INDIVIDUAL INFLUENCE OF Al₂O₃ AND Nb₂O₅ ON GRAIN GROWTH OF UO₂ SINTERED PELLETS MANUFACTURED AT INB

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ABSTRACT

The effects of alumina and niobia on densification and grain growth of UO₂ sintered pellets have been investigated. The UO₂ powder used was produced at INB by commercial AUC route. The U₃O₈ sample was obtained by oxidation of a mix of both defected pellets and grinding sludge at 380°C in air atmosphere for 20 h. Two tests were carried out: the first one using only UO₂, lubricant and dopant; and the other adding U₃O₈ to the last blend. Samples of 0.1-0.5 wt% of both Al₂O₃ and Nb₂O₅-doped pellets were sintered at 1760°C for 5.7 h in a commercial sintering furnace, at INB Pelletizing Process, under wet hydrogen atmosphere. Al₂O₃ addition decreased the sintered density in a rate of 0.03 g/cm³ for each 0.1 wt% added and 0.2-0.5 wt% of Nb₂O₅ increased the density. 12 wt% of U₃O₈ addition decreased the densities by about 0.20 g/cm³ in each doping tests. Comparing with undoped UO₂ pellets, the grain growth enhanced and the grain sizes became larger as the niobia content increased, reaching a maximum value of about 30 µm (0.5 wt%), 135.2 % higher than the undoped one (Z test). Such effect may be attributed to the increased concentration of uranium vacancies, which are formed by the interstitial Nb⁴⁺ ion in UO₂ lattice. The addition of alumina was less effective on grain growth than niobia. The maximum value obtained for Al₂O₃ was almost 15 µm, 16.7 % higher than the Z test.

1. INTRODUCTION

Nowadays, one of the major challenges for nuclear energy industries is to increase the fuel discharged burn-up while enhancing the safety features. This fact is very important because it can reduce the maintenance and fuel cycle cost [2]. Regarding these points, so many studies have been carried out in order to obtain an improvement in the fuel pellets microstructures [7, 11, 12, 15]. The aim of this improvement is to increase the fuel matrix average grain size and fuel plasticity. In this way, the fission gas release (FGR) is reduced and the pellet-cladding interaction (PCI) margins are increased [12].

Different processes for UO₂ pellets production, with large grains sizes, have been studied. Many authors have investigated the effect of process parameters on the grain growth, which mainly include: sintering temperature, time and atmosphere, chemical additives (dopants) and recycled material (U₃O₈) as well [1, 3, 12, 13]. It has been very common the use of doping technology, which consists in a small addition of dopants in the UO₂ non-sintered pellets, to improve the grain growth of the pellets. The additives facilitate densification and diffusion during sintering, which results in a higher density and larger grain size. Nevertheless, the introduction of chemical additives in UO₂ fuel could change the in-reactor fuel performance. In order to use the doped UO₂ fuel in reactor, long-term verifications of the pellets are required [15].
Concerning those issues, INB (Indústrias Nucleares do Brasil S.A.) has started a research program in doping technology to develop sintered pellets with large average grain size. In this study, alumina and niobia with 0.1-0.5 wt% (gMetal/gU) were used. The UO\textsubscript{2} powder used to manufacture the pellets was obtained at INB Reconversion Plant by commercial Ammonium Uranium Carbonate (AUC) route.

In this work, INB has made various experiments in lab-scale in order to know the individual influence of alumina and niobia on the average grain size of UO\textsubscript{2} sintered pellets. Before this study, INB had performed tests at INB Pelletizing Plant and had obtained good results for both additives. Additionally, the influence of both dopants on sintered density and average pore size was also analyzed in this paper.

2. MANUFACTURING PROCESS

2.1. Preparation of UO\textsubscript{2} and U\textsubscript{3}O\textsubscript{8} Powders

The UO\textsubscript{2} powder used in this study was produced by commercial Ammonium Uranyl Carbonate (AUC) route at INB Reconversion Plant. The U\textsubscript{3}O\textsubscript{8} powder was obtained by the oxidation of a mix of defected UO\textsubscript{2} pellets and grinding sludge (mass ratio: 0.6/0.4, respectively), during 20 hours at 380°C in air atmosphere. The orthorhombic U\textsubscript{3}O\textsubscript{8} phase has an about 30\% larger lattice volume than the cubic UO\textsubscript{2} phase, so UO\textsubscript{2} defected pellets are spontaneously pulverized by the stress involved in the oxidation process [8].

