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# Effect of $Al(OH)_3$ on the sintering of $UO_2$–$Gd_2O_3$ fuel pellets with addition of $U_3O_8$ from recycle

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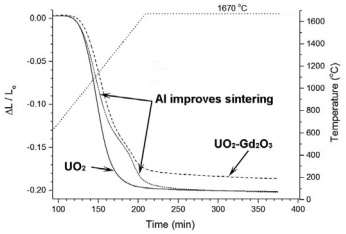
## HIGHLIGHTS

- Sintering tests for $UO_2$-7wt%$Gd_2O_3$ were performed with additions of $Al(OH)_3$ and $U_3O_8$.
- $U_3O_8$ addition does not interfere in the sintering behavior of the $UO_2$-$Gd_2O_3$ system when aluminum is added as a sintering aid.
- The presence of aluminum greatly improves the sinterability of the $UO_2$-$Gd_2O_3$ system.
- The characteristics of $UO_2$-7wt% $Gd_2O_3$ pellets are adequate for use as fuel when $Al(OH)_3$ and $U_3O_8$ are added to the $UO_2$-$Gd_2O_3$.

## GRAPHICAL ABSTRACT

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## ABSTRACT

The incorporation of gadolinium as burnable poison directly into nuclear fuel is important for reactivity compensation, which enables longer fuel cycles. The function of the burnable poison fuel is to control the neutron population in the reactor core during its startup and the beginning of the fuel burning cycle to extend the use of the fuel. The implementation of $UO_2$-$Gd_2O_3$ poisoned fuel in Brazil has been proposed according to the future requirements established for the Angra-2 nuclear power plant. The $UO_2$ powder used is produced from the Ammonium Uranyl Carbonate (AUC). The incorporation of $Gd_2O_3$ powder directly into the AUC-derived $UO_2$ powder by dry mechanical blending is the most attractive process, because of its simplicity. Nevertheless, processing by this method leads to difficulties while obtaining sintered pellets with the minimum required density. The cause of the low densities is the bad sintering behavior of the $UO_2$-$Gd_2O_3$ mixed fuel, which shows a blockage in the sintering process that hinders the densification. This effect has been overcome by microdoping of the fuel with small quantities of aluminum. The process for manufacturing the fuel inevitably generates uranium-rich scraps from various sources. This residue is reincorporated into the production process in the form of $U_3O_8$ powder additions. The addition of $U_3O_8$ also hinders densification in sintering. This study was carried out to investigate the influence of both aluminum and $U_3O_8$ additives on the density of fuel pellets after sintering. As the effects of these additives are counterposed, this work studied the combined effect thereof, seeking to find an applicable composition for the production process. The experimental results demonstrated the effectiveness of aluminum, in the form of $Al(OH)_3$, as an additive to promote increase in the densification

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of the (U,Gd)$O_2$ pellets during sintering, even with high additions of $U_3O_8$ recycled from the manufacturing process.



## 1. Introduction

Demands for extended fuel cycles and higher target burnups are a strong incentive to use $Gd_2O_3$ as a burnable poison in modern Pressurized Water Reactors. The use of a burnable poison in nuclear reactors provides the necessary negative moderator reactivity coefficient at the beginning of core life and helps shape core power distributions [1]. From a nuclear viewpoint, gadolinia is an excellent burnable poison, possessing a high-neutron absorption cross-section coupled to a burn-up rate that, if properly designed, can closely match $^{235}U$ depletion, minimizing the reactivity penalty at the end-of-cycle (EOC) [2,3]. For these reasons, the implantation of $UO_2$-$Gd_2O_3$ poisoned fuel in Brazil has been proposed in the future requirements established for the Angra-2 nuclear power plant.

From the different methods for the conversion of $UF_6$ to ceramic grade $UO_2$ on an industrial scale [4], the Ammonium Uranyl Carbonate (AUC) process [5] is the most attractive due to the smallest number of process steps involved. Due to the good characteristics of $UO_2$ powder derived from AUC, the fabrication process of $UO_2$-$Gd_2O_3$ fuel adopts the dry mechanical blending method to prepare the mixed powders. In this process, the $Gd_2O_3$ powder is incorporated to $UO_2$ powder and homogenized with no additional milling, prepressing and granulating steps, which are necessary when $UO_2$ powder is derived from other methods for the conversion of $UF_6$ [6,7]. Following this route, $Gd_2O_3$ powder is incorporated directly into $UO_2$ powder by mechanically dry mixing $UO_2$ and $Gd_2O_3$ powders, the so-called dry mechanical blending method. After blending, the $UO_2$-$Gd_2O_3$ mixed powders are pressed into pellet form, following sintering under reducing hydrogen atmosphere.

Experimental results [7–9] have shown that the incorporation of $Gd_2O_3$ powder into the AUC-derived $UO_2$ powder by the most attractive commercial method of dry mechanical blending leads to difficulties while obtaining sintered $UO_2$-$Gd_2O_3$ pellets with the minimum required density due to the deleterious effect of the $Gd_2O_3$ on the traditional $UO_2$ sintering behavior. Several studies have investigated the sintering of $UO_2$-$Gd_2O_3$ mixed oxides. The results have shown difficulties in sintering fuel pellets with the minimum specified density, of around 94% of the theoretical density. The sintering curves available in the literature show that the lower sintered densities are due to the abnormal sintering behavior of the $UO_2$-$Gd_2O_3$ fuel compared to the sintering behavior of the traditional $UO_2$ fuel. Dilatometric analyses show that at temperatures around 1100–1400 °C, the shrinkage of the $UO_2$-$Gd_2O_3$ pellets is delayed, the sintering rate decreases, and densification shifts to higher temperatures [7,9–11]. Previous work revealed the typical sintering curve showing this abnormal sintering behavior, as illustrated in Fig. 1 [9].

To overcome the problem of low densification of the $UO_2$-$Gd_2O_3$ pellets in the sintering, Assmann et al. proposed the use of aluminum as a sintering aid [8]. The aluminum was added as $Al(OH)_3$ powder in the step of dry mixing of the $UO_2$ and $Gd_2O_3$ powders. The maximum aluminum concentration used was 200 ppm and depended on the concentration of $Gd_2O_3$ added to the fuel.

In a commercial $UO_2$ fuel pellet manufacturing process, defective sintered and green pellets are produced and they should be reused. A common recycling method is to oxidize them in the air to make recycled $U_3O_8$ powder, which is then added to $UO_2$ powder. INB (Indústrias Nucleares do Brasil S.A.) is the producer of $UO_2$ fuel pellets for the Brazilian nuclear power reactors. INB oxidizes the pellets at 380 °C during 20 h in an air atmosphere for dry recycling of defective $UO_2$ pellets. The pellets are spontaneously pulverized by the stress involved in the oxidation process. The $U_3O_8$ formed is then sieved through a sieve of 350 μm [12].

In this recycling process, however, the addition of $U_3O_8$ to $UO_2$ leads to a drop in the pellet density because the recycled $U_3O_8$ powder has a small surface area and thus poor sinterability compared to the raw $UO_2$. In other words, the $U_3O_8$ addition decreases the sintered densities of $UO_2$ pellets because the specific surface area of the $U_3O_8$ powder is much lower (6.1 times) than that of $UO_2$ powder [12].

