ABSTRACT

The use of gadolinium and uranium mixed oxide as a nuclear fuel aims to obtain a fuel with a performance better than that of UO\textsubscript{2} fuel. In this work, seeding method was used to improve ionic diffusity during sintering to produce high density pellets containing coarse grains by co-precipitation and mechanical mixing processes. Sintered UO\textsubscript{2}-10wt\% Gd\textsubscript{2}O\textsubscript{3} pellets were obtained using the reference processes with 2wt\% and 5wt\% UO\textsubscript{2} seeds with two granulometries, less than 20 µm and between 20 and 38 µm. Characterisation was carried out by chemical analysis, surface area, X-ray diffraction, SEM, WDS, image analysis, and densitometry. The seeding method using mechanical mixing process was more effective than the co-precipitation method. Furthermore, mechanical mixing process resulted in an increase in density of UO\textsubscript{2}-10wt\% Gd\textsubscript{2}O\textsubscript{3} with seeds in relation to that of UO\textsubscript{2}-10wt\% Gd\textsubscript{2}O\textsubscript{3} without seeds.

Key words: seeding, grain size, AUC Co-precipitation, (U,Gd)O\textsubscript{2} nuclear fuel
I. INTRODUCTION

The use of gadolinium and uranium mixed oxide as a nuclear fuel aims to obtain a fuel with a performance better than that of UO₂ fuel. Gadolinium, a burnable absorber, presents many advantages when used as a part of a nuclear fuel. One of the most important advantages is that gadolinium has a high neutron absorption cross section and presents a better efficiency than boron does at the beginning of the burning cycle. Among other advantages, the use of gadolinium extends fuel cycles, increases burnup, and optimizes power density distribution.

In the study of (U,Gd)O₂ fuel development by powder mechanical mixing and co-precipitation processes, Lima’s¹ and ² results showed that the (U,Gd)O₂ pellet density only reached the project density of 95% of the theoretical solid solution density (U,Gd)O₂ for 2% Gd₂O₃ weight composition. For the most used compositions, those with contents of 5 and 10% Gd₂O₃, the densities obtained were below specification. The best results were obtained with uranium and gadolinium co-precipitation experiments. In fact, in this case, it was obtained high densities, between 91 and 93 TD%; however, they are still insufficient for PWR reactor use. Furthermore, another adverse result was that the (U,Gd)O₂ pellets grain size was smaller than 8-12 µm, which is commonly obtained for UO₂ pellets³. The literature⁴ and ⁵ mentions that large grains reduce the release of fission gaseous products and thus enhance the fuel performance.

There are many different processes to obtain denser and coarser grains in (U,Gd)O₂ matrix such as the use of dopants, high temperatures, and long processing times⁶⁻¹¹. However, these techniques are expensive. Although each of these processes may produce fuels containing gadolinium with high densities and large grains, production considerations may prevail over their benefits. In this work, it was chosen the study by seeding aiming at promoting grain growth and raising densification. There is a large number of publications on non-nuclear ceramics obtained by seeding¹²⁻¹⁶.

In the nuclear material field, two recent works report the development of a simple UO₂ matrix by seeding aiming to promote grain growth³ and ¹². Densification was not analyzed since the wanted UO₂ matrix density is easily obtainable. In this seeding technique, it was used only direct physical mixing of UO₂ powders and seeds. Other alternatives such as the largely used non-nuclear ceramic matrices were not explored¹²⁻¹⁶. It was sought to apply this innovative development to the uranium oxide matrix containing gadolinium in an attempt to improve densification and simultaneously afford UO₂-10%Gd₂O₃ fuel grain growth. The seeds were obtained from sintered UO₂ pellets produced by the AUC process. The co-precipitation and mechanical mixing processes were used as references. Sintered UO₂-10wt% Gd₂O₃ pellets
were obtained using the reference processes with 2wt% and 5wt% UO$_2$ seeds with two granulometries, less than 20 µm and between 20 and 38 µm. The results of the two processes are discussed in this work and compared to those of UO$_2$-10wt% Gd$_2$O$_3$ without seeds$^{1-3}$.

