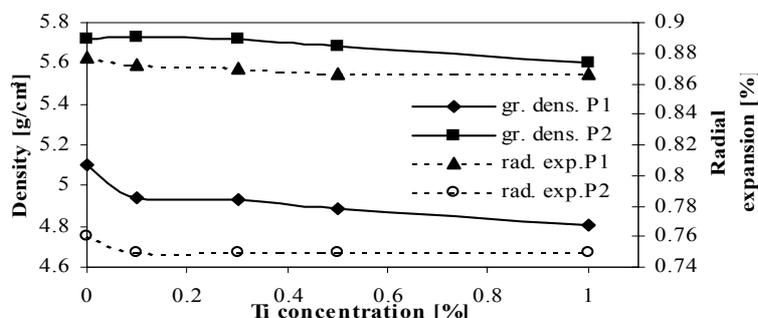


Figure 3. Green density and radial expansion versus Ti concentration

The mean value of green density and radial expansion for each dopants concentration are presented in the curves from Figures 1, 2 and 3. The green density is strongly dependent on powder type. The difference between green pellets density manufactured from P1 powder (ADU route) and P2 powder (IDR route) is about 0.8 g/cm³. Nevertheless, the difference between radial expansions for the same powder is only 0.1%.

The Nb₂O₅ addition in the powders does not modify very much the green density (Figure 1) but a little tendency to decrease with dopant percentage increasing exists. Cr₂O₃ addition has an influence appreciatively the same like Nb₂O₅, maybe a little more for P1 powder. TiO₂ addition has a pregnant influence on green pellets density comparatively to Nb₂O₅ addition (Figure 2). The dopants concentration increasing from zero up to 1% induces green pellets density decrease especially for P1 powder (Figure 3).

The radial expansion curves for all dopants have appreciatively the same form comparatively with green density curves, respectively.

The behavior of doped powders to pressing is dependent on dopant and powders microstructural and physical properties. The powders, being obtained by different routes, have different microstructural and physical properties and aptitude for pressing. Similarly, obtaining methods for dopants manufacturing are different.

SINTERED PELLETS DENSITY AND RADIAL CONTRACTION

The variation in density of Nb₂O₅ - doped UO₂ pellets as a function of Nb content is presented in Figure 4. A very small concentration of Nb₂O₅ (0-0.1%Nb/U) leads to a minimum value of the UO₂ pellet density. The density of UO₂ pellets increases with the increase of the Nb content for low concentrations (0.1 ÷ 0.2% Nb/U). At concentrations higher than 0.2%Nb/U, the density values are different, depending on the manufacturing routes: the increase of the Nb concentration slowly diminishes the density (P₁ -ADU route) or remains constant (P₂ - IDR route).

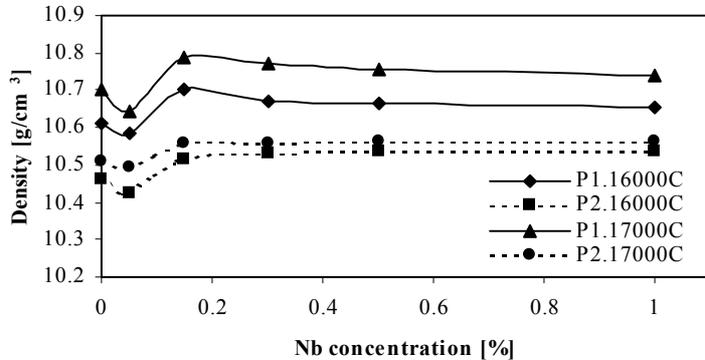


Figure 4. Sintered pellets density versus Nb concentration

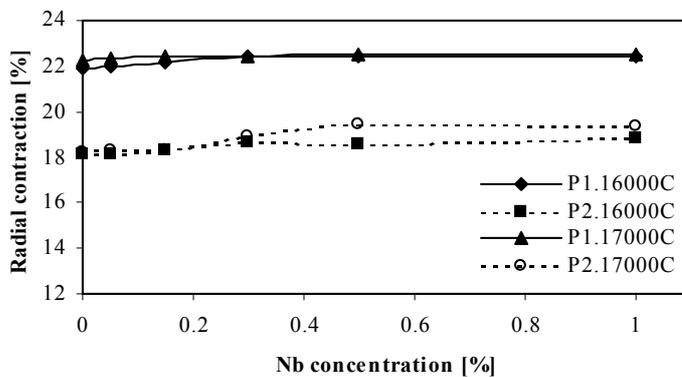


Figure 5. Radial contraction versus Nb concentration

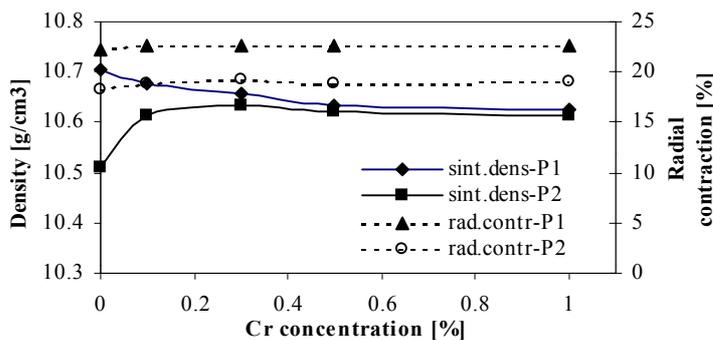


Figure 6. Sintered pellets density and radial contraction versus Cr concentration

