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THERMAL STABILITY TEST OF UO_2-DOPED PELLET MANUFACTURED AT INB

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ABSTRACT

The thermal stability test of UO_2-doped pellet manufactured at INB was carried out in order to analyze the resintering behavior. This analysis is fundamental for predicting dimensional behavior during irradiation. INB commonly performs resintering test to qualify its production lots, and the same methodology was applied to UO_2-doped pellets. In this preliminary study, three sets of experiments have been made: 1) without any chemical additive (Z test, the standard UO_2 pellets - undoped); 2) UO_2 pellets doped with 0.1, 0.2 and 0.3 wt% of Al_2O_3; and 3) 0.1, 0.2 and 0.3 wt% of Nb_2O_5. The preliminary results showed an increase in sintered density in all resintering experiments. So as to obtain the percentage increase, the theoretical densities (g/cm^3 and %TD) were calculated based on the undoped UO_2 pellets. All samples increased in a range of 0.27 to 0.32 %TD the out-pile densification during the resintering process. However, the Z(Nb)3 test showed the lowest value of 0.08 %TD, which is not in agreement with the INB specification limits. The sintered density of this test (0.3 wt% niobia) was 96.15% TD. This fact might be related to the competitive mechanism between Kirkendall effect, forming porosity owing to niobium solubilization on UO_2 matrix, and densification process as a result of uranium diffusivity. Thus, the densification was only 0.08 %TD in Z(Nb)3 sample. All the other samples were in agreement with INB specification.

1. INTRODUCTION

One of the major challenges for nuclear energy industries today 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 [1]. Regarding these points, so many studies have been carried out in order to obtain an improvement in the fuel pellets microstructures [2,3,4,5,6]. The goal of this improvement is to increase the fuel matrix average grain size and fuel plasticity, causing the reduction of fission gas release (FGR) and increasing the pellet-cladding interaction (PCI) margins [5].

Different production processes of UO_2 pellets, 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 (U_3O_8) as well [5,7,8,9,10,11,12,13]. The doping technology is becoming

popular, being basically the addition of calculated amounts of dopants in the UO_2 non-sintered pellets, to improve their grain growth. 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 UO_2 fuel could change the in-reactor fuel performance. Hence the long-term verifications of the pellets are required [6].

Thermal stability test, which correlates the resintering process at constant temperature to the stability of UO_2 pellet during thermal heating in operation, is fundamental for predicting dimensional behavior during irradiation of UO_2 fuel pellets. There are, basically, two ways of perform it: i) quantitative analysis of sintered density, pore structure and model calculation. If the porosity decreases a lot, the sintered density will be higher and the pellet will not present stability during thermal heating in operation; and ii) thermal resintering test, which applies a predicting correlation between the changes in both sintered density and in-pile densification. INB commonly performs resintering test to qualify its production lots.

Concerning those issues, a work team from INB (*Indústrias Nucleares do Brasil S.A.*) has started a research program in doping technology to develop sintered pellets with large average grain size. This work presents planned experiments focusing on knowing the individual influence of alumina and niobia (0.1, 0.2 and 0.3 wt%) on thermal stability of UO_2 pellets. Primarily results of sintered density after resintering test were analyzed and are described as follow.

2. MANUFACTURING PROCESS

2.1. Preparation of UO_2 Powder

The UO_2 powder used in this study was produced by commercial Ammonium Uranyl Carbonate (AUC) route at INB Reconversion Plant. Afterwards, the UO_2 powder 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 resintering behavior of dopants on UO_2 pellets sintered density, three experiments were made. The first one was called "Z", in which only UO_2 and aluminum distearate (ADS), a solid lubricant, were used (UO_2 + 0.2 wt% ADS); the second and third ones by adding 0.1, 0.2 and 0.3 wt% of alumina or niobia to the sample Z, respectively. The blends were prepared using Al_2O_3 (> 99.5%, ALCOA calcined alumina – APC G) and Nb_2O_5 (> 99.0%, MERK) powders as additives to UO_2, mixed in a Laboratory Mixer for 25 min to guarantee the homogeneity. Table 1 shows the samples and their identifications.