II. LITERATURE REVIEW

Sintered nuclear fuel pellet production from powders obtained by precipitation and co-precipitation are described, as well as the seeding technique.

II.1. Production of UO$_2$-xGd$_2$O$_3$ Powder by Co-precipitation Process

Co-precipitation and the production of UO$_2$-xGd$_2$O$_3$ powder by co-precipitation of ammonium tricarbonate containing uranium and gadolinium is carried out similarly to the precipitation of ammonium tricarbonate containing uranium (AUC) to obtain UO$_2$. For such, it is only necessary to add gadolinium to the AUC solution as a salt in solution. The resulting solution is co-precipitated as an ammonium tricarbonate compound containing uranium and gadolinium$^{1, 3, 7, 10, 11, 17, 17$ and $18}$.

It is known that nuclear ceramic oxide powders, UO$_2$, reach high density, around 95% of the theoretical value, during sintering in neutral or oxidizing atmosphere. This density is obtained at temperatures 300 to 400 °C lower than those used in sintering in reducing atmosphere. Dörre’s$^{19}$ sintering kinetics study revealed that densification in oxidizing atmosphere is larger than in reducing atmosphere is, since the uranium diffusivity in the network is larger due to the larger concentration of vacancy defects in the UO$_2$ network under sintering in oxidizing atmosphere$^{1, 3, 7-9, 11, 18 and 19}$.

The greatest difficulty in sintering UO$_2$ at low temperatures is that the product is not stoichiometric, unless hydrogen reduction stage is introduced during cooling. Due to the fuel behaviour under irradiation in the power reactor, the nuclear oxide fuel pellets must be stoichiometric$^{1-3, 7-9, 11, 18 and 20-23}$.

The UO$_2$-xGd$_2$O$_3$ pellet sintering steps are similar to those of UO$_2$ pellets. Only recently have UO$_2$-xGd$_2$O$_3$ sintered pellet kinetics been studied more systematically. These investigations have been carried out with samples obtained by mechanical mixing. Studies to investigate the sintering kinetics and mechanisms more closely using pellets produced by co-precipitation process are recent$^{1, 3, 7, 9, 11 and 21}$.

The investigations show that the solid (U,Gd)O$_2$ solution densification rate is influenced both by the sintering atmosphere and the Gd$_2$O$_3$ content in the solid solution. The UO$_2$ pellet densification increases with the increase in the oxygen potential in the sintering atmosphere,
while the densification of UO$_2$-xGd$_2$O$_3$ pellets sintered in oxidizing atmosphere in the intermediate and final step was delayed, comparatively to that of UO$_2$ pellets. According to Yuda$^7$, the final density of UO$_2$-xGd$_2$O$_3$ pellets sintered at high temperatures (~1700 °C/2 h) is lower than that of UO$_2$. The same experiments showed that the density values of UO$_2$-xGd$_2$O$_3$ pellets sintered in oxidizing atmosphere were due to the formation of large closed pores generated by non-uniform local volumetric changes resulting from the different densification rates of the reactions between the UO$_2$ and de Gd$_2$O$_3$ powder particles. Obviously, due to the microstructure homogeneity, the densification rates of pellets obtained by co-precipitation must diverge significantly in relation to those due associated to the mechanical mixing.

II.2. Seeding technique

The seeding process parameters define the microstructure and it directly influences the material properties. The grain structure has a strong influence on the pellet and coating interaction mechanisms: small grains contribute to a large release of fission products, while large grains reduce the fuel plasticity; therefore, its structure must be well controlled. Large nuclear fuel pellet grains, 20-25 $\mu$m$^{20}$, perform better in operation. Large grains may be obtained by several processes: at high temperatures, with long sintering time, and in oxidizing atmosphere either with or without dopant. The two first methods affect the process economy and productivity, while the use of dopants introduces impurities. The use of oxidizing atmosphere requires special ovens that are difficult to adapt for industrial use$^{20-24}$.