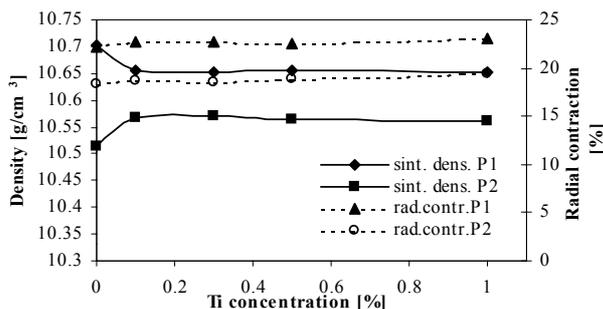


Figure 7. Sintered pellets density and radial contraction versus Ti concentration

At concentrations higher than 0.2%Nb/U, the density values are different, depending on the manufacturing routes: the increase of the Nb concentration slowly diminishes the density (P₁ -ADU route) or remains constant (P₂ - IDR route).

The sintering temperature has an impact on UO₂ sintered pellets density. The decrease of sintering temperature can observe the diminishing of sintered pellets density. However, the influence of dopant concentration is similar.

The importance of powders quality can be observed following Figure 1and Figure 4. Nevertheless, the pellets green density from P2 powder is better than pellets green density from P1 powder, the sintered pellets density from P1 powder are better than sintered pellets density from P2 powder.

The radial contraction of doped green pellets in the sintering process can be seen in Figure 5. In concordance with sintered pellets density, radial contraction for green pellets manufactured from P1 powder is better that radial contraction for green pellets manufactured from P2 powder. The presence of Nb₂O₅ in UO₂ powder and temperature decrease by 100⁰C have little influence on green pellets radial contraction.

The influence of Cr₂O₃ dopant on sinterability of both powders is showed in Figure 6. The behavior of doped powders is different. Increasing of Cr₂O₃ content in P1 type powder determines a continuous decrease of UO₂ sintered pellets density. Little quantities of Cr₂O₃ dopant (< 0.3%) in P2 powder type determine the increasing of UO₂ sintered pellets density. After that, increasing of Cr₂O₃ quantities determines a very slow decrease of sintered pellets density. The influence of Cr₂O₃ content on radial contraction is negligible.

The presence of TiO₂ dopant in both powders has the same impact on UO₂ sintered pellets density like Cr₂O₃ (Figure7). Hereby, TiO₂ content up to 0.1% in P1 powder type determine a visible decrease of UO₂ sintered pellets density. After that the decreasing of sintered density with the increase of TiO₂ content is almost indistinguishable. Concentrations of TiO₂ up to 0.1% in P1 powder type determine a visible increasing of UO₂ sintered pellets density. The TiO₂ content increasing determines a very slowly decrease of UO₂ sintered pellets density.

The modifying of radial contraction function of TiO_2 content is undistinguishable.

DOPANT INFLUENCE ON THE GRAIN SIZE OF UO_2 SINTERED PELLETS

The influence of Nb_2O_5 dopant on grain size of UO_2 sintered pellets is showed in Figure 8. The dopant addition