Later than the oxidation process, the U\textsubscript{3}O\textsubscript{8} formed was then sieved in a sieve of 350 mesh. So, samples were collected for quality control and a sufficient amount was picked up from the production lot (number LO 003/13) to carry out all the experiments.

After preparing both UO\textsubscript{2} and U\textsubscript{3}O\textsubscript{8}, samples were sent to Physical Characterization and Chemical Laboratories at INB to evaluate the following characteristics: chemical impurities, humidity, enrichment, O/U ratio and uranium quantity at Chemical Laboratory. Yet, flowability, bulk density, specific surface area and mean particle size at Physical Characterization Laboratory.

2.2. Preparation of the Blends

In order to analyze the effects of the dopants on UO\textsubscript{2} pellets microstructure and sintered density, two background experiments were made. The first one was called “Z”, in which only UO\textsubscript{2} and aluminum distearate (ADS), a solid lubricant, were used (UO\textsubscript{2} + 0.2 wt% ADS). The second one was named as “M”, in which U\textsubscript{3}O\textsubscript{8} was added to the mixture Z to obtain another blend with the following composition: 89.8 wt% UO\textsubscript{2} + 0.2 wt% ADS + 12.0 wt% U\textsubscript{3}O\textsubscript{8}. This blend is identical to the large scale production of INB Pelletizing Process. Not only the individual influence of additives on sintered density and microstructure could be analyzed, but also the influence of U\textsubscript{3}O\textsubscript{8}.

The blends were prepared using Al\textsubscript{2}O\textsubscript{3} (> 99.5\%, ALCOA calcined alumina – APC G) and Nb\textsubscript{2}O\textsubscript{5} (> 99.0\%, MERK) powders as additives. To the sample Z, some quantities of both dopants (0.1-0.5 wt%) were added and then mixed in a Tubular Mixer for 25 min to guarantee the homogeneity. At the same way, the additives were mixed with the sample M. Table 1 shows the samples and their identifications.
Table 1: Samples identifications

<table>
<thead>
<tr>
<th>Dopants wt % (g Metal/g U)</th>
<th>Z^a</th>
<th>M^a</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Al_2O_3</td>
<td>Nb_2O_5</td>
</tr>
<tr>
<td>0.1</td>
<td>Z(Al)1</td>
<td>Z(Nb)1</td>
</tr>
<tr>
<td>0.2</td>
<td>Z(Al)2</td>
<td>Z(Nb)1</td>
</tr>
<tr>
<td>0.3</td>
<td>Z(Al)3</td>
<td>Z(Nb)1</td>
</tr>
<tr>
<td>0.5</td>
<td>Z(Al)5</td>
<td>Z(Nb)1</td>
</tr>
</tbody>
</table>

a. backgrounds for both tests.

2.3. Pelletizing Process

A significant amount of pellets, with green density of 5.75 ±0.05 g/cm³, were manufactured in a lab press machine with one axial position and die-wall lubrication. The compression force and the mass of each pellet were about 5000 kgf and 7.90 g, respectively. The green densities were calculated using an INB program based on the mass and geometrical shape of the pellets.

After pressing, the pellets were sintered in a commercial sintered furnace with five temperatures zones: 500, 750, 1760, 1760 e 1760°C for 5.7h in a moisture hydrogen atmosphere with dew point about -30°C (ratio of H_2O to H_2 gas corresponded to 5.0 x 10⁻³). Afterwards, samples of UO_2 pellets were sent to the Physical Characterization Laboratory to quantify the sintered density and the average pore and grain sizes. The first one was performed by water immersion method. Sintered pellets were sectioned longitudinally and then polished. In order to observe the microstructures, thermal etching was carried out at 1400°C for 3 h in carbon dioxide gas and then analyzed in an optical microscope.

3. RESULTS

All the UO_2 and U_3O_8 powders used in this study were collected from the same production lot (L 002/13 and LO 003/13, respectively). Fig. 1 shows the morphological shapes of UO_2 ex-AUC powder, performed by Scanning Electron Microscopy at INB Physical Characterization Laboratory.

Figure 1: Morphology of UO_2 powder.
The UO\textsubscript{2} particles have a round shape and smooth surface, as the typical UO\textsubscript{2} ex-AUC powder.