Table 1: Samples identifications

Dopants wt % (g Metal/g U)	Z[a]	
	Al_2O_3	Nb_2O_5
0.1	Z(Al)1	Z(Nb)1
0.2	Z(Al)2	Z(Nb)1
0.3	Z(Al)3	Z(Nb)1

a. standard test (undoped UO_2 pellet)

2.3. Pelletizing Process

A significant number of pellets were manufactured by pressing the powder mixtures 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 (5.70 – 5.80 g/cm^3) using an INB program based on the mass and geometrical shape of the pellets.

2.4. Sintering Process

The green 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 5.0×10^{-4}). Samples of UO_2 pellets were sent to the Physical Characterization Laboratory to quantify the sintered density and the average pore size. The first one was performed by water immersion method and the second one started from the longitudinal section of the pellet followed by polishing.

2.5. Resintering Process

The thermal stability test (resintering) was performed by heating the UO_2 pellets at 4°C/min until 1708°C in a pure hydrogen atmosphere, kept at this temperature for 24 h and then cooled down at 6°C/min till room temperature. The UO_2 pellet densification must be higher than 0.2 % and lower than 1.3 % of the UO_2 theoretical density (TD = 10.97 g/cm^3) to be considered qualified, according to INB product specification limits. The water immersion method was used to determine the sintered densities before and after the resintering test in all experiments. The procedures described regarding the UO_2-doped are the same used in large scale production lots at INB. In this preliminary study, three sets of experiments have been made: 1) without any chemical additive (Z test). This is considered the standard UO_2 pellets (undoped); 2) UO_2 pellets doped with 0.1, 0.2 and 0.3 wt% of Al_2O_3 or 3) Nb_2O_5, as showed in Table 1.

3. RESULTS AND DICUSSIONS

3.1. Characterization of Chemical Properties

The chemical properties of UO_2 powder were analyzed. 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 2: Chemical impurities of UO_2 powder

	Impurities (μg/gU)[b]									
Oxides	F	Al	B	Gd	Ca	Fe	Ni	Si	C	N
UO_2	16	1.77	<0.2[a]	<0.2[a]	2.71	6.19	0.28	6.63	-[c]	-[c]

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

Also, humidity, enrichment, O/U ratio and uranium quantity were measured at INB Chemical Laboratory and their values are described in Table 3.

Table 3: Chemical analysis of UO_2 powder

Analysis	UO_2[a]	Methods
Humidity (wt%)	0.19	Karl Fisher Titration
Enrichment (U^{235} wt%)	1.915	Gamma Spectroscopy
O/U ratio	2.15	Thermogravimetry
U quantity (U wt%)	87.4	Thermogravimetry

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

In the same way, all the results are within the 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_2 was made. Table 4 lists these values. It shows that all the values are in agreement with the specification.

Table 4: Physical analysis of UO_2 powder

Analysis	Values	Specification[b]	Methods
Flowability (s/50g)	2.3	50 g ≤ 10 s	Funnel and time
Bulk density (g/cm^3)	2.3	2.0 – 2.6	Funnel and weight
Specific surface (m^2/g)	4.9	2.5 – 6.0	B.E.T.
Mean Particle Size (μm)	26.3	-[a]	Laser diffraction

a. not evaluated as specification parameters.
b. specification limits for UO_2.

3.3. Sintering and Resintering Behaviors

The UO_2 pellets were manufactured and identified according to the Table 1. The average results for sintered and resintered densities, as well as the variation between them as a function of the UO_2 theoretical density (Δ %TD), were calculated and the values are dated in Table 5.