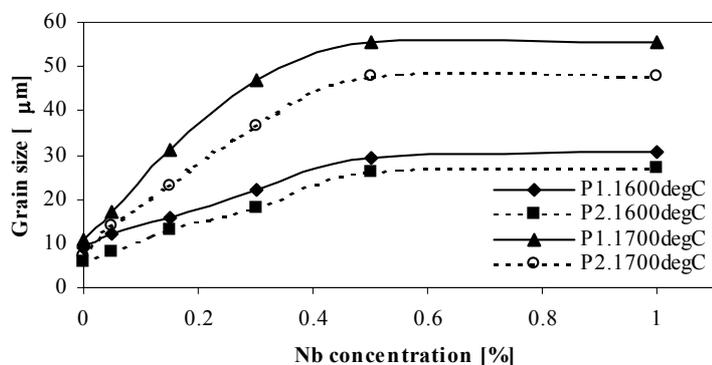


Figure 8. Grain size versus Nb concentration

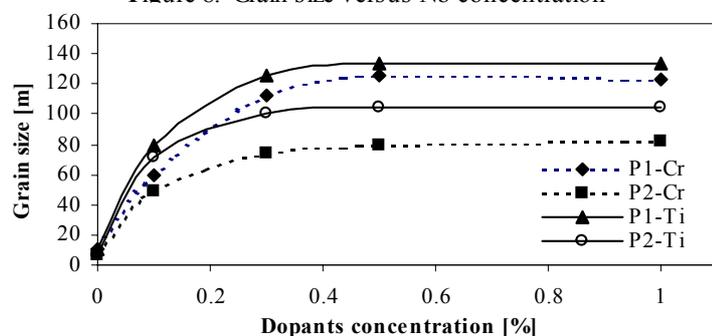


Figure 9. Grain size dependence from dopants concentration

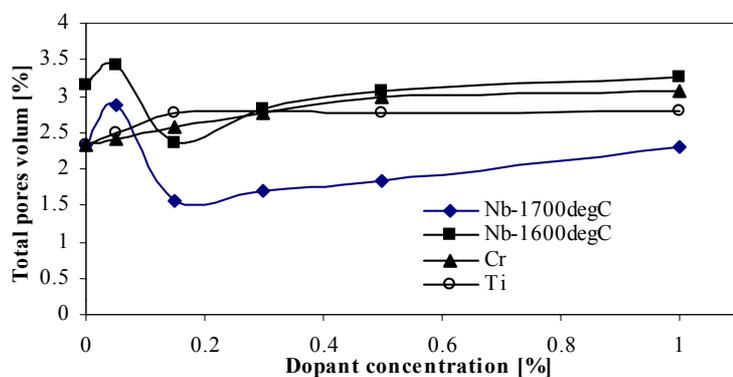


Figure 10. Total pores volum versus dopant concentration

determines a significant grain growth. The increasing of Nb_2O_5 content (up to 0.5%) determines the increasing of grain size up to 56 μm for P1 powder type and up to 48 μm for P2 powder type sintered at 1700 $^{\circ}\text{C}$. In the same conditions, but sintered at 1600 $^{\circ}\text{C}$, the grain size is 31 μm and 27 μm for P1 and P2 powder type, respectively.

The temperature influence on the grain size growth in the presence of Nb_2O_5 dopant is significant. For P1 powder type doped with 0.5% Nb_2O_5 , the difference between grain sizes sintered at 1700 $^{\circ}\text{C}$ and 1600 $^{\circ}\text{C}$ is 25 μm .

The increasing of Nb_2O_5 content does not produce important grain size modifications.

The influence of Cr_2O_3 and TiO_2 dopants is presented in Figure 9. The increasing of Cr_2O_3 content up to 0.5% induces a grain size growth up to 126 μm for P1 powder type and up to 80 μm for P2 powder type. Grain size growth, when Cr_2O_3 content increases up to 1%, is undistinguishable. The increasing of TiO_2 content up to 0.5% induces a grain size growth up to 133 μm for P1 powder type and up to 104 μm for P2 powder type. When increasing of TiO_2 content over 0.5% no eloquent growth appears.

The total pores volume dependency on nature and concentration of dopants for P1 powder type is presented in Figure 10. The total pores volume of sintered pellets (1700 $^{\circ}\text{C}$) doped with Nb_2O_5 has the following evolution: increase from 2.4% (undoped) to 2.8% (0.05% Nb_2O_5), decrease to 1.6% (0.1% Nb_2O_5), after that slowly increase up to 2.3% (1% Nb_2O_5). The decreasing of sintering temperature at 1600 $^{\circ}\text{C}$ determines the follow total pores volume evolution: increase from 3.2% (undoped) to 3.4% (0.05% Nb_2O_5), decrease to 2.8% (0.1% Nb_2O_5), after that slowly increase up to 3.2% (1% Nb_2O_5).

The influence of Cr_2O_3 and TiO_2 dopant on total pores volume is not very much. Hereby, the total pores volume increase slowly from 2.34% (undoped) up to 3.05% and 2.8% (1% dopant) for Cr and Ti respectively.

BENEFICIAL EFFECTS

A program covering the manufacturing, irradiation and post-irradiation examination (PIE) of niobia doped fuel at two dopant levels (0.25% and 0.4% by weight of Nb/U) was performed [21]

The fuel was manufactured by BNFL using binderless IDR/CONPOR route. The as-manufactured grain sizes were: 6-8 μm - undoped pellets, 36 μm - 0.25% Nb doped pellets and 45 μm - 0.4% Nb doped pellets.

The fuel was irradiated in the commercial Dodewaard BWR (Netherlands) at various mean burn-ups: 25-26 MWd/kgU (4 cycles) - fuel rods with 0.25% Nb doped pellets and 36-39 MWd/kgU (6 cycles) - fuel rods with 0.4% Nb doped pellets.

Using poolside facilities at the Dodewaard reactor and the hot cells at Winfrith, Berkeley and Harwel carried out the post-irradiation examination. Puncturing and krypton counting determined the fission gas release. The fuel rod

puncturing showed the fission gas release for the niobia-doped rods in all cases to be lower than their sibling undoped rods. The difference was a factor of 1.4 to 2.1 for the fuel rods with 0.25% Nb doped pellets and 1.1 to 1.2 for the fuel rods with 0.4% Nb doped pellets.

CONCLUSIONS

Large grain size pellets can be a solution to increase fuel burn-up by diminishing the elements internal pressure. The manufacturing of large grain size pellets is not a very elaborate process. The dopant addition in UO_2 powder is a possibility.

The main factors affecting the large grain size structure of UO_2 sintered pellets are: nature and concentration of dopants, powder sinterability and sintering temperature. By combination of this factors can to obtain any sintered pellets structure: density, grain size, pores volume, function of needs for sintered pellets design.

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