### 3.1. Characterization of Chemical Properties

The chemical properties of UO\textsubscript{2} and U\textsubscript{3}O\textsubscript{8} powders, from production lots L002/13 and LO 003/13, respectively, were analyzed in agreement with the technical specifications. Table 2 shows the observed values, which were calculated using an inductively coupled plasma optical emission spectrometry (ICP-OES), at INB Chemical Laboratory. Fluorine quantities were calculated by ion chromatography.

<table>
<thead>
<tr>
<th>Oxides</th>
<th>F</th>
<th>Al</th>
<th>B</th>
<th>Gd</th>
<th>Ca</th>
<th>Fe</th>
<th>Ni</th>
<th>Si</th>
<th>C</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>UO\textsubscript{2}</td>
<td>16</td>
<td>1.77</td>
<td>&lt;0.2\textsuperscript{a}</td>
<td>&lt;0.2\textsuperscript{a}</td>
<td>2.71</td>
<td>6.19</td>
<td>0.28</td>
<td>6.63</td>
<td>c</td>
<td>-</td>
</tr>
<tr>
<td>U\textsubscript{3}O\textsubscript{8}</td>
<td>2</td>
<td>36</td>
<td>&lt;0.2\textsuperscript{a}</td>
<td>-c</td>
<td>3.96</td>
<td>23.94</td>
<td>4.61</td>
<td>7.35</td>
<td>4</td>
<td>46</td>
</tr>
</tbody>
</table>

a. under detection limit.
b. all values are under the specification limits.
c. not evaluated as a specification parameters.

As presented in Table 2 observation, all the contaminants are under the specification limits for both oxides. Therefore, they were used as certified materials to manufacture the pellets.

Others chemical analyses were made in order to know the chemical characteristics of UO\textsubscript{2} and U\textsubscript{3}O\textsubscript{8} powders. Humidity, enrichment, O/U ratio and uranium quantity were evaluated and their values are described in Table 3. All these analysis were performed at INB Chemical Laboratory as well.

<table>
<thead>
<tr>
<th>Analysis</th>
<th>UO\textsubscript{2}\textsuperscript{a}</th>
<th>U\textsubscript{3}O\textsubscript{8}\textsuperscript{a}</th>
<th>Methods</th>
</tr>
</thead>
<tbody>
<tr>
<td>Humidity (wt%)</td>
<td>0.19</td>
<td>0.09</td>
<td>Karl Fisher Titration</td>
</tr>
<tr>
<td>Enrichment (U\textsuperscript{235} wt%)</td>
<td>1.915</td>
<td>1.909</td>
<td>Gamma Spectroscopy</td>
</tr>
<tr>
<td>O/U ratio</td>
<td>2.15</td>
<td>2.68</td>
<td>Thermogravimetry</td>
</tr>
<tr>
<td>U quantity (U wt%)</td>
<td>87.4</td>
<td>84.2</td>
<td>Thermogravimetry</td>
</tr>
</tbody>
</table>

a. all values are in agreement with the specification limits.

In the same way, all the results are in according to specification limits for both oxides.

### 3.2. Characterization of Physical Properties

Characterization of physical properties like flowability, bulk density, specific surface area and mean particle size for UO\textsubscript{2} was made. Table 4 lists these values. It shows that all the values are in agreement with the specification. For U\textsubscript{3}O\textsubscript{8}, the result of specific surface area,
performed by B.E.T. method, was 0.8 m$^2$/g. This value is 6.1 times lower than the UO$_2$ powder result (4.9 m$^2$/g), which means a lower sinterability of U$_3$O$_8$ than UO$_2$.

**Table 4: Physical analysis of UO$_2$ powder**

<table>
<thead>
<tr>
<th>Analysis</th>
<th>Values</th>
<th>Specification</th>
<th>Methods</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flowability (s/50g)</td>
<td>2.3</td>
<td>50 g ≤ 10 s</td>
<td>Funnel and time</td>
</tr>
<tr>
<td>Bulk density (g/cm$^3$)</td>
<td>2.3</td>
<td>2.0 – 2.6</td>
<td>Funnel and weight</td>
</tr>
<tr>
<td>Specific surface (m$^2$/g)</td>
<td>4.9</td>
<td>2.5 – 6.0</td>
<td>B.E.T.</td>
</tr>
<tr>
<td>Mean Particle Size (μm)</td>
<td>26.3</td>
<td>^a</td>
<td>Laser diffraction</td>
</tr>
</tbody>
</table>

a. not evaluated as a specification parameter.
b. specification limits for UO$_2$.