The seeding technique consists in providing formed nuclei so that the energy spent to form them is transferred to the nucleus growth process. In this way, the presence of nuclei affects the transformation kinetics favourably and reduces the sintering temperature$^{20-24}$.

Seeding makes it possible to obtain large grain sizes without the addition of impurities and without changing the industrial nuclear fuel production technology. Another advantage of the use of UO$_2$ as a seed is the possibility of using nuclear industry wastes, since the seeds have the same chemical composition as that of the pellets used in the industry. In seeding, it is important to select the proper particle size and amount of seeds to be added to the mixture to obtain pellets with large grains in the appropriate size. As previously said, the appropriate grain size for nuclear application is 20-25 $\mu$m$^{20}$ and the seed amount more commonly used ranges from 2 to 5% weight of the pellet chemical composition. Amounts lower than 1% weight are also used$^{5, 12, 13, 24}$. Seeds in the form of crystals and with appropriate sizes may be added in two ways: in the powder homogenization stage and in the liquid reagent homogenization stage of the chemical process of production of the powders$^{2, 5, 20-24}$.
III. EXPERIMENTAL METHOD

Sintered UO$_2$-10wt% Gd$_2$O$_3$ fuel pellets were obtained using the co-precipitation and mechanical mixing processes with 2wt% and 5wt% UO$_2$ seeds with two granulometries, less than 20 µm and between 20 and 38 µm.

Seeds were obtained from sintered pellets produced by precipitation process after milling in agate mortar and classification by sieving$^{15, 20-24}$. The seeds were sieved under absolute purity ethyl alcohol and afterwards dried in oven at 80 °C for 24 h.

The reactants used in the co-precipitation process were uranyl hexahydrated nitrate, gadolinium hexahydrated nitrate with 99.9% purity (from Aldrich Chemical Company, Inc), ammonium carbonate (absolute purity product from ECIBRA), deionized water, and seeds. The seeds, hexahydrated uranyl and hexahydrated gadolinium nitrates and the reaction water were added to a volumetric balloon. Ammonium carbonate diluted in 1 L deionized water was dripped into the ballon. Then, the solution was mechanically agitated for 1 h at 60 °C. The precipitates were filtered in vacuum, washed with absolute purity ethyl alcohol, and dried in oven in the temperature range from 40 to 50 °C for 21 h. This reactant addition order was different from the one used in previous works by Lima$^1$ and$^2$ because of the addition of the seeds.

Calcination was performed in air at 450 °C for 12 h. The powders were reduced at 600 °C in a chamber under rotation at 12 rpm in commercial H$_2$ atmosphere for 4 h, followed by passivation in CO$_2$ atmosphere during cooling down to room temperature.

For mechanical mixing, it was used the UO$_2$ powder from the AUC precipitation process and Gd$_2$O$_3$ powder, purity 99.9%, from Merck. The powders were homogenized in a rotating Ronrad mixer. First, the powders were homogenized in the proportion of 1:1 in order to obtain a master mixture. After that, a quantity of UO$_2$ mass equal to that of the master mixture was added and homogenized again. This process was repeated until the target concentrations$^{1, 2, 8, 11}$ and$^{18}$ were obtained. The powders were homogenized five times. The powders were mixed for 30 min under rotation each time. The total powder homogenization time for each mixture was 2:30 h.

To determine the specific surface area of the powders (BET method), it was used a NOVA 2200 apparatus from Quantachrome Corporation.

The green pellets were compacted using a double action hydraulic press from CIOLA with compaction pressures of 30, 40, and 50 KN/cm$^2$. It was used a powder mass of 6 g and the green pellets obtained had a diameter of 9 mm. Three pellets were made for each working condition.

Sintering was carried out in pure hydrogen atmosphere at 1700 °C for 3 h at 5 °C/min heating rate and 67 °C/min cooling rate.
The morphological characterization of co-precipitation process powders, seeds and of the microstructure of the sintered pellets obtained by the two processes was carried out using a scanning electronic microscope, JSM-840C.

The chemical analyses were made using X-ray energy spectrometry (Kevex).

The ceramography of the sintered pellets was made by grinding and polishing.