Therefore, both the addition of $Gd_2O_3$ (as burnable poison) and $U_3O_8$ (as recycling material) to the $UO_2$ powder causes the final density of the sintered pellets to decrease. As the use of $Al(OH)_3$ as a

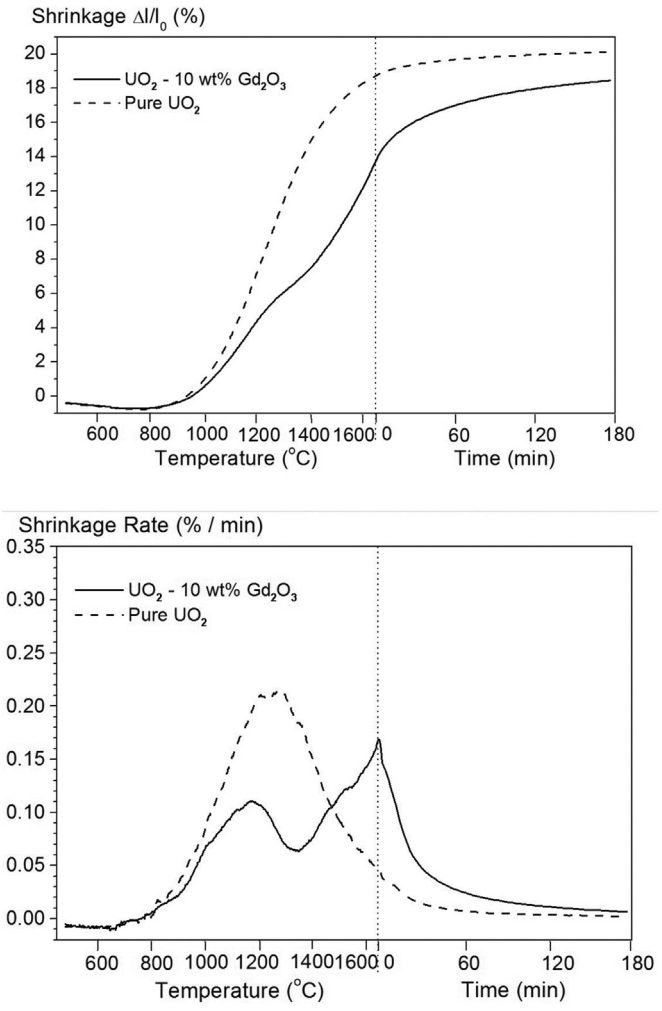


**Fig. 1.** Effect of $Gd_2O_3$ on the sintering behavior of $UO_2$-$Gd_2O_3$ fuel pellets [9].

sintering aid has been demonstrated to be effective for $Gd_2O_3$ additions to the $UO_2$ [8], this work amplified previous studies [13,14] on the effect of $Al(OH)_3$ doping on the sintering of $UO_2$ pellets with combined additions of $Gd_2O_3$ and recycled $U_3O_8$ generated from defective $UO_2$-$Gd_2O_3$ pellets. The objective was to develop $UO_2$-$Gd_2O_3$ burnable poison containing pellets by using the mechanical blending of $Al(OH)_3$ as a sintering aid and $U_3O_8$ from the recycling of scrap.

## 2. Experimental

The process adopted to prepare $UO_2$-$Gd_2O_3$ pellets was through the dry mechanical mixing of $UO_2$ and $Gd_2O_3$ powders, together with densification additive $Al(OH)_3$ and fuel scrap as $U_3O_8$. The concentration of 7 wt% $Gd_2O_3$ was used in order to meet the specification for Angra-2 power plant. The concentrations of $Al(OH)_3$ and $U_3O_8$ as fuel scrap recycled are presented in Table 1. Two types of scrap were utilized in the study, green (GP) and sintered (SP) $UO_2$–$Gd_2O_3$ pellets (7 wt% $Gd_2O_3$). These are the main sources of recycling material in a typical manufacturing process. The $U_3O_8$ was produced by oxidation of scraps at 380 °C during 20 h, according to INB procedures [12].

The physical-chemical characteristics of $UO_2$ powder are typical for the powder derived from the AUC reconversion route [8]. The main impurities and physical characteristics of the $UO_2$ powder are listed in Table 2. The $Gd_2O_3$ powder was supplied by Alfa-Aesar (reference 11290) with purity 99.99%, particle size < 10 μm. The $Al(OH)_3$ was also supplied by Alfa-Aesar (reference 12366).

The mixtures were prepared by using a Tubular Mixer for one hour to guarantee the homogeneity. The mixed powders were pressed under pressure of 400 MPa to produce green pellets 11.3 mm in diameter and about 12.7 mm in height. The green densities varied from 5.5 to 5.7 g/cm$^3$ (50–52% of the $UO_2$ theoretical density, 10.96 g/cm$^3$) and were calculated based on the mass and geometrical shape of the pellets.

The pellets were sintered under commercially pure hydrogen (>99.95%) at 1750 °C during 4 h. Triplicate samples from each testing conditions were sintered. The main characteristics desired for the $UO_2$-$Gd_2O_3$ sintered pellets for use in the Angra-2 Pressurized Water Reactor are presented in Table 3. These were the parameters analyzed in this work.

**Table 1**
Concentration of additives added to the $UO_2$-7wt%$Gd_2O_3$ powder.

| $Al(OH)_3$ (wt%) | $U_3O_8$ (wt%) | |
|---|---|---|
| | GP (recycled green pellets) | SP (recycled sintered pellets) |
| 0 | 0 | 0 |
| | 3 | 3 |
| | 7 | 7 |
| | 10 | 10 |
| 0.10 | 0 | 0 |
| | 3 | 3 |
| | 7 | 7 |
| | 10 | 10 |
| 0.15 | 0 | 0 |
| | 3 | 3 |
| | 7 | 7 |
| | 10 | 10 |
| 0.20 | 0 | 0 |
| | 3 | 3 |
| | 7 | 7 |
| | 10 | 10 |
| 0.25 | 0 | 0 |
| | 3 | 3 |
| | 7 | 7 |
| | 10 | 10 |
| 0.30 | 0 | 0 |
| | 3 | 3 |
| | 7 | 7 |
| | 10 | 10 |

**Table 2**
Physical-chemical characteristics of $UO_2$ powder.

| Impurity | (μg/g) |
|---|---|
| Si | <0.112 |
| Ca | <0.016 |
| Fe | 1.472 ± 0.126 |
| Ni | 0.224 ± 0.053 |
| Zn | <1.223 |
| Cl | <0.50 |
| F | 9.98 ± 1.60 |
| N | 13.42 ± 0.10 |
| C | 163.25 ± 11.57 |
| **Other** | |
| O/U | 2.25 |
| Total U (%) | 87.50 ± 0.50 |
| Bulk Density (g/cm$^3$) | 2.43 ± 0.01 |
| Specific Surface Area (BET) (m$^2$/g) | 5.24 ± 0.16 |
| Average Particle Size (μm) | 10.30 ± 0.71 |

The sintered pellets' density was determined by the immersion method. The method is based on the determination of the pellet volume and the volume of open and closed pores by measurement of the dry mass, the saturated mass and the immersed mass of the samples, according to the ISO 9278 standard [15]. Xylol was used as penetration immersion liquid.