The UO$_2$ pellets were manufactured and identified according to the Table 1. The average results for green density, sintered density and average pore and grain size were calculated and the values are dated in Table 5.

**Table 5: Average values of green density, sintered density and pore and grain size for UO$_2$ undoped (Z and M) and doped sintered pellets**

<table>
<thead>
<tr>
<th>Samples</th>
<th>Green Density$^a$ (g/cm$^3$)</th>
<th>Sintered Density$^a$ (g/cm$^3$)</th>
<th>Grain Size$^{b,c}$ (μm)</th>
<th>Pore Size$^{b,d}$ (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z</td>
<td>5.77</td>
<td>10.58</td>
<td>12.5</td>
<td>2.6</td>
</tr>
<tr>
<td>Z(Al)1</td>
<td>5.75</td>
<td>10.53</td>
<td>10.8</td>
<td>2.5</td>
</tr>
<tr>
<td>Z(Al)2</td>
<td>5.78</td>
<td>10.50</td>
<td>13.9</td>
<td>2.5</td>
</tr>
<tr>
<td>Z(Al)3</td>
<td>5.77</td>
<td>10.47</td>
<td>14.5</td>
<td>2.5</td>
</tr>
<tr>
<td>Z(Al)5</td>
<td>5.79</td>
<td>10.44</td>
<td>12.1</td>
<td>3.6</td>
</tr>
<tr>
<td>Z(Nb)1</td>
<td>5.78</td>
<td>10.53</td>
<td>15.7</td>
<td>2.6</td>
</tr>
<tr>
<td>Z(Nb)2</td>
<td>5.75</td>
<td>10.50</td>
<td>18.9</td>
<td>3.0</td>
</tr>
<tr>
<td>Z(Nb)3</td>
<td>5.75</td>
<td>10.54</td>
<td>27.7</td>
<td>4.5</td>
</tr>
<tr>
<td>Z(Nb)5</td>
<td>5.75</td>
<td>10.61</td>
<td>29.3</td>
<td>3.6</td>
</tr>
<tr>
<td>M</td>
<td>5.76</td>
<td>10.51</td>
<td>9.5</td>
<td>2.6</td>
</tr>
<tr>
<td>M(Al)1</td>
<td>5.76</td>
<td>10.35</td>
<td>19.0</td>
<td>2.8</td>
</tr>
<tr>
<td>M(Al)2</td>
<td>5.74</td>
<td>10.33</td>
<td>9.0</td>
<td>2.9</td>
</tr>
<tr>
<td>M(Al)3</td>
<td>5.77</td>
<td>10.30</td>
<td>9.4</td>
<td>3.0</td>
</tr>
<tr>
<td>M(Al)5</td>
<td>5.75</td>
<td>10.25</td>
<td>10.5</td>
<td>3.0</td>
</tr>
<tr>
<td>M(Nb)1</td>
<td>5.76</td>
<td>10.32</td>
<td>13.0</td>
<td>2.8</td>
</tr>
<tr>
<td>M(Nb)2</td>
<td>5.77</td>
<td>10.30</td>
<td>16.5</td>
<td>2.8</td>
</tr>
<tr>
<td>M(Nb)3</td>
<td>5.78</td>
<td>10.36</td>
<td>17.7</td>
<td>3.5</td>
</tr>
<tr>
<td>M(Nb)5</td>
<td>5.77</td>
<td>10.40</td>
<td>19.4</td>
<td>3.0</td>
</tr>
</tbody>
</table>

a. average value of six pellets.
b. average sizes.
c. specification limits: 9 – 35 μm.
d. specification limits: < 100 μm with only 10% > 100 μm; and it is forbidden > 500 μm.
4. DISCUSSION

It is evident that both sinterability and microstructure of UO$_2$ pellets can be modified to a significant extent by low levels of sintering aid additions. In some cases the sintered density may increase, while in others it may decrease. These behaviors will depend on the kind of additive used, their concentrations and the homogeneity of the blend. In this work, both behaviors are present.

4.1. Sintered Pellets Density

The data presented in Table 5 are plotted in Fig. 2, where is shown the variation of sintered density with both dopants and U$_3$O$_8$ additions.