Powder and sintered pellets phase was characterized by X-ray diffraction analysis. The UO₂ powder obtained by precipitation process and the as-obtained Gd₂O₃ powder (from Merk) were used as references. The same working conditions were used in all trials, 0.05º pass and 25 s counting time. These trials were carried out using a semi-automatic X-ray diffractometer, Rigaku, Geigerflex model, with graphite curve crystal monochromator and a CuKα X-ray tube.

The sintered pellet density was measured by xylol penetration and immersion method. For the two processes, EDS and WDS analyses were made using an electronic microprobe, JEOL JXA-8690RL, in order to investigate the chemical composition homogeneity through the polished surfaces of sintered pellets obtained with 50 KN/cm² compaction pressure.

Thermal etching was carried out to show the sintered fuel pellets grains. Working conditions: CO₂ atmosphere at 1250 °C for 1 h and N₂ heating and cooling atmosphere.

Grain diameter was measured by image analysis using the Quantikov software. Six fields were analyzed by working condition, totaling 250 fields for the fuel pellets obtained with 50kN/cm² compaction pressure.

IV. RESULTS AND DISCUSSIONS

IV.1. Seed and powder Characterizations

Figs. 1 (a) and (b) present the UO₂ seed aspect. It shows the presence of pores, which certainly influences the density of the final products. In Fig. 1 (a), it can be noted a large amount of particles with sizes smaller than 20 µm and fewer with sizes close to 20 µm. These results are due to the larger efficiency of the agate mortar grinding in the production of fine particles. The very fine material, smaller than 10 µm, is considered too small to generate large recrystallized grains. In the granulometric range of (20-38) µm, Fig. 1 (b), the particle sizes are quite close.

The BET surface area analysis of the seeds shows that those smaller than 20 µm and between 20 and 38 µm gave results of 1.4616 m²/g and 0.1843 m²/g, respectively. These data are in agreement with those in the literature as sintered UO₂ pellets present very low surface area values. It is observed that for granulometry smaller than 20 µm, the specific surface value is slightly larger, which confirms that the powder is finer.
As shown in Figs. 1a) and (b), the presence of seed pores is observed. For the two types of seeds, most pores present approximately the same mean diameter, 58.717 Å, for seeds with granulometry smaller than 20 µm, and 59.945 Å, for seeds with granulometry in the range (20-38) µm.

The chemical analysis results of the powders obtained by co-precipitation in the different working conditions are presented in Table I. For the powder in co-precipitate state, the analysis results are exactly half as the theoretically predicted due to the presence of hydrated products, ammonium carbonate, and co-precipitation by-products.

Table I – Chemical composition of UO$_2$ – 10wt%Gd$_2$O$_3$ powders obtained by co-precipitation process. Analysis of the Gd$_2$O$_3$ weight percentage

<table>
<thead>
<tr>
<th>Nominal Chemical Composition</th>
<th>Co-Precipitated Powder</th>
<th>Reduced Powder</th>
</tr>
</thead>
<tbody>
<tr>
<td>UO$_2$-10wt%Gd$_2$O$_3$ (seeds: 2wt% - &lt;20 µm)</td>
<td>5</td>
<td>9.7</td>
</tr>
<tr>
<td>UO$_2$-10wt%Gd$_2$O$_3$ (seeds: 5wt% - &lt;20 µm)</td>
<td>5.1</td>
<td>10.6</td>
</tr>
<tr>
<td>UO$_2$-10wt%Gd$_2$O$_3$ (seeds: 2wt% - (20-38) µm)</td>
<td>5.6</td>
<td>9.8</td>
</tr>
<tr>
<td>UO$_2$-10wt%Gd$_2$O$_3$ (seeds: 5wt% - (20-38) µm)</td>
<td>4.0</td>
<td>9.9</td>
</tr>
</tbody>
</table>

The BET specific surface area results of UO$_2$ obtained by co-precipitation process and of Gd$_2$O$_3$ powders were 8.4455 m$^2$/g and 1.3831 m$^2$/g, respectively. The BET specific surface area results of UO$_2$ – 10wt%Gd$_2$O$_3$ powders obtained with different percent amounts and seed sizes by the two processes are presented in Table II. It is known that UO$_2$ powders produced by AUC process present typical surface area values between 4 and 6.5 m$^2$/g\textsuperscript{10}. Table II shows that the values found are close to the upper limit reported in literature or a little higher. This is probably due to the smaller granulometry of the powders obtained here.