The grain and pore sizes were determined by analyzing sections of the sintered pellets. The sintered pellets were sectioned axially and the sections were ground and polished according to traditional metallographic techniques. One sample of each combination of additive concentration was analyzed. Ten fields of each sample were analyzed. The mean grain size was determined by the linear intercept method (Heyn) according to the ASTM E112 standard [16]. The mean diameters of pores were measured directly from the polished sections of the sample by an image analysis system. The images were obtained with a scanning electron microscope using secondary electrons. Thermal etching was used to distinguish grain boundary. Thermal etching was carried out at 1400 °C for 3 h in a carbon dioxide atmosphere [12].

## 3. Results and discussion

Table 4 presents the results obtained for $UO_2$-7wt%$Gd_2O_3$ pellets with additions of 0, 3, 7 and 10 wt% of fuel scrap recycle. No addition of $Al(OH)_3$ was added to the samples. The specification for density has not been met, which is in agreement with the literature [8] and proved that it is necessary to use a sintering aid when $Gd_2O_3$ is incorporated into the $UO_2$ fuel. Fig. 2 shows that the final density achieved after sintering $UO_2$-7wt%$Gd_2O_3$ pellets without the addition of $Al(OH)_3$ did not meet the minimum specified value. The additions of $U_3O_8$ recycle further decrease the density of the pellets after sintering, even for small amounts of added $U_3O_8$. This behavior was also observed by Song et al. [17] and Yang et al. [18], who concluded that the $UO_2$ pellet density decreases almost linearly with the addition of $U_3O_8$. Fig. 2 also shows that the reduction of the sintered density was more pronounced in the case of the addition of $U_3O_8$ recycled from green pellets.

Fig. 3 shows a scanning electron micrograph illustrating the microstructure of a $UO_2$-7wt%$Gd_2O_3$ pellet in which 10 wt% of $U_3O_8$ SP recycle was added, with no addition of $Al(OH)_3$. A high fraction of large pores can be seen due to the low density achieved after

**Table 3**
Main specifications for the $UO_2$-7wt%$Gd_2O_3$ sintered pellets.

| | |
|---|---|
| density | 9.98–10.28 g/cm$^3$ |
| open porosity | ≤3.0 vol% |
| average grain size | 7 to 35 μm in at least 90% of the cut surface |
| average size of pores | average diameter ≤100 μm in at least 90% of the cut surface |
| resintering | change in density after annealing at 1700 °C during 24 h in a reducing atmosphere shall not be greater than 0.142 g/cm$^3$ |

**Table 4**
Physical characteristics of $UO_2$-7wt%$Gd_2O_3$ sintered pellets without using densification additive Al $(OH)_3$.

| $U_3O_8$ (%) | | density (g/cm$^3$) | open porosity(%) | average pore size (μm) | average grain size (μm) |
|---|---|---|---|---|---|
| SP | GP | | | | |
| 0 | 0 | 9.81 ± 0.02 | 4.02 ± 0.28 | 5.0 ± 4.1 | 4.4 ± 3.0 |
| 3 | – | 9.71 ± 0.02 | 3.64 ± 0.04 | 4.6 ± 3.6 | 4.7 ± 2.8 |
| 7 | – | 9.70 ± 0.01 | 3.74 ± 0.12 | 4.2 ± 3.5 | 3.9 ± 2.6 |
| 10 | – | 9.69 ± 0.00 | 3.78 ± 0.15 | 4.2 ± 3.0 | 4.4 ± 2.9 |
| – | 3 | 9.68 ± 0.01 | 3.89 ± 0.04 | 5.3 ± 4.2 | 4.0 ± 2.8 |
| – | 7 | 9.64 ± 0.01 | 4.17 ± 0.05 | 4.2 ± 3.5 | 4.5 ± 2.9 |
| – | 10 | 9.60 ± 0.01 | 4.55 ± 0.12 | 4.5 ± 3.7 | 4.2 ± 2.8 |

GP - recycled green pellets SP - recycled sintered pellets.

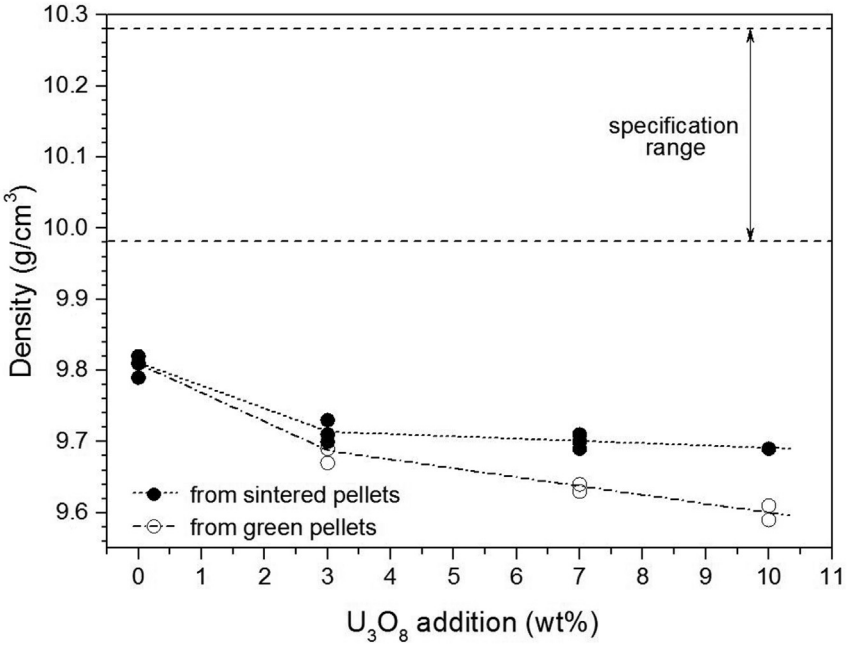


**Fig. 2.** Sintered densities of $UO_2$–7wt%$Gd_2O_3$ pellets with the addition of $U_3O_8$ recycle and no addition of Al$(OH)_3$.

sintering. The average grain size is smaller than the minimum value specified. Yang et al. [18] attributed the small grain size when $U_3O_8$ is added to the $UO_2$ to the presence of grapelike pore clusters that would not only reduce the density but also might act as obstacles to grain boundary migration, so grain growth could be impeded. This should be the cause for inhibiting the grain growth when $U_3O_8$ is added, although the pores were not observed in Fig. 3.

Table 5 presents the results obtained for $UO_2$-7wt%$Gd_2O_3$ pellets in which only Al$(OH)_3$ was added at concentrations of 0.10, 0.15, 0.20, 0.25 and 0.30 wt%. No $U_3O_8$ recycle was added. All $UO_2$-7wt% $Gd_2O_3$ sintered pellets showed physical characteristics in accordance with the specification. The addition of Al$(OH)_3$ promoted the densification in sintering and also the grain growth. Fig. 4 shows that the final density achieved after sintering $UO_2$-7wt%$Gd_2O_3$ pellets with the addition of Al$(OH)_3$ as a sintering aid met the minimum specified value for density. The values fit comfortably within the specified range even for small Al$(OH)_3$ addition, such as 0.10 wt%.