Table 5: Values of both sintered and resintered densities for UO_2 undoped (Z) and doped pellets

Samples	Sintered Density (g/cm^3)	Resintered Density (g/cm^3)	Δ Density (%TD)
Z	10.65	10.68	0.26
Z(Al)1	10.53	10.56	0.26
Z(Al)2	10.51	10.54	0.32
Z(Al)3	10.47	10.51	0.30
Z(Nb)1	10.54	10.57	0.31
Z(Nb)2	10.50	10.53	0.27
Z(Nb)3	10.54	10.55	0.08

It is evident that the densities of resintered pellets increased in all experiments. The results were very similar to the standard pellet except in Z(Nb)3, which has the lowest increase in density. The data presented in Table 5 are plotted in Fig. 1 and Fig. 2.

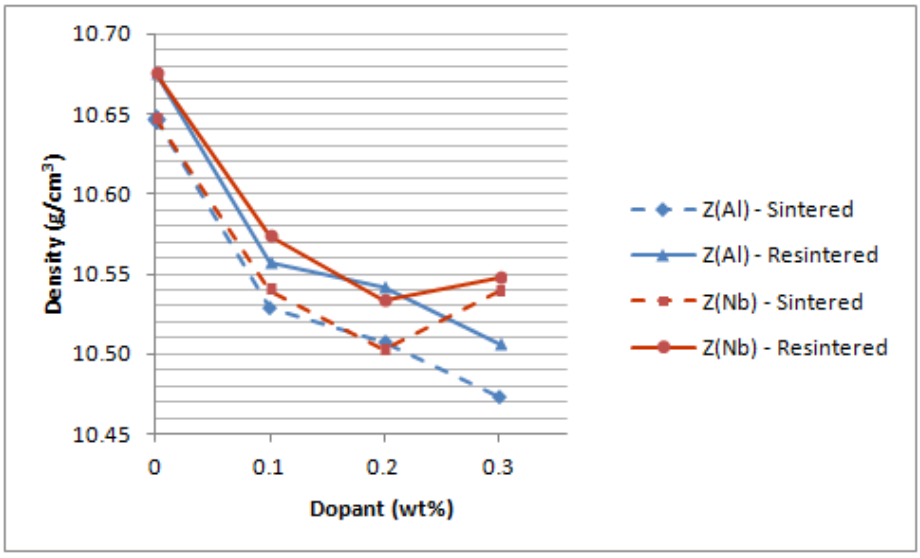

Figure 1: Variation of sintered and resintered densities with dopant additions.

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 to 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 0.3 wt%. Earlier studies have shown similar behaviors [4,9,14].

The decrease in sintered density observed in Fig. 1 might be explained by the Kirkendall effect [15], which relates pore formation concerning the difference between the solubility of dopant on UO_2 matrix and vice-versa. When the cation from dopant enters into UO_2 matrix, the original state (or shape) from the oxide generate a pore, decreasing thus the sintered density. The higher the dopant addition, the lower the sintered density, except by the Z(Nb)3 sample.

It is a fact that the ratio of H_2O to H_2 in the sintering atmosphere affects sintered density. 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, resulting in difference on solubility. A previous work [14] 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 $5.0x10^{-4}$, a stable niobium oxide was Nb_2O_5 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 in reducing atmosphere.

The behavior of Z(Nb)3 sample might be explained by the higher increase in U diffusion atoms by niobium solubilization on UO_2 matrix than pore formation by Kirkendall effect, which would imply in a faster difusional effect than pore formation. Since the substitution of the Nb^{4+} for the U^{4+} ions do 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 implies increases in uranium ions diffusion, resulting a higher densification. Bellow 0.2 wt% of this additive, the mechanism of pore former by Kirkendall effect might be faster than the difusional effect of uranium ions, which would explain the slight decrease of density from 10.54 to 10.50 g/cm^3 for Z(Nb) samples.

Regarding the resintering behavior, it is clear that, for Al_2O_3 addition, the behavior after 24 h in H_2 atmosphere under 1708ºC followed almost the same rule of sintered pellets; the higher the alumina content, the lower the resintered densities (Fig. 1).

