# INFLUENCE OF ADDITIVES ON THE AVERAGE GRAIN SIZE IN $UO_2$ SINTERED PELLETS

*MARIANA POSTELNICU, ALEXANDRU MUŞAT, EMANUEL BĂDULESCU*

Institute for Nuclear Research (RATEN ICN) Piteşti, Romania
*e-mail: mariana.postelnicu@nuclear.ro*

*Abstract*

The paper presents the influence of the chromium (III) oxide and aluminium oxide added to the $UO_2$ powder on the grain size of the sintered pellets. The reason why dopants are added to $UO_2$ fuel is to improve the retention of fission products and provide enhanced resistance to stress corrosion cracking due to the pellet-clad interaction. A batch of uranyl nitrate hexahydratate was used to obtain the $UO_2$ powder, which was produced through ADU (Ammonium Diuranate) route. The mixing of $UO_2$ powder with dopants was done in two stages, because the amount of added dopants is very small. The green pellets were obtained by bilateral pressing of the powder in a mould. The pellets were then sintered at 1700 °C for 2 hours in a hydrogen atmosphere. The density of the sintered pellets was determined using immersion method. The sintered compacts microstructure was analyzed by optical microstructure investigations. Grain size has being measured by taking optical microscope images and then using the Heyn linear intercept method. The additive level of the $UO_2$ powder influences the grains size in the sintered pellets, so that with the increase in the concentration of dopant added to the powder, an increase in the size of the grains was observed. Based on the obtained results, it can be concluded that the size of the grains in the doped $UO_2$ pellets increased 5-6 times compared to the size of the grains in the undoped $UO_2$ pellet.

***Keywords:*** *Accident tolerant fuel, Doped $UO_2$ pellets, Grain size*

## Introduction

The Three Mile Island and Fukushima Daiichi accidents have shown that the current fuel designs are vulnerable under such extreme conditions, so there is are new interest in alternative fuel designs that not only increase the safety of reactors, but also improve plant performance at a crucial time for the nuclear industry. This alternative fuel is called Accident tolerant fuel (ATF). There are extensive programs all over the world supporting and promoting the development of Accident tolerant fuel. ATF may incorporate the use of new materials and designs for cladding and fuel pellets [1].

Fuel pellets doping technology is showing promising results with respect to enhancing densities and enlarging grain size. However, in order to bring this technology from lab-scale to mass-scale fuel production, the following points need to be addressed:

- Develop an improved understanding of the mechanism of grain enlargement and density improvement due to the addition of dopants;
- Develop confidence in in-pile behaviour of doped fuel with respect to fission gas retention without swelling [2].

One of the most accepted concepts is the use of accident-tolerant fuel made by improving the fuel microstructure by adding dopants. There have been efforts by several different research groups to study the effects of doping on properties of uranium dioxide. These efforts have being focused on how dopants affect properties such as thermal diffusivity, fission gas release, grain size, and creep strength. Several papers have specifically shown that adding minute amounts (from 0.05 to 0.2 wt%) of different oxides to uranium dioxide will noticeably alter material's thermo-mechanical and microstructural properties [3].

The motivation for adding dopants to $UO_2$ fuels is best addressed in some references mentioning that $Cr_2O_3$ and $Al_2O_3$-$Cr_2O_3$ dopants improve retention of fission product gas and provide enhanced resistance to stress corrosion cracking due to the pellet-clad interaction [4].

The objective of this paper was focused on establishing the influence on the grain size of the sintered pellets due to the adding of chromium (III) oxide and aluminium oxides to the $UO_2$ powder.

## Experimental works

A batch of uranyl nitrate hexahydratate was used to obtain the $UO_2$ powder, which was produced through ADU (Ammonium Diuranate) route.

The main stages in the $UO_2$ powder manufacture were:

- dissolving yellow crystals of uranyl nitrate;
- precipitation of uranyl nitrate solution with ammonia solution;
- vacuum filtration of ammonium diuranate;
- calcination of ADU (ammonium diuranate) to $U_3O_8$;
- reduction of $U_3O_8$ powder to $UO_2$;
- passivation of $UO_2$ powder.

The additives used for doping the obtained powder were chromium oxide and aluminium oxide. The main characteristics of $Cr_2O_3$ and $Al_2O_3$ powders are shown in Table 1.