These results are in accordance with the results presented by Assmann et al. [8], where microdoping with 100 ppm of aluminum was enough to get the specified density after sintering $UO_2$-$Gd_2O_3$ pellets with 7 wt% $Gd_2O_3$. The results presented in Fig. 4 showed that only 0.10 wt% of Al$(OH)_3$ (1000 ppm) is enough to meet the specification for the sintered density. This concentration is equivalent to 350 ppm of aluminum. The specification of the minimum density would be met with the addition of 190 ppm of aluminum, as illustrated in the graph. This is in accordance with what was stated by Assmann et al. [8].

Fig. 5 presents dilatometric curves illustrating the sintering behavior of $UO_2$-7wt% $Gd_2O_3$ pellet with the addition of 0.20 wt%

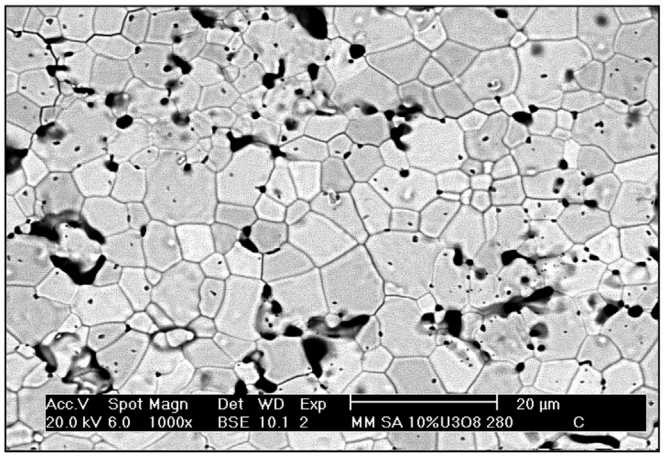


**Fig. 3.** Micrograph illustrating the microstructure of $UO_2$–7wt%$Gd_2O_3$ sintered pellet with the addition of $U_3O_8$ recycle SP and no addition of $Al(OH)_3$.

$Al(OH)_3$, which is the level of addition to achieve maximum densification of the system, as illustrated in Fig. 4. The dilatometric curves for $UO_2$-7wt% $Gd_2O_3$ pellet without $Al(OH)_3$ and for pure $UO_2$ pellet were also presented for comparison. The sintering behavior of $UO_2$-7wt% $Gd_2O_3$ and pure $UO_2$ pellets closely reproduced the results obtained in a previous work [9]. When $Al(OH)_3$ was added to the $UO_2$-7wt% $Gd_2O_3$ pellet, the densification before the abrupt decrease in shrinkage due to the presence of $Gd_2O_3$ (sintering "blockage") was shifted towards lower temperatures, approaching the $UO_2$ curve. This demonstrates that the aluminum acted as a sintering aid.

Previous studies demonstrated that the retardation of shrinkage due to the presence of $Gd_2O_3$ is caused by the formation of pores during sintering. These new pores are formed due to the Kirkendall effect that occurs during the solubilization of gadolinium in the fluorite lattice of $UO_2$ [19]. The aluminum added as dopant also acts after the formation of the new pores due to the Kirkendall effect, recovering the densification in the final stage of sintering. As a result, the new pores would be eliminated and the total shrinkage during sintering approximates that achieved for pure $UO_2$, as illustrated in Fig. 5.

Fig. 6 shows a scanning electron micrograph illustrating the microstructure of a $UO_2$-7wt%$Gd_2O_3$ pellet in which 0.20 wt% of $Al(OH)_3$ was added, with no addition of $U_3O_8$. The average grain size was increased and the pore fraction was decreased compared with the pellet sintered without $Al(OH)_3$ addition (Fig. 3). This behavior is in accordance with other results from literature, which show that aluminum as a dopant improves grain growth in sintered $UO_2$ pellets, as well as other dopants such as $Nb_2O_5$ [18,20,21]. The microstructure is comparable to the microstructure of a typical pure ex-AUC $UO_2$ sintered pellet (Fig. 7) but with a slightly larger grain size.

Table 6 Presents the results obtained for sintered $UO_2$-7wt% $Gd_2O_3$ pellets where the combined effects of both additives $Al(OH)_3$

**Table 5**
Physical characteristics of $UO_2$–7wt%$Gd_2O_3$ sintered pellets using $Al(OH)_3$ additive, without using $U_3O_8$ recycle.

| $Al(OH)_3$ (%) | density ($g/cm^3$) | open porosity (%) | average pore size (µm) | average grain size (µm) |
|---|---|---|---|---|
| 0.10 | 10.12 ± 0.02 | 0.20 ± 0.22 | 4.5 ± 3.7 | 10.0 ± 8.4 |
| 0.15 | 10.13 ± 0.03 | 0.11 ± 0.06 | 5.2 ± 4.1 | 8.6 ± 6.4 |
| 0.20 | 10.18 ± 0.03 | 0.15 ± 0.09 | 4.9 ± 4.4 | 10.4 ± 6.8 |
| 0.25 | 10.17 ± 0.02 | 0.20 ± 0.16 | 5.9 ± 4.3 | 10.9 ± 8.0 |
| 0.30 | 10.17 ± 0.02 | 0.20 ± 0.09 | 5.3 ± 4.9 | 9.9 ± 9.1 |

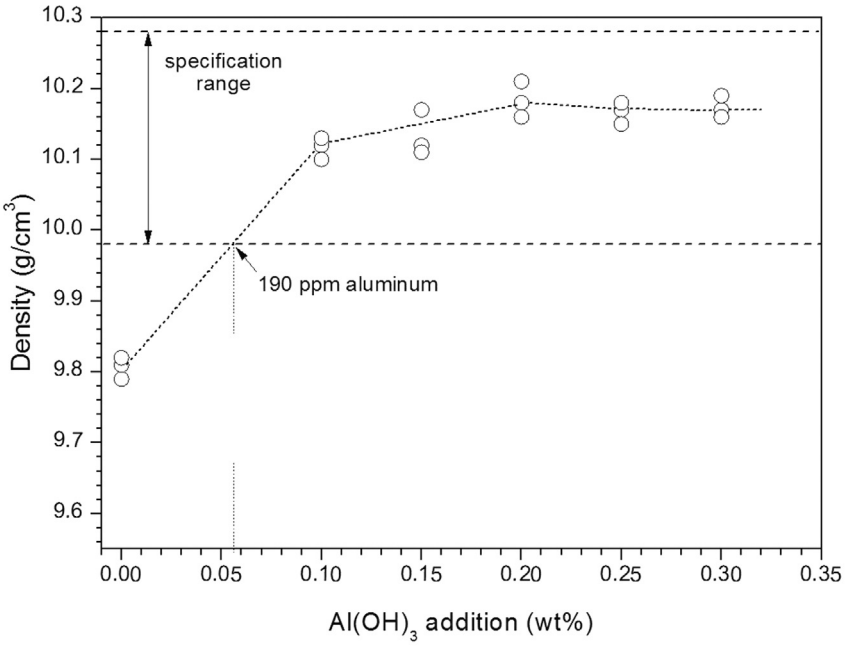


**Fig. 4.** Sintered densities of $UO_2$–7wt%$Gd_2O_3$ pellets with the addition of $Al(OH)_3$ and no addition of $U_3O_8$ recycle.