The niobia-doped pellets showed similar behavior but a difference with 0.3 wt%, the lowest densification. Fig. 2 shows the difference between the resintered and sintered densities as a function of dopant addition. The variations are almost the same for both dopants until 0.2 wt and, after that, for niobia addition, the value decrease drastically till 0.08 wt%. This result indicates that the sample Z(Nb)3 did not densify as expected and the result is not in agreement with INB specification limit.

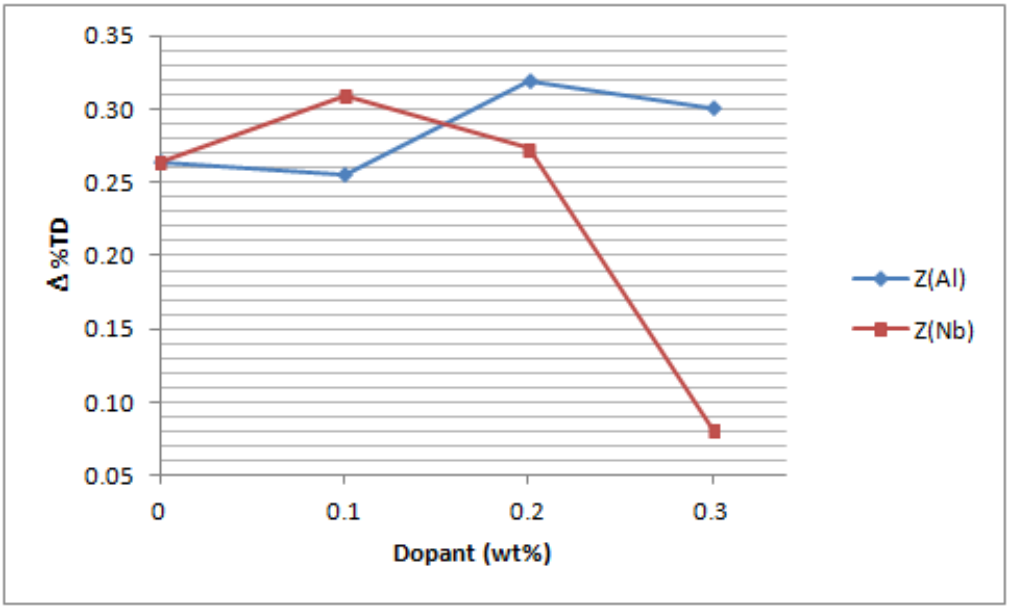

Figure 2: Variation of difference between resintered and sintered densities (Δ %TD) as a function of dopants additions.

Fig. 3 shows the values of sintering variation (%TD) emphasizing the INB specification limits (red lines).