The Gd$_2$O$_3$ powder used in the mechanical mixing process presented a flaky aspect with reasonable difference in particle sizes, see Fig. 1 (c). While the UO$_2$ powder obtained by AUC process by the mechanical mixing process presented a typical monoclinic crystal aspect, see Fig. 1 (d).

As said before, to obtain powders with seeds by co-precipitation, it was necessary to modify the reagent addition order due to practical problems with the procedure different from that described by Lima\textsuperscript{1} and \textsuperscript{2}. As a result, the powders obtained presented a large difference in
particle size, which probably influenced the densification and size of the grains of the sintered products, see Fig. 2 (a).

Table II – Specific surface area of UO$_2$-10%Gd$_2$O$_3$ powders with seeds (m$^2$/g)

<table>
<thead>
<tr>
<th>Mixture Proportion</th>
<th>Co-precipitation Process</th>
<th>Mechanical Mixing Process</th>
</tr>
</thead>
<tbody>
<tr>
<td>UO$_2$ – 10wt%Gd$_2$O$_3$ (seeds: 2wt% - &lt;20 $\mu$m)</td>
<td>6.7381</td>
<td>7.1514</td>
</tr>
<tr>
<td>UO$_2$ – 10wt%Gd$_2$O$_3$ (seeds: 5wt% - &lt;20 $\mu$m)</td>
<td>10.1143</td>
<td>6.4598</td>
</tr>
<tr>
<td>UO$_2$ – 10wt%Gd$_2$O$_3$ (seeds: 2wt% - (20-38) $\mu$m)</td>
<td>9.7798</td>
<td>7.7817</td>
</tr>
<tr>
<td>UO$_2$ – 10wt%Gd$_2$O$_3$ (seeds: 5wt% - (20-38) $\mu$m)</td>
<td>6.9065</td>
<td>7.604</td>
</tr>
</tbody>
</table>

Figure 1. UO$_2$ seed and powder morphology. (a) <20 $\mu$m and (b) (20-38) $\mu$m. Powder Morphology: (c) Gd$_2$O$_3$ and (d) AUC. SEM

Fig. 2 (b) shows the typical morphology of the powders used in the mechanical mixing process. These powder sizes are nearer than those of the powders used in co-precipitation process, as compared that shown in Figs 2 (a) and (b). This fact certainly influenced the grain size and the density of the sintered pellets. It is noticed that the powder surface presents some porosity.

IV.2. X-Ray Diffraction of Powders and Sintered Fuel Pellets

Figs. 3 (a) and (b) present the diffractograms of the UO$_2$ and Gd$_2$O$_3$ powders taken as references.

After reduction, the powders containing gadolinium presented only peaks relative to the UO$_2$ phase, because the peaks of this compound are very strong and overlap those of the gadolinium-containing compound such as observed in other works$^{1-3,8,18}$. The X-ray
dифрактометрических образцов зерен, полученных с помощью процесса синтеза и механического смешивания.

Фигура 2: Сравнение микроструктуры образцов UO₂-10%Gd₂O₃, полученных с помощью процессов синтеза и механического смешивания. (a) Процесс синтеза - добавки: 5% < 20 µm и (b) процесс механического смешивания - добавки: 5% (20-38) µm

Фигура 3: Рентгеновские дифрактограммы образцов UO₂ и Gd₂O₃.

IV.3. Chemical Analysis of Sintered Pellets

The chemical analysis results of the sintered pellets are presented in Table III. Some variations are slightly larger than the nominal values, possibly due to the accuracy of the method used.
Figure 4. X-ray diffractograms of sintered fuel pellets obtained by co-precipitation process

Figure 5. X-ray diffractograms of sintered fuel pellets obtained by mechanical mixing process
Table III – Chemical composition of UO₂ – 10wt%Gd₂O₃ sintered fuel pellets with seeds.