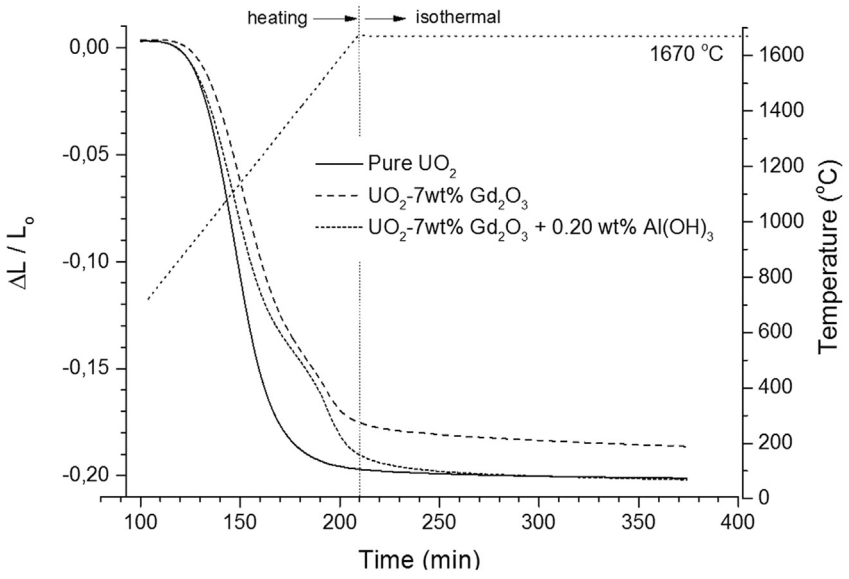


**Fig. 5.** Effect of $Al(OH)_3$ on the sintering behavior of $UO_2$–7wt%$Gd_2O_3$ pellets.

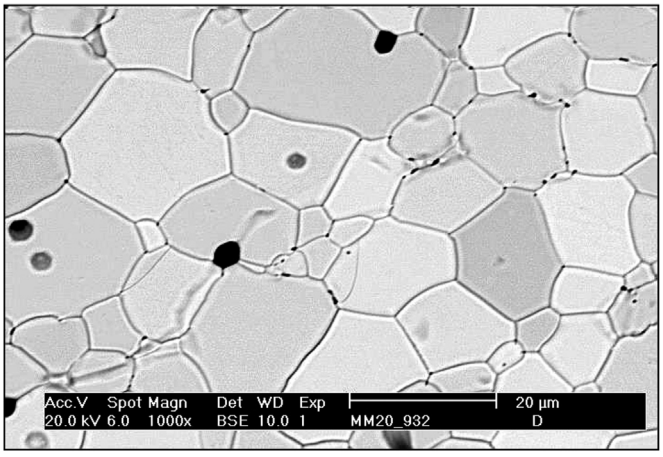


**Fig. 6.** Micrograph illustrating the microstructure of $UO_2$-7wt%$Gd_2O_3$ sintered pellet with addition of 0.20 wt% $Al(OH)_3$ and no addition of $U_3O_8$ recycle.

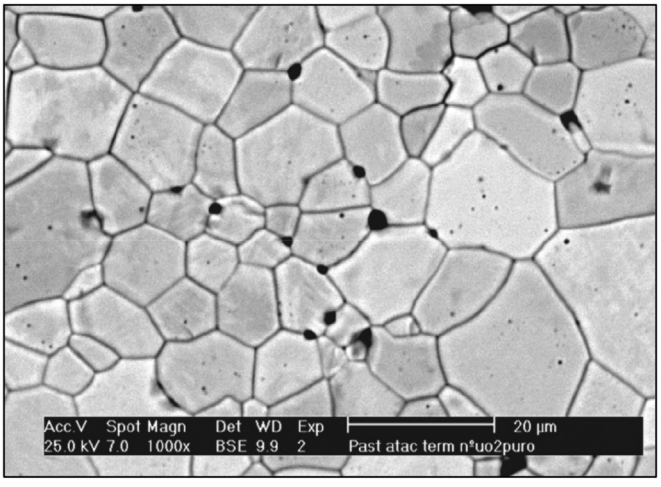


**Fig. 7.** Micrograph illustrating the typical microstructure of ex-AUC $UO_2$ sintered pellet.

and $U_3O_8$ recycled from sintered pellets (SP) were evaluated.

It can be noted that the effects of the additives seem to be independent. The addition of $Al(OH)_3$ sufficiently increased the sintered density of $UO_2$-7wt%$Gd_2O_3$ for all levels of $U_3O_8$ additions. The specification for the density of all sintered pellets containing $U_3O_8$ recycle SP was met. A general lowering of the sintered densities was observed when $U_3O_8$ was added to the pellets doped with $Al(OH)_3$. Fig. 8 better illustrated this effect. The curves showed that the increasing of $U_3O_8$ concentration causes a decrease in the sintered density for all levels of $Al(OH)_3$ additions. For $Al(OH)_3$ additions higher than 0.20 wt%, the sintered densities tend to decrease for all concentrations of $U_3O_8$ added. For high $U_3O_8$ additions (7 and 10 wt%) and high addition of $Al(OH)_3$ (0.30 wt%), the sintered densities tend to decrease close to the minimum specified value. The highest densities were achieved for 0.20 wt% of $Al(OH)_3$ addition. For this level of $Al(OH)_3$ addition the density after sintering was placed comfortably within the specification range even for high concentrations of $U_3O_8$ added. Also, when 0.20 wt% of $Al(OH)_3$ was used as a sintering aid at the same time as $U_3O_8$ recycled from sintered pellets is added, the open porosity is lower than the maximum specified and the average grain size is higher than the minimum specified.

Fig. 9 illustrates the microstructure of a $UO_2$-7wt%$Gd_2O_3$ pellet with additions of both $Al(OH)_3$ and $U_3O_8$ from sintered pellets (SP). The grain growth is expected with aluminum additions [18,20,21], even with the presence of $Gd_2O_3$ and $U_3O_8$, as can be seen in the microstructure. The microstructure shows regions with the grapelike pore clusters reported by Yang et al. [18], which would explain the lower sintered density when compared with the density achieved for pellets without $U_3O_8$ additions. A possible mechanism to explain the presence of the grapelike pore clusters could be the presence of $U_3O_8$ as agglomerates in the $UO_2$ powder after homogenization. After the reduction of $U_3O_8$ to $UO_2$ during the sintering cycle, these agglomerates would form a cluster of pores in a region where $UO_2$ would have low activity, which would make it difficult to eliminate this type of pores.