![Figure 2: Variation of sintered density with both dopants and U$_3$O$_8$ additions.](image)

Without any addition of U$_3$O$_8$, the sintered density obtained was 10.58 g/cm$^3$ for Z test (0% of additive). This value was reduced to 10.51 g/cm$^3$ owing to the U$_3$O$_8$ addition.

It is known that the U$_3$O$_8$ addition decreases the sintered density. Previous authors [14] have studied the U$_3$O$_8$ powder morphology only modifying the oxidizing temperature. The oxides were prepared with 325 and 450°C. They have used 0, 3, 5 and 10 wt% of this oxide and observed that, with the increase of U$_3$O$_8$ wt%, the density of UO$_2$ sintered pellets have decreased. Moreover, they have concluded that with the increase of the oxidizing temperature, the powder has become more sinter-active (large BET surface area and small particle sizes), which implies that, with the same quantity of U$_3$O$_8$, the sintered density will decrease more when the oxidizing temperature is higher.

The densities of Z(Al) samples decreased almost linearly with the Al content and the rate was about 0.03 g/cm$^3$ for each 0.1 wt% of alumina added, which are directly related with the moderated increase in sample porosity. Meanwhile, the Z(Nb) sample had a different behavior with niobia content higher than 0.2 wt%. The figure above shows an increase in densities with the addition of niobia from 0.2 to 0.5 wt%. Earlier studies have shown similar behaviors [6, 9, 11].

It is a fact that the ratio of H$_2$O to H$_2$ in the sintering atmosphere affects both sintered density and grain growth. It also determines whether niobium oxide is fully dissolved in UO$_2$ or not.
Therefore, it is supposed that the oxidation state of niobium in the niobium oxide varies according to the gas ratio and resultantly the solubility of niobium oxide is influenced. A previous work [9] has shown that the stable form of niobium oxides changes in accordance with the sintering temperature, even under a fixed gas ratio. When it was $5.0 \times 10^{-4}$, a stable niobium oxide was Nb$_2$O$_3$ bellow 500°C, NbO$_2$ in the temperature range between 500 and 1050°C, and NbO above 1050°C, which indicates that the last one is mainly operative during the sintering. In this way, the partially dissolved niobium oxide is NbO, because the sintering temperature used in this study was 1760°C.

Although NbO$_2$ acts at lower temperature than NbO, it can be dissolved in UO$_2$ more than NbO since the size of Nb$^{4+}$ ion (0.83 Å) is smaller than Nb$^{2+}$ (0.85 Å) [5]. It is supposed that the partial dissolution of niobium oxide is attributed to the reduction of Nb$_2$O$_3$ to NbO before the complete dissolution of NbO$_2$, which happens up to about 1500°C. Considering that the substitution of the Nb$^{4+}$ for the U$^{4+}$ ions does not cause the creation of any extrinsic defects in UO$_2$, it is assumed that the Nb$^{4+}$ ions enter interstitially in the UO$_2$ lattice and, resultantly, uranium vacancy may be formed [9]. Increases in concentration of uranium vacancies give increases in uranium ions diffusion, explaining the enhancement in densification with concentration of niobia higher than 0.2 wt%. Bellow 0.2 wt% of this additive, the mechanism of pore former might be faster than the difusional effect of uranium ions, which would explain the decrease of density from 10.58 g/cm$^3$ to 10.5 g/cm$^3$ for Z(Nb) samples.

Regarding the U$_3$O$_8$ and dopants addition, it is clear that the densities decreased in both M(Al) and M(Nb) tests. As mentioned above, 12 wt% of U$_3$O$_8$ decreased the density from 10.58 (Z test) to 10.51 g/cm$^3$ (M test). The behavior of M(Al) and M(Nb) was very similar to Z(Al) and Z(Nb), respectively, separated by a variation of about 0.20 g/cm$^3$ for each 0.1 wt% of dopants added. In other words, the U$_3$O$_8$ addition decreased the sintered densities of both samples in a factor of about 0.20 g/cm$^3$. This reduction is associated to the fact that the specific surface area of the U$_3$O$_8$ powder is much lower than UO$_2$ powder (6.1 times lower in this study), resulting in a powder with lower sinterability [10].