Analysis of the Gd₂O₃ weight percentage

<table>
<thead>
<tr>
<th>Nominal Chemical Composition</th>
<th>Co-Precipitated Process</th>
<th>Mechanical Mixing Process</th>
</tr>
</thead>
<tbody>
<tr>
<td>UO₂-10wt%Gd₂O₃ (seeds: 2wt% - &lt;20 µm)</td>
<td>9.8 ± 0.3</td>
<td>10.0 ± 0.3</td>
</tr>
<tr>
<td>UO₂-10wt%Gd₂O₃ (seeds: 5wt% - &lt;20 µm)</td>
<td>10.5 ± 0.3</td>
<td>10.0 ± 0.3</td>
</tr>
<tr>
<td>UO₂-10wt%Gd₂O₃ (seeds: 2wt% - (20-38) µm)</td>
<td>9.8 ± 0.3</td>
<td>11.3 ±0.3</td>
</tr>
<tr>
<td>UO₂-10wt%Gd₂O₃ (seeds: 5wt% - (20-38) µm)</td>
<td>9.9 ± 0.3</td>
<td>9.9 ± 0.3</td>
</tr>
</tbody>
</table>

IV.4. Microstructural Characterization

Figs 6 and 7 show the microstructures of the sintered pellets obtained with 50 KN/cm² compaction pressure. All samples presented some porosity. The pellets obtained by co-precipitation process became more porous with the increase in the quantity of seeds. The mechanical mixing process resulted in less and the same degree of porosity for all samples. The seed sizes and powders used in the mechanical mixing process resulted in better pellet densification, in agreement with the density shown in section IV.8.

Figure 6. Sintered fuel pellets obtained by co-precipitation process. Seeds: (a) 2% - <20 µm, (b) 5% - <20 µm, (c) 2% - (20-38) µm, and (d) 5% - (20-38) µm. Compaction pressure: 50 KN/cm²

SEM
Figure 7. Sintered fuel pellets obtained by mechanical mixing process. Seeds: (a) 2% - <20 µm, (b) 5% - <20 µm, (c) 2% - (20-38) µm, and (d) 5% - (20-38) µm. Compaction pressure: 50 KN/cm² - SEM

Line profiles were performed in longitudinal sections with quantitative chemical analysis in weight percentage of U (converted to UO₂) and Gd (converted to Gd₂O₃) in sintered pellets obtained via co-precipitation process and mechanical mixing, respectively. It was observed that the peak intensities are homogeneous along the lines for all the chemical compositions. As to the presence of Gd, it is observed that the distribution was homogeneous along the lines. However, it is observed a large peak intensity variation for the co-precipitation process due to the larger porosity of these samples. Fig. 8 illustrates all cases. Specifically in Fig. 8 (a), it can be noted a high peak due to the porosity. According to Durazzo⁸, the porosity of (U,Gd)O₂ systems is due to the Kirkendall effect. Basically, charge compensation upon the addition of Gd³⁺ to UO₂ may occur by oxygen vacancy oxidation of U⁴⁺ to U⁵⁺ or U⁶⁺, interstitial formation, or a combination of these types of defects, depending on the sintering atmosphere. As a consequence, pores are formed where there are Gd₂O₃ clusters simultaneously to sintering. In this way, poor (UO₂-Gd₂O₃) mixed powder homogeneity causes insufficient densification. As in a previous paper², some sample regions are rich in gadolinium and others in uranium. However, the matrix presented near nominal chemical composition.

The X-ray maps for the several working conditions for the co-precipitation and mechanical mixing processes were similar. In these maps, the light colour indicates that the element under analysis is present in large amounts, see Fig. 9. The comparison of the photomicrographies in Fig. 9 (a) and (b) reveals that in the mechanical mixing process, the microstructure is more homogeneous, while that of the co-precipitation process presents larger regions with high concentrations of the element under analysis. However, for the same sample, it is observed a homogeneous distribution of the elements along the area presented. Thus, it can be said that for
the processing conditions used in this work, homogenization is less satisfactory in the co-precipitation process.