Table 7 presents the results obtained for sintered $UO_2$-7wt% $Gd_2O_3$ pellets where the effects of $U_3O_8$ recycled from green pellets (GP) were evaluated. The results were similar to the results obtained from $U_3O_8$ recycled from sintered pellets (SP). However, when the added $U_3O_8$ is recycled from green pellets, the density

**Table 6**
Physical characteristics of $UO_2$-7wt%$Gd_2O_3$ sintered pellets using $Al(OH)_3$ and $U_3O_8$ recycled from sintered pellets (SP).

| composition | | density (g/cm$^3$) | open porosity (%) | average pore size (μm) | average grain size (μm) |
|---|---|---|---|---|---|
| $Al(OH)_3$ (wt%) | $U_3O_8$ - SP (wt%) | | | | |
| 0.10 | 3 | 10.08 ± 0.02 | 0.21 ± 0.11 | 4.4 ± 3.6 | 9.3 ± 7.6 |
| | 7 | 10.07 ± 0.01 | 0.16 ± 0.06 | 4.3 ± 3.6 | 8.9 ± 7.6 |
| | 10 | 10.05 ± 0.02 | 0.14 ± 0.05 | 4.6 ± 3.8 | 8.5 ± 7.7 |
| 0.15 | 3 | 10.11 ± 0.02 | 0.16 ± 0.06 | 5.1 ± 4.1 | 7.8 ± 6.1 |
| | 7 | 10.10 ± 0.05 | 0.12 ± 0.06 | 5.2 ± 3.9 | 8.9 ± 9.3 |
| | 10 | 10.05 ± 0.06 | 0.48 ± 0.63 | 5.1 ± 4.0 | 8.5 ± 6.0 |
| 0.20 | 3 | 10.14 ± 0.01 | 0.17 ± 0.07 | 4.9 ± 4.6 | 9.5 ± 7.0 |
| | 7 | 10.12 ± 0.05 | 0.12 ± 0.03 | 5.1 ± 4.6 | 9.3 ± 6.4 |
| | 10 | 10.09 ± 0.02 | 0.14 ± 0.07 | 5.2 ± 4.5 | 9.6 ± 6.7 |
| 0.25 | 3 | 10.11 ± 0.02 | 0.19 ± 0.07 | 6.1 ± 4.6 | 10.4 ± 8.2 |
| | 7 | 10.08 ± 0.02 | 0.33 ± 0.17 | 5.9 ± 4.4 | 9.7 ± 7.9 |
| | 10 | 10.07 ± 0.03 | 0.12 ± 0.04 | 5.9 ± 4.4 | 10.6 ± 7.8 |
| 0.30 | 3 | 10.07 ± 0.06 | 0.13 ± 0.01 | 4.9 ± 4.5 | 9.5 ± 7.2 |
| | 7 | 10.03 ± 0.04 | 0.21 ± 0.18 | 5.2 ± 4.6 | 8.5 ± 6.3 |
| | 10 | 10.03 ± 0.03 | 0.35 ± 0.13 | 6.3 ± 6.4 | 9.4 ± 5.4 |

SP - recycled from sintered pellets.

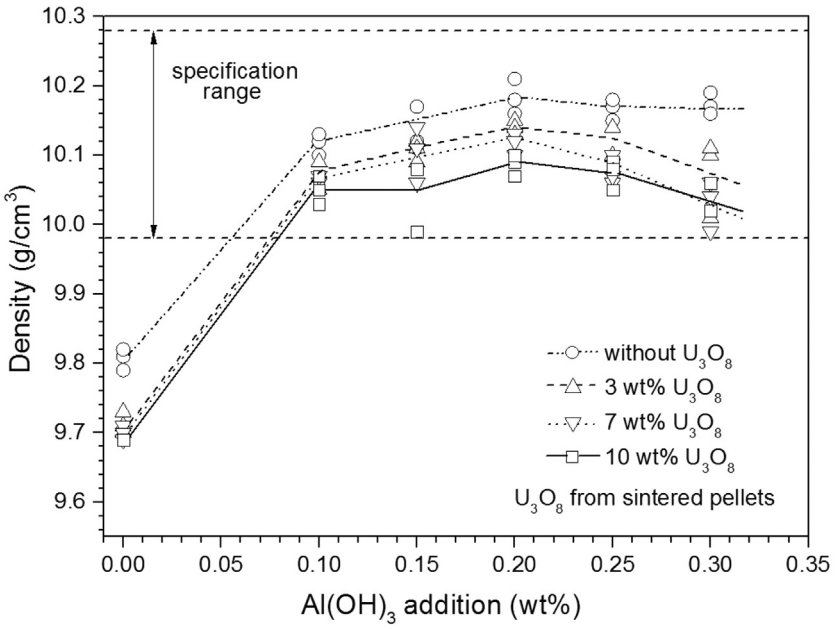


**Fig. 8.** Sintered densities of $UO_2$-7wt%$Gd_2O_3$ pellets with addition of $Al(OH)_3$ and $U_3O_8$ recycled from sintered pellets.

decreasing is more accentuated for high $U_3O_8$ concentrations (7 and 10 wt%) and for low (0.10 wt%) and high (0.30 wt%) $Al(OH)_3$ additions. Fig. 10 illustrates these results. For intermediate additions of $Al(OH)_3$ (0.15–0.25 wt%) the densities of the sintered pellets were within the specified range.

The effects of the addition of $U_3O_8$ prepared from green (GP) and sintered (SP) pellets were similar. However, when the recycled $U_3O_8$ powder comes from green pellets, lower densities after sintering were observed for small additions of $Al(OH)_3$ (0.10 wt%). This could indicate that the amount of aluminum added was insufficient to improve the sintering of the system to compensate for the decrease in sintering caused by the addition of $U_3O_8$ from green pellets. An unexpected increase in dispersion of the results obtained for high concentrations of $U_3O_8$ (10 wt%) and $Al(OH)_3$ (0.30 wt%) was also observed. These observations could be related to the pore structure revealed by the microstructures. In general, a larger number of regions with grapelike pore clusters were observed, as illustrated in Fig. 11. Also, some regions with grapelike pore clusters were too large, as illustrated in Fig. 12. The pore structures suggest that high quantity of agglomerates were present when $U_3O_8$ from green pellets was added to the $UO_2$ powder. In addition, the size of $U_3O_8$ agglomerates from green pellets would be larger than the agglomerates from sintered pellets. This could be explained by a higher tendency to agglomerate for the $U_3O_8$ powder prepared from green pellets or by a higher resistance of these agglomerates to be disaggregated in the homogenization with $UO_2$ powder.

Fig. 13 presents dilatometric curves illustrating the sintering behavior of $UO_2$-7wt% $Gd_2O_3$ pellet with additions of 0.20 wt% $Al(OH)_3$ and 7 wt% of $U_3O_8$ prepared from both sintered and green pellets. All the sintering curves were very similar, including the curve for the pellet without the addition of $U_3O_8$. This shows that the presence of $U_3O_8$ did not alter the mechanism related to the presence of $Gd_2O_3$ and the role of aluminum in this mechanism.