Table 1. Physical and chemical properties of $Cr_2O_3$ and $Al_2O_3$

| | **$Cr_2O_3$** | **$Al_2O_3$** |
|---|---|---|
| Physical condition | powder | powder |
| Colour | green | white |
| Melting point | 2435 °C | 2040 °C |
| Boiling point | 4000 °C | 2980 °C |
| Water solubility | insoluble | insoluble |
| Density | 5.22 g/cm$^3$ | 3.94 g/cm$^3$ |

Determination of the particle size distribution of $UO_2$, $Cr_2O_3$ and $Al_2O_3$ powders was performed using Horiba Partica LA 950 V2 particle analyser, which allows both the determination of the particle sizes and their distribution by size class. The mean particle size for each type of powder is presented in Table 2.

Table 2. Average particle size for considered powders

| Powder | **$UO_2$** | **$Cr_2O_3$** | **$Al_2O_3$** |
|---|---|---|---|
| Particle size [μm] | 14.84 | 6.21 | 9.72 |

A pellet was pressed from the batch of the obtained $UO_2$ powder, and the rest of the powder was divided into three approximately equal quantities, each quantity being mixed with chromium oxide and aluminium oxide according to the mass percentages shown in Table 3.

Table 3. Considered mass percentages Metal/Uranium

| **Batch no.** | **wt% Al/U** | **wt% Cr/U** |
|---|---|---|
| 1 | 0.02 | 0.05 |
| 2 | 0.02 | 0.10 |
| 3 | 0.02 | 0.16 |

While the mass percentage Al/U remained constant in all the three batches, the mass percentage Cr/U was different.

The additives facilitate densification and diffusion during sintering. Data show that $Al_2O_3$ enhances the grain size enlarging effect of $Cr_2O_3$. Aluminium oxide can be viewed as a way to lower the total amount of dopant [4].

Based on the parametric studies, chromium content is specified at an optimum value of 0.16 wt% corresponding to the solubility limit of the dopant in $UO_2$ at the applicable sintering conditions. Beyond this solubility limit, excess dopant remains as inclusions in the grain boundaries. The presence of such precipitates inhibits the growth of the grain.

For a given optimized chromium content level, large grains favorably increase $Cr_2O_3$-doped fuel visco-plasticity. These features provide a lower stress-resistance capability of $Cr_2O_3$-doped fuel, as compared to reference $UO_2$ fuel [4, 5].

Additive levels were kept low because the level of impurities and the effective neutron absorption section in the nuclear fuel must remain low [6].

The mixing of $UO_2$ powder with dopants was done in two stages, due to the very small amount of added dopants. Thus, a premix was made from the dopant and ~10% of the powder quantity, followed by the homogenization of the premix with the remaining powder.

The green pellets were obtained by bilateral pressing of the powder in a mould lubricated with zinc stearate diluted in acetone. A mould with an inner diameter of 13.5 mm was used; the compaction pressure of 280 MN/m$^2$ was applied to the powder for 10 seconds. In order to determine the geometrical density, the green pellets were weighed and dimensionally measured. The geometrical density values of green pellets were in the range 5-6 g/cm$^3$.

The sintering heat treatment of the green pellets was performed in following experimental conditions:

- heat rate: 240 °C/ h;
- temperature: 1700 °C for 2 hours;
- cooling rate: 600 °C/ h;
- dynamic hydrogen atmosphere.

The sintered pellets density was determined using the immersion method. The density was determined using a dedicated density determination kit which is a part of additional equipment intended for laboratory balance. Each sintered pellet is weighed in air and then in demineralised water. The density of each sintered pellet was in the range 98.4 - 98.9% TD (theoretical density).

Each sintered pellet was sectioned longitudinally and polished on hydro-resistant abrasive paper. Then, in order to examine the microstructure, the samples were chemically attacked with an oxidizing solution consisting of hydrogen peroxide and concentrated sulphuric acid.

The microstructure of the sintered compacts was analysed using optical microstructure investigations with CARL ZEISS optical microscope. The surfaces of the analyzed samples were not polished with diamond paste and for this reason the images obtained are not very clear.

**Results and discussions**

In the analyzed samples, grain size has been measured by taking optical microscope images and then using the Heyn linear intercept method. This method estimates the average grain size by counting (on the ground-glass screen, on a photomicrograph of a representative field of the specimen, a monitor or on the specimen itself) the number of grains intercepted by one or more straight lines sufficiently long to yield at least 50 intercepts. It is desirable to select a combination of test line length and magnification such that a single field will yield the required number of intercepts. The precision of grain size estimated by the intercept method depending on the number of grain interceptions counted [7].