![Graph of Co-Precipitation Process - UO₂-10%Gd₂O₃ and Mechanical Mixing Process - UO₂-10%Gd₂O₃](image)

(a) Co-Precipitation Process - UO₂-10%Gd₂O₃
Seeds: 2wt% (20-38) µm

(b) Mechanical Mixing Process - UO₂-10%Gd₂O₃
Seeds: 2wt% (20-38) µm

Figure 8. Electron microprobe diagram of UO₂-10wt%Gd₂O₃ sintered fuel pellets. Seeds: 2wt% (20-38) µm. (a) Co-precipitation process and (b) mechanical mixing process

WDS analyses were carried out in the regions in evidence. The blue regions in the Gd analysis map are very rich in U. The white regions present high amounts of Gd. The percentage of the elements in the matrix varies around the nominal composition. Therefore, it can be concluded that, as in other works, some sample regions are not homogeneous, with regions rich in UO₂ and others rich in Gd₂O₃.

![X-ray difraction maps of UO₂-10wt%Gd₂O₃](image)

(a) Co-precipitation process
(b) Mechanical Mixing process

Figure 9. X-ray difraction maps of UO₂-10wt%Gd₂O₃ sintered fuel pellets. Seeds: 2wt% (20-38) µm. a) Co-precipitation process and b) mechanical mixing process

Figs. 10 and 11 present the microstructure of the sintered pellets obtained with compaction pressure of 50 KN/cm². All pellets required 5000 X enlargement for the observation of the grains, as they were very small.
Figure 10. Grain size of sintered fuel pellets obtained by co-precipitation process. Seeds: (a) 2% - <20 µm, (b) 5% - <20 µm, (c) 2% - (20-38) µm, and (d) 5% - (20-38) µm. Compaction pressure: 50 KN/cm² - SEM

Figure 11. Grain size of sintered fuel pellets obtained by mechanical mixing process. Seeds: (a) 2% - <20 µm, (b) 5% - <20 µm, (c) 2% - (20-38) µm and (d) 5% - (20-38) µm. Compaction pressure: 50 KN/cm² - SEM

Table IV gives the mean grain diameter of the pellets presented in Figs. 10 and 11. The grain size of the pellets obtained by the mechanical mixing process is slightly larger than those obtained by the co-precipitation process.

<table>
<thead>
<tr>
<th>Chemical Composition</th>
<th>Co-precipitation Process</th>
<th>Mechanical Mixing process</th>
</tr>
</thead>
<tbody>
<tr>
<td>UO₂-10wt%Gd₂O₃ (seeds: 2wt% - &lt;20 µm)</td>
<td>1.0612 ± 0.3064</td>
<td>1.4251 ± 0.454</td>
</tr>
<tr>
<td>UO₂-10wt%Gd₂O₃ (seeds: 5wt% - &lt;20 µm)</td>
<td>1.2674 ± 0.4822</td>
<td>1.5147 ± 0.5819</td>
</tr>
<tr>
<td>UO₂-10wt%Gd₂O₃ (seeds: 2wt% - (20-38) µm)</td>
<td>1.2642 ± 0.4234</td>
<td>1.3494 ± 0.4359</td>
</tr>
<tr>
<td>UO₂-10wt%Gd₂O₃ (seeds: 5wt% - (20-38) µm)</td>
<td>1.273 ± 0.5363</td>
<td>1.3023 ± 0.5298</td>
</tr>
</tbody>
</table>
However, comparatively to the results of a previous work by Lima\textsuperscript{2} in similar conditions without the addition of seeds, it was obtained slightly larger grain sizes ($3 \pm 1$ $\mu$m for the composition prepared by the mechanical mixing process. In terms of grain growth, the addition of 2 and 5% seeds to the powder mixture interfered with the grain growth process, as the grain growth kinetics became slower. These results confirm that the small size seed fractions and powders caused small particle-particle interferences with a subsequent reduction in grain size increase as the growth then proceeded according to conventional kinetics\textsuperscript{24}. In addition, longer times or higher temperatures might help to solve this problem\textsuperscript{24 and 26}. Other solutions might be the use of either dopants\textsuperscript{24 and 26} or oxidizing atmosphere with or without dopants\textsuperscript{21, 24 and 26}.