### 4.2. Average Pore Size

It is well known that the pore sizes are impacted by dopants addition. Fig. 3 shows the variations of average pore sizes with dopants and U$_3$O$_8$ addition.

![Figure 3: Variation of average pore size with dopants and U$_3$O$_8$ additions.](image-url)
The results show peaks in 0.3 wt% addition of niobia in both Z and M tests. The data for Z(Nb)3 was almost 72.0 % higher than the undoped Z test and, for M(Nb)3, about 36.5 % upper than M value. Until 0.2 wt%, the average pore sizes were a little bit increased for M(Nb) and M(Al) samples. In contrast, the values for Z(Al) tests slight decreased with 0.1 wt% and reached the highest value in 0.5 wt% (almost 39.0 % higher than the undoped one). Fig. 4 portrays the microstructures for Z and M pellets.

![Figure 4](image)

**Figure 4:** Pore structures of (a) Z and (b) M samples for undoped UO₂ pellets.

It is possible to see in Fig. 4(a) and (b) that the undoped UO₂ pellet has two kinds of pores: irregular (elliptical and triangular) and round shape. The typical half-moon pore for UO₂ undoped pellets and the fine round pores shape can be seen. This last one probably came from the interspaces and/or inhomogeneities of UO₂ crystallite structure (spherical pore diameter ~ 1-3 μm). The largest uniform round pores (~ 9-12 μm) in Fig. 4(a) may be associated with both UO₂ particles interspaces and/or lubricant. The irregular pores in Fig. 4(b) are mainly formed by black U₃O₈ with different particle sizes. Fig. 5 shows the microstructure of both alumina and niobia doped UO₂ pellets with 0.3 wt% of additive.

![Figure 5](image)

**Figure 5:** Pore structures of 0.3 wt% alumina and niobia (Z and M) doped pellets.
Increasing the additive level, a more pronounced sweeping of the fine pores was observed. It was more evident when the additives content was higher than 0.2 wt% in all samples. Large round pores (> 50 µm) could be seen in Fig. 5(a). Yet, the pore density appears to be remarkably increased when additives were added (comparing Fig. 4 and 5).

In addition, big and round pores appeared in both doped pellets. The largest one (> 150 µm) was found in Z(Nb)3 (Fig. 5(b)) and it is believed to be formed at the original sites of niobium oxide, because Nb ions enter interstitially the surrounding UO2 lattice, leaving the biggest and round pores [6]. In M(Nb)3, presented in Fig. 5(d), this effect was not so significant but it was also present in lowest values (40-50 µm). It is thought that the homogeneity of Z(Nb)3, specifically, could not have been effective as the others samples. The largest pores might be formed by the sintering of the non-homogeneity agglomerates of niobium oxide (agglomerated size ~ 200 µm).

4.3. Average Grain Size

The average grain sizes of UO2 sintered pellets were obtained in order to evaluated the individual influence of each dopant on grain growth. Fig. 6 shows the evolution of the average grain sizes as a function of dopant content (wt%).

![Figure 6: Variation of average grain size with dopants additions.](image)

Concerning the alumina doped pellets, it is clear to see a maximum value of about 15 µm with 0.3 wt% of Z(Al) test. However, when U3O8 was added, the grain size decreased in all alumina experiments. It could be seen a slight increase on average grain size in a range of 0.1-0.3 wt%, in Z(Al) test, and 0.3-0.5 wt% in M(Al) test, but they were not significant as the niobia samples. For instance, the Z(Nb)5 test (~ 30 µm) was 2.4 times higher than Z(Al)5 test (~ 12 µm). It exemplifies that the niobia is the most promising additive to improve the grain growth.

Fig. 7 portrays a comparison between the undoped and alumina doped UO2 pellets microstructures for Z and M samples.
The microstructures above show an evolution on grain sizes with the increase of Al content. In both tests, the density of pore on grain boundaries increased with the alumina quantity. Similar result on literature has shown similar pore shape distribution but with a higher average grain size (15-18 µm). The authors have used 0.03 wt% of alumina in a mix of UO₂ (by commercial Dry Conversion process), 8 wt% of U₃O₈, 0.3 wt% of AZB (pore former) and 0.2 wt% of ACRAWAX (lubricant) [15]. It suggests that alumina is more effectiveness to promote grain growth in DC UO₂ powder than in AUC powder.