The resintering test consists of subjecting the pellets to high temperature for a long time aiming to simulate the shrinkage

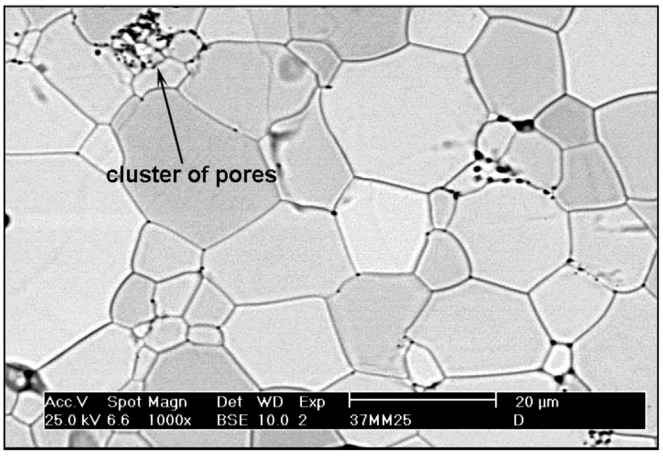


**Fig. 9.** Micrograph illustrating the microstructure of $UO_2$-7wt%$Gd_2O_3$ sintered pellet with the addition of 0.20 wt% $Al(OH)_3$ and 7 wt% of $U_3O_8$ recycled from sintered pellets (SP).

during operation in the reactor core. The analysis is made by measuring the variation of the density of the sintered pellet after the resintering test. The test was performed at a temperature of 1720 °C for 24 h in a reducing atmosphere. The increase in density after resintering is expected to be less than 0.142 g/cm$^3$, as recommended for the fuel to be used in the Angra-2 power reactor. Due to the experimental limitation in view of the high temperature of the resintering test and the long residence time at that temperature, only one sample was submitted to this test.

The resintering test was conducted using all the concentrations of the two types of $U_3O_8$ recycle (3, 7 and 10 wt%/SP and GP) combined with the concentration of 0.20 wt% $Al(OH)_3$. For the other concentrations of $Al(OH)_3$ (0.10, 0.15, 0.25 and 0.30 wt%), the concentration of $U_3O_8$ was fixed in 7 wt% for each type of $U_3O_8$ recycle (SP and GP). Table 8 presents the results obtained with the resintering test. The results showed that the densities measured after the resintering test were very close to the densities of the pellets before the test. The maximum variation was 0.04 g/cm$^3$, well below the maximum recommended variation of 0.142 g/cm$^3$.

**Table 7**
Physical characteristics of $UO_2$–7wt%$Gd_2O_3$ sintered pellets using $Al(OH)_3$ and $U_3O_8$ recycled from green pellets (GP).

| composition | | density (g/cm$^3$) | open porosity (%) | average pore size (µm) | average grain size (µm) |
|---|---|---|---|---|---|
| $Al(OH)_3$ (wt%) | $U_3O_8$ - GP (wt%) | | | | |
| 0.10 | 3 | 10.07 ± 0.01 | 0.18 ± 0.15 | 4.6 ± 4.2 | 9.8 ± 8.2 |
| | 7 | 10.00 ± 0.03 | 0.27 ± 0.06 | 4.7 ± 4.2 | 9.2 ± 7.3 |
| | 10 | 9.94 ± 0.02 | 0.69 ± 0.16 | 4.7 ± 4.0 | 8.7 ± 6.7 |
| 0.15 | 3 | 10.10 ± 0.02 | 0.33 ± 0.25 | 5.2 ± 4.2 | 8.9 ± 5.9 |
| | 7 | 10.08 ± 0.02 | 0.20 ± 0.07 | 5.0 ± 4.0 | 9.2 ± 6.0 |
| | 10 | 10.07 ± 0.02 | 0.16 ± 0.04 | 4.8 ± 4.0 | 9.1 ± 6.0 |
| 0.20 | 3 | 10.16 ± 0.01 | 0.15 ± 0.02 | 5.3 ± 4.9 | 10.3 ± 7.0 |
| | 7 | 10.15 ± 0.02 | 0.24 ± 0.08 | 5.9 ± 4.8 | 9.0 ± 6.9 |
| | 10 | 10.14 ± 0.04 | 0.20 ± 0.16 | 5.1 ± 4.1 | 8.0 ± 6.0 |
| 0.25 | 3 | 10.15 ± 0.03 | 0.15 ± 0.10 | 6.0 ± 4.5 | 10.8 ± 8.1 |
| | 7 | 10.11 ± 0.02 | 0.32 ± 0.05 | 5.9 ± 4.7 | 10.4 ± 8.1 |
| | 10 | 10.10 ± 0.01 | 0.18 ± 0.02 | 6.0 ± 4.5 | 10.6 ± 7.7 |
| 0.30 | 3 | 10.14 ± 0.03 | 0.17 ± 0.16 | 4.4 ± 3.6 | 8.4 ± 6.4 |
| | 7 | 10.09 ± 0.01 | 0.24 ± 0.07 | 6.5 ± 5.7 | 8.2 ± 7.0 |
| | 10 | 9.94 ± 0.12 | 0.42 ± 0.21 | 6.3 ± 4.9 | 7.6 ± 5.8 |

GP - recycled from green pellets.

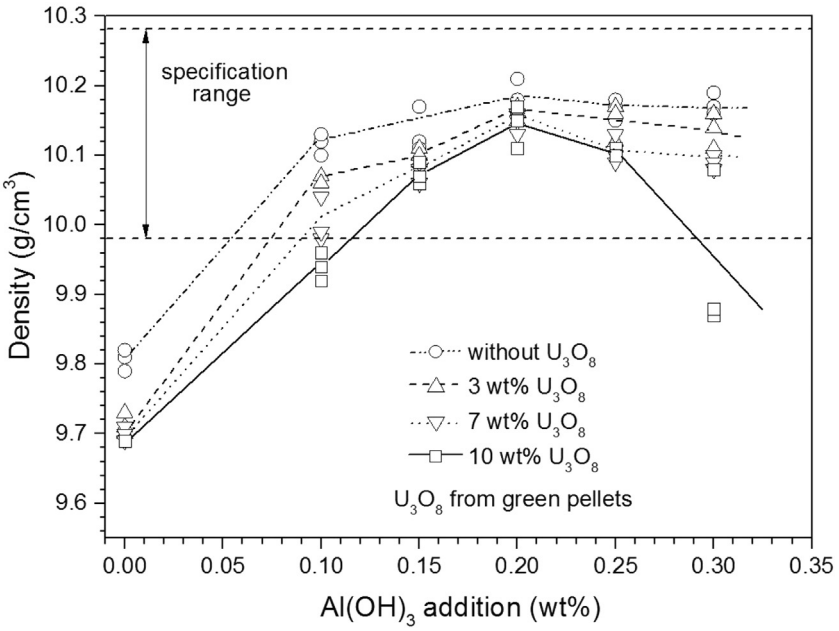


**Fig. 10.** Sintered densities of $UO_2$-7wt%$Gd_2O_3$ pellets with the addition of $Al(OH)_3$ and $U_3O_8$ recycled from green pellets.

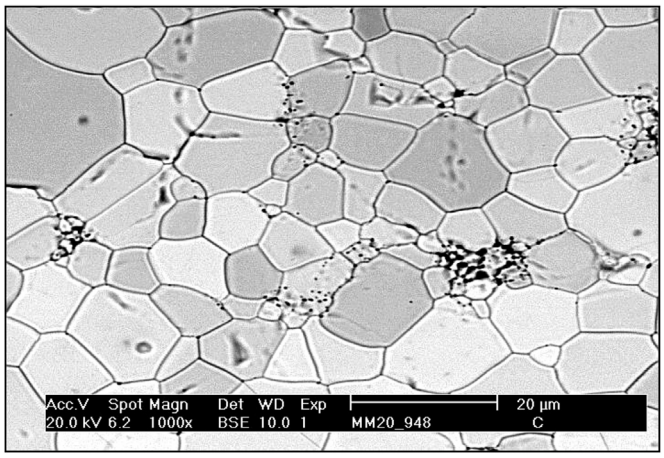


**Fig. 11.** Micrograph illustrating the microstructure of $UO_2$-7wt%$Gd_2O_3$ sintered pellet with the addition of 0.20 wt% $Al(OH)_3$ and 7 wt% of $U_3O_8$ recycled from green pellets (GP). Many grapelike pore clusters regions can be seen.