Figures 1÷7 show micrographs of the analyzed samples.

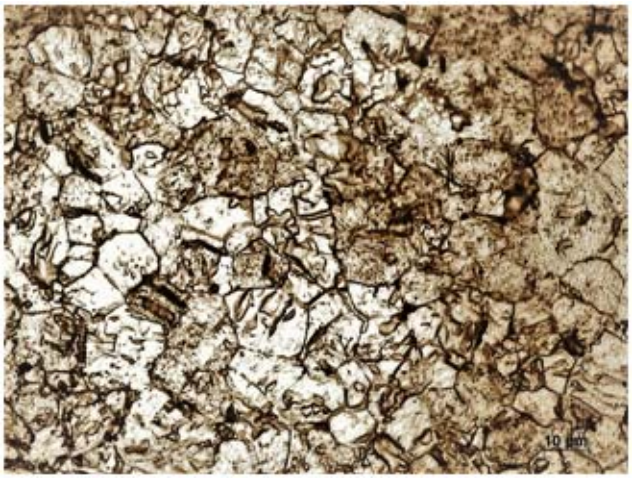


Fig.1. Image of undoped sintered pellet (no.0)



Fig. 2. Image of pellet (no.1) doped with 0.02% Al and 0.05% Cr



Fig. 3. Image of pellet (no.2) doped with 0.02% Al and 0.05% Cr



Fig. 4. Image of pellet (no.3) doped with 0.02% Al and 0.1% Cr

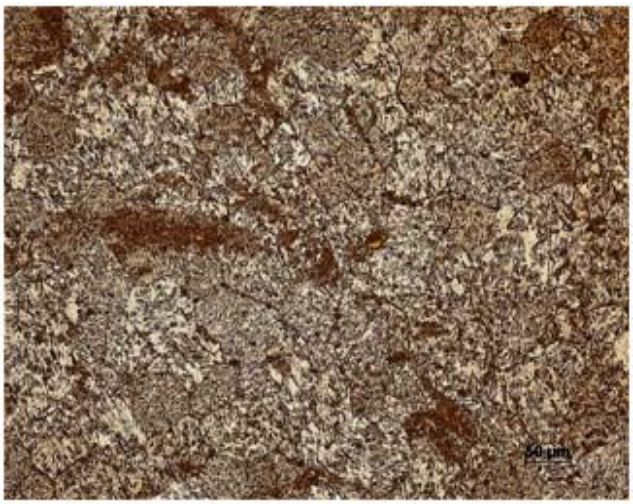


Fig. 5. Image of pellet (no.4) doped with 0.02% Al and 0.1% Cr

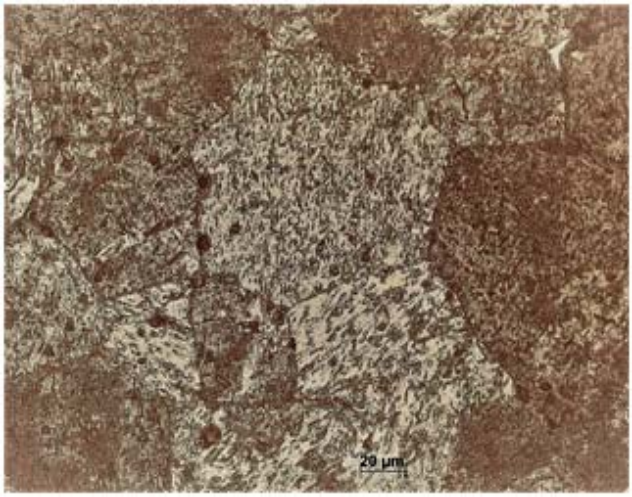


Fig. 6. Image of pellet (no.5) doped with 0.02% Al and 0.16% Cr

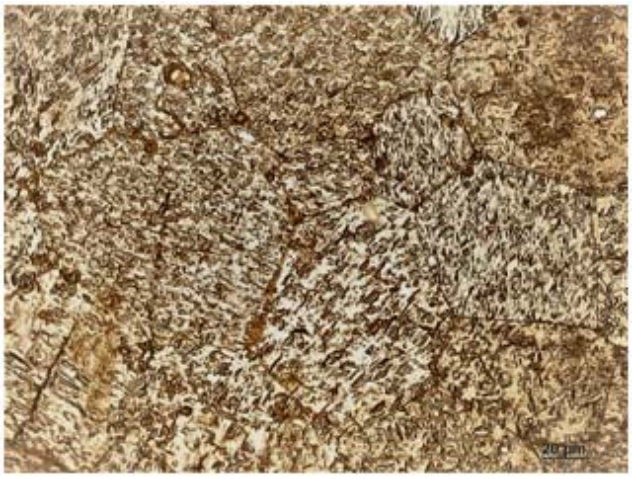


Fig. 7. Fig. 6. Image of pellet (no.6) doped with 0.02% Al and 0.16% Cr

No determination of average grain size can be exactly measured and due to this reason the determinations are not complete without calculating the standard deviation.

Six test lines were drawn on each micrograph, the magnitude was calculated and the average grain size and standard deviation were determined. The confidence interval for the mean ($\bar{d}$) with a 95% confidence level is presented in the Table 4.

Table 4. Average grain size

| Sample no. | Level of doping [%] | Average grain size [µm] |
|---|---|---|
| 0 | - | $8 \leq \bar{d} \leq 10$ |
| 1 | 0.02 Al+ 0.05Cr | $40 \leq \bar{d} \leq 46$ |
| 2 | 0.02 Al+ 0.05Cr | $40 \leq \bar{d} \leq 46$ |
| 3 | 0.02 Al+ 0.1 Cr | $49 \leq \bar{d} \leq 56$ |
| 4 | 0.02 Al+ 0.1Cr | $49 \leq \bar{d} \leq 56$ |
| 5 | 0.02 Al+ 0.16Cr | $60 \leq \bar{d} \leq 63$ |
| 6 | 0.02 Al+ 0.16Cr | $60 \leq \bar{d} \leq 63$ |

## Conclusions

The present study was performed aiming to bring in attention the accident tolerant fuel. The goal was to establishing the influence on the grain size of the sintered pellets due to the addition of dopant Chromium (III) and Aluminium oxides to the $UO_2$ powder.

The density and microstructure of the pellets made from the powder are significantly influenced by the quality of the nuclear material used to prepare the $UO_2$ powder.