Niobia has been used extensively as chemical additive for UO₂-doped pellets with large average grain size [4, 6, 7, 10, 11]. In agreement with these literature results, INB has manufactured niobia-doped pellets with large grain size in both Z(Nb) and M(Nb) tests. Fig. 8 presents these data.

The behavior of Z(Nb) samples shows a significant increase on average grain size even in small quantities (0.1 wt%) of niobia (about 16.0 µm, higher than the largest alumina doped value). The maximum value was almost 30.0 µm with 0.5 wt%, which means 135.2 % higher
than the undoped one (Z). The top limit of INB Specification is 35 μm and the historical average grain size for large scale production is about 9.5-10.0 μm, which is very low when compared with Nb-doped pellets. Regarding the U₃O₈ addition, it showed a negative effect on grain growth on M(Nb) samples. It was almost 10 μm less than Z(Nb) test with 0.3 and 0.5 wt% of niobia.

It is well known that both gas ratio and temperature of sintering influence the grain growth of UO₂ doped pellets [7, 15]. As presented previously, the stable form of niobium oxides, with dew point of -30°C (H₂O/H₂ = 5.0x10⁻⁴), is Nb₂O₅ bellow 500°C, NbO₂ in the temperature range between 500 and 1050°C, and NbO above 1050°C, which indicates that the last one is mainly operative during the sintering process. Yet, the substitution of Nb⁴⁺ ion for the U⁴⁺ ion does not cause the creation of any extrinsic defects in UO₂ structure. This way, the enhancement in grain growth cannot be explained by this mechanism. So, it is supposed that the Nb⁴⁺ ion enters interstitially in the UO₂ lattice and then uranium vacancy may be formed [9]. An increase in concentration of the uranium vacancy increases the uranium diffusion ion, explaining the enhancement in grain growth obtained in both Z(Nb) and M(Nb) tests.

Analyzing the Fig. 8, the microstructures show that pores are mostly located on grain boundaries in Fig. 8(c) but small quantities are separated from grain boundaries in Fig. 8(b), (d) and (g), which means that the grain boundary was so mobile that pores could not catch up with it. Yet in Fig. 8(c), it is found a grain boundary separation for Z(Nb)³ sample. Similar behavior was found in previous work [4]. Additionally, with high content of niobia in both A and M test (> 0.3 wt%), a presence of a second phase might be formed (the “round” inclusions), as presented in Fig. 8(c), (d), (g) and (h). These defects look like to those presented earlier by others authors [9, 10]. In those studies, they have found a second phase on grains in 0.5 wt% niobia-doped UO₂ pellets. The niobium concentration profile across this phase has indicated that it has had a higher niobium concentration than the matrix. The quantitative analysis of uranium, niobium and oxygen was performed by EPMA, and the results have suggested that the second phase might be an oxide compound whose compositions have corresponded to near Nb₂UO₆ (U: 11.024 at%, Nb: 20.886 at% and O: 68.091 at%). So, further analysis are necessary to prove the supposition (and what is the precipitate) of the second phase in both Z and M niobia-doped samples.

4. CONCLUSIONS

UO₂-doped pellets were successfully manufactured at INB. The alumina addition decreased the sintered density in a rate of 0.03 g/cm³ for each 0.1 wt% added and the niobia showed a different behavior above 0.2 wt%; the values increased up to 10.61 g/cm³ in Z(Nb)5 sample. The U₃O₈ addition decreased the sintered densities of both samples in a factor of about 0.20 g/cm³, because the specific surface area of the U₃O₈ powder is much lower (6.1 times) than UO₂ powder, resulting in a powder with lower sinterability. With 0.3 wt% of niobia, large and round pores were found on pellets structure and it might be associated to a presence of non-homogeneity agglomerates of niobium oxide in the blend.

Comparing with those undoped UO₂ pellets (Z and M tests), the grain growth enhanced and the grain sizes became larger as the niobia content increased, reaching a maximum value of about 30 μm, 135.2 % (with 0.5 wt%) higher than the undoped one (Z). Such effect may be attributed to the increased concentration of uranium vacancy, which is formed by the interstitial Nb⁴⁺ ion in UO₂ lattice. The alumina was less effective on grain growth than
niobia. The maximum value obtained was almost 15 μm, about 16.7% higher than the undoped one (Z). So, niobia was the most promising additive because it significantly increased both density and grain growth, even with U₃O₈ addition.

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