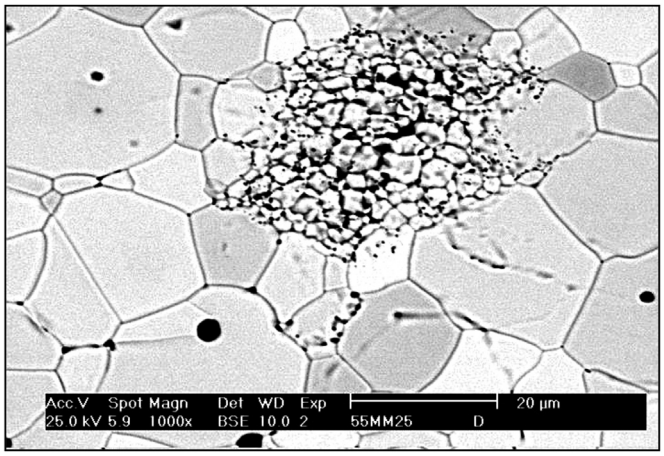


**Fig. 12.** Micrograph illustrating the microstructure of $UO_2$-7wt%$Gd_2O_3$ sintered pellet with the addition of 0.30 wt% $Al(OH)_3$ and 10 wt% of $U_3O_8$ recycled from green pellets (GP). Large size grapelike pore clusters region can be seen.

**Table 8**
Density variation for $UO_2$-7wt%$Gd_2O_3$ sintered pellets after resintering.

| $Al(OH)_3$ (wt%) | $U_3O_8$ (wt%) | | sintered density ($g/cm^3$) | resintered density ($g/cm^3$) | density variation ($g/cm^3$) |
|---|---|---|---|---|---|
| | SP | GP | | | |
| 0.10 | 7 | – | 10.07 | 10.09 | 0.02 |
| 0.10 | – | 7 | 9.99 | 10.00 | 0.01 |
| 0.15 | 7 | – | 10.11 | 10.11 | 0.00 |
| 0.15 | – | 7 | 10.08 | 10.09 | 0.01 |
| 0.20 | no U3O8 addition | | 10.18 | 10.18 | 0.00 |
| 0.20 | 3 | – | 10.14 | 10.16 | 0.02 |
| 0.20 | 7 | – | 10.12 | 10.12 | 0.00 |
| 0.20 | 10 | – | 10.09 | 10.11 | 0.02 |
| 0.20 | – | 3 | 10.15 | 10.16 | 0.01 |
| 0.20 | – | 7 | 10.13 | 10.14 | 0.01 |
| 0.20 | – | 10 | 10.18 | 10.18 | 0.00 |
| 0.25 | 7 | – | 10.06 | 10.10 | 0.04 |
| 0.25 | – | 7 | 10.09 | 10.13 | 0.04 |
| 0.30 | 7 | – | 10.04 | 10.07 | 0.03 |
| 0.30 | – | 7 | 10.10 | 10.13 | 0.03 |

## 4. Conclusions

The experimental results showed the effectiveness of the $Al(OH)_3$ as an additive to promote the increase in the densification of the $(U.Gd)O_2$ pellets during sintering. It was found that the addition of $Al(OH)_3$ is essential to reach the desired density and open porosity. By using additions between 0.15 and 0.25 wt% $Al(OH)_3$, all the recommended features of the $UO_2$-7wt%$Gd_2O_3$ sintered pellets were achieved. The densities after sintering fit comfortably within the desired range even for $U_3O_8$ additions as large as 10 wt%. Furthermore, the open porosity, as well as the average size of pores, has complied with the recommendations for the fuel for the Angra-2 power reactor. This is valid for $U_3O_8$ recycled from both green and sintered $UO_2$-7wt%$Gd_2O_3$ defective pellets.

Regarding the average grain size, considering the values obtained and the error associated with them, it cannot be safely concluded that the recommendation for Angra-2 fuel was met. A complementary work regarding the dependence of grain size on the additives studied in this work is necessary.

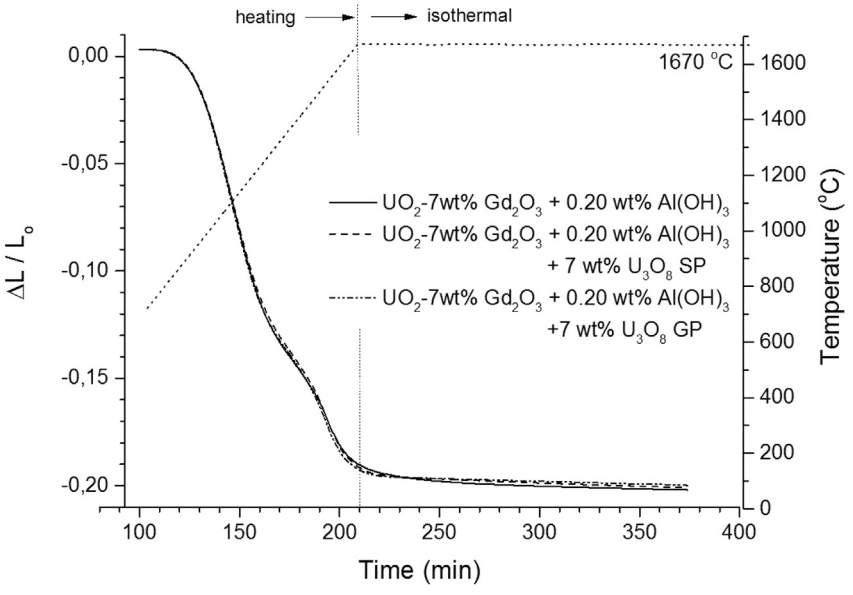


**Fig. 13.** Effect of $U_3O_8$ on the sintering behavior of $UO_2$–7wt%$Gd_2O_3$ pellets doped with 0.20 wt% $Al(OH)_3$.

From the observations from the experimental sintering curves, it can be inferred that the aluminum acts in the sintering process both before and after pore formation due to the Kirkendall effect, which occurs when the gadolinium is solubilized in the fluorite lattice of $UO_2$. When aluminum is added, the densification before the gadolinium solubilization is shifted towards lower temperatures, approaching the $UO_2$ curve. After the formation of the new pores due to the Kirkendall effect, the aluminum acts recovering the densification in the final stage of sintering. The experimental results also showed that the presence of $U_3O_8$ does not alter the mechanism related to the presence of $Gd_2O_3$ and the role of aluminum in this mechanism. The sintering curves are very similar and the decrease in shrinkage during sintering due to the presence of $U_3O_8$ is negligible.

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