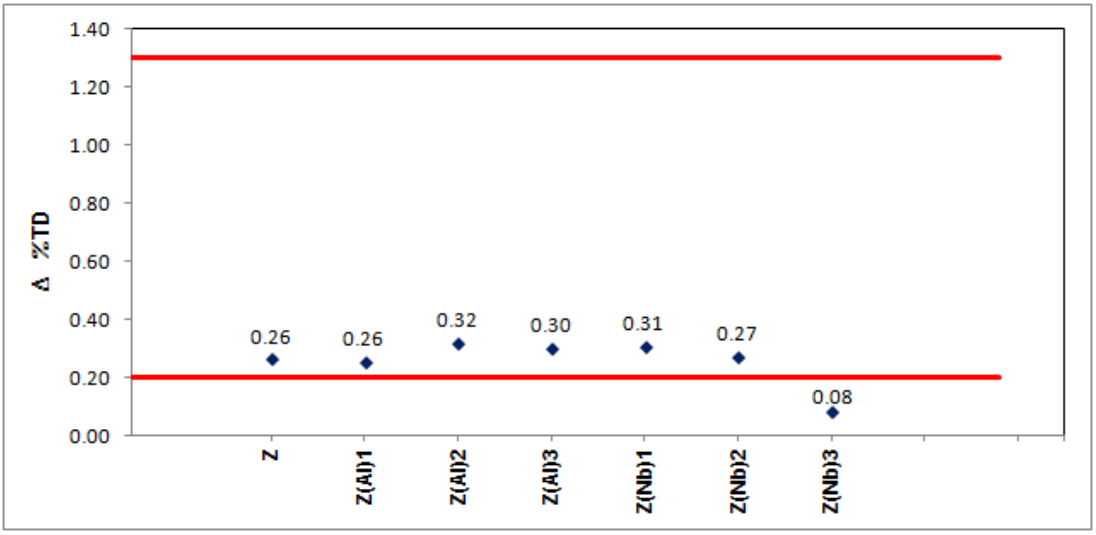

Figure 3: Variation of difference between resintered and sintered densities (Δ %TD) emphasizing the INB specification limits (red lines).

The results indicate that all samples are in accordance with INB specification limits except by one, the Z(Nb)3 test. This result excludes the possibility of using this percentage in a production line since the thermal stability test must be satisfied. The diffusion of U ion in this sample might be suppressed by the continuity of Kirkendall effect of niobium precipitates formed during sintering, as showed as white spots in optical microscopy presented in Fig. 4. Therefore, the net effect would be the sum of densification through increasing in U diffusion [16] (lower at this stage because the lower solubility of Nb-rich phase precipitate when compared to niobium oxide) and the pore formation by Kirkendall

effect with the higher impact of pore formation. Another set of experiments are under development to better understand the phenomenon.

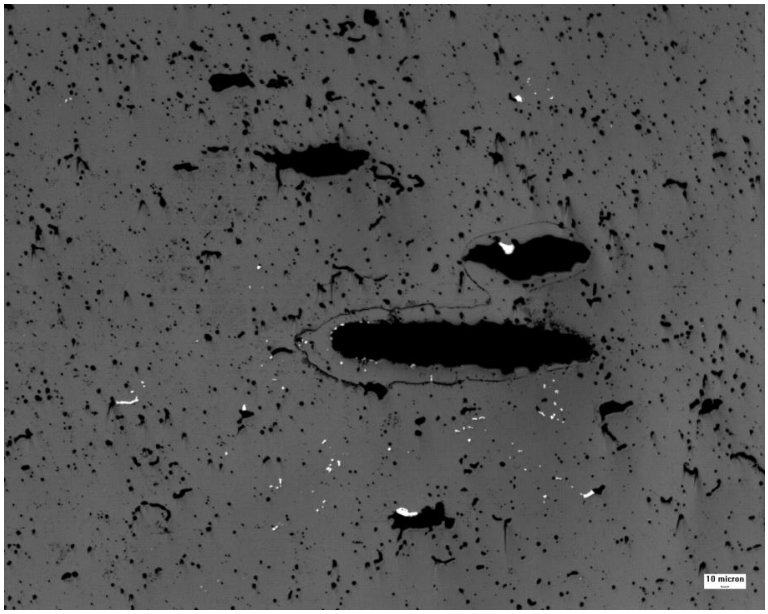

Figure 4: Precipitates and pore shapes presented in Z(Nb)3 samples before resintering process.

4. CONCLUSIONS

The thermal stability test of UO_2-doped pellets was successfully carried out at INB. The results of sintered densities indicate that the alumina addition decreases the density in a rate of about 0.03 g/cm^3 for each 0.1 wt% added, and the niobia showed a different behavior above 0.2 wt%; the value increases up to 10.54 g/cm^3 in Z(Nb)3 sintered sample. The density decrease in sintered pellets might be related to the Kirkendall effect, where porosity is formed as the difusional processes occurs.

The resintering behavior showed that all samples were in agreement with INB specification and, therefore, could be used as a dopant at INB large scale plant. Only Z(Nb)3 sample showed a different behavior; the resintering density was the lowest one and might be related to the suppress of densification by Kirkendall effect, mainly owing to the precipitates observed on Z(Nb)3 samples. New experiments are under development in order to understand better the system.

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