The addition of seeds in the co-precipitation process did not promote grain growth either. For this co-precipitation process without the addition of seeds, the mean grain size was ($4 \pm 2$) $\mu$m\textsuperscript{2}. It is believed that the large amount of small particles present in the powders used may have been the main cause of the reduction of grain size in this process.

In nuclear fuels, large pellet grains, 20-25 $\mu$m\textsuperscript{22}, perform better in operation. Large grains reduce the release of gaseous fission products and thus improve the fuel performance\textsuperscript{19 and 23}. For the processing conditions employed in this work, the grain size obtained is below the desirable value for industrial application\textsuperscript{19 and 23}. The advantage of the use of seeds in sintered pellets is associated to the possibility of using nuclear industry wastes. As said before, other techniques may be used as well\textsuperscript{5, 20, 22, 24 and 26}.

IV.5. Density

Fig. 12 presents the density values as a theoretical density percentage of nuclear fuel sintered pellets with seeds obtained by co-precipitation and mechanical mixing processes.

![Figure 12. Density of sintered fuel pellets with seeds. (a) co-precipitation process and (b) mechanical mixing process](image-url)
For the co-precipitation process, Fig. 12 (a), it was observed that the large difference in particle size of co-precipitated powders influenced the sintering process significantly, reducing the density in relation to the process without the addition of seeds\(^2\).

It is known that the density specification for nuclear fuel is \((95 \pm 1.5)\%\) of the theoretical value\(^{21}\) and \(^{24}\). For the co-precipitation process, the density values were even higher as the compaction pressure increased. However, for the largest compaction pressure, 50 KN/cm\(^2\), the density values were close to the low theoretical density specification limit for nuclear fuels. For this compaction pressure, it is believed that a larger sintering time would result in a larger theoretical density value.

For the mechanical mixing process, Fig. 12 (b), the density values obtained were quite close to the low theoretical density specification limit for nuclear fuels for all compaction pressures. This is probably related to the small difference in particle size of the powders used in this process. Supposedly, a larger sintering time would affect the theoretical density values as well.

A good result of this work is related to the improved densification of the sintered pellets with the use of mechanical mixing with seeds. As this process is used in the industry to obtain fuel pellets, the better result obtained with this process in relation to that of the co-precipitation process is important. Furthermore, the comparison of this process with that previously carried out without the addition of seeds reveals that the density did not vary with the compaction pressure. Additionally, for the compaction pressure of 50 KN/cm\(^2\), the density values rose from 89 TD\(^%\)\(^2\) to 91 TD\(^%\) in this work.

Figs. 12 (a) and (b) show that the density value tends to decrease with the increase in the seed amount.

**V. CONCLUSIONS**

From the results of this work, it can be inferred that:

- Powders with seeds presented a near-nominal chemical composition and specific surface area typical of UO\(_2\) powders.
- The chemical composition of sintered fuel pellets was homogeneous throughout the pellets.
- The mechanical mixing process was more effective in terms of crystallization than the co-precipitation process was.
- The seeding method using mechanical mixing process was more effective in terms of densification than the co-precipitation process was.
For the co-precipitation process, the density reached values close to the theoretical one only for compaction pressure of 50 KN/cm².

For the mechanical mixing process, the density reached values close to the theoretical one for all compaction pressures.

The mechanical mixing process resulted in a larger increase in the density of UO₂-10wt% Gd₂O₃ with seeds in relation to that of UO₂-10wt% Gd₂O₃ without seeds.

The samples did not present an ideal grain size for nuclear fuel pellets and grain size and density decreased with the seed size and quantity.

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VII. REFERENCES