The obtained sintered pellets have a density greater than 10.80 g/cm$^3$, value indicating a low porosity.

The additive level of the $UO_2$ powder influences the grains size in the sintered pellets, so that with the increase in the concentration of dopant added to the powder, an increase in the size of the grains is observed.

Based on the obtained results, it can be concluded that the size of the grains in the doped $UO_2$ pellets increased 5-6 times compared to the size of the grains in the undoped $UO_2$ pellet.

## References

[1] Munoz-Reja Ruiz, C., Romero, J., Quecedo, M., Oelrich, R.L. (2019) ″Fuel Engineering Innovation. The development of the enhanced accident tolerant fuels (ATF)″, *Nuclear Espana*, No. 403, pp. 20-24.

[2] International Atomic Energy Agency (2004) ″Advanced fuel pellet materials and designs for water cooled reactors″, IAEA-TECDOC-1416, Proceed. of a technical committee meeting held 2003 in Brussels, Belgium.

[3] McDonald, R. (2014) *″An Evaluation of the Mechanical Properties and Microstructure in Uranium Dioxide Doped with Oxide Additives″*, MSc thesis, Arizona State University.

[4] Khatib-Rahbar, M., Krall, A., Yuan, Z., Zavisca, M. (2020) ″Review of accident tolerant fuel concepts with implications to severe accident progression and radiological releases″, Energy Research Inc. report. ERI/NRC 20-209, prepared for US Nuclear Regulatory Commission, USA.

[5] Perez, A.M., Bonales, L.J., Rodriguez Villagra, N., Fernadez, S., Baonza, V.G., Cobos, J. (2021) ″Raman spectroscopy cupled to principal component analysis for studying $UO_2$ nuclear fuels with different grain sizes due to the chromia addition″, *Journal of Nuclear Materials*, Vol. 543, paper 152581, https://doi.org/10.1016/j.jnucmat.2020.152581

[6] Diaconu, D. (1999) *″Contribution to modelling the growth of $UO_2$ crystallites in additive nuclear fuels″*, PhD thesis, University of Bucharest (in Romanian)

[7] ASTM International (2012) *″Standard Test. Methods for Determining Average Grain Size″*, ASTME 112-12.