EFFECTS OF U₃O₈ ADDITION ON MICROSTRUCTURE OF UO₂-DOPED AND UNDOPED CERAMIC FUEL PELLETS

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ABSTRACT

The effects of U₃O₈ addition (recycled material) on microstructure of UO₂-doped and undoped pellets have been investigated. The U₃O₈ powder was obtained by oxidation of a mix of defected pellets and grinding sludge, at 380°C in air atmosphere, for 20 h. Two tests were carried out: 1) tests “Z”: UO₂, ADS (0.2 wt%) and dopants (0.1-0.5 wt% of Al₂O₃ and Nb₂O₅); and 2) tests “M”: adding U₃O₈ (12 wt%) to the Z tests. The pellets were pressed and then sintered at 1760°C during for 5.7h under wet hydrogen atmosphere. The results showed that 12 wt% of U₃O₈ decreased the densities by about 0.20 g/cm³ in all tests. Regarding the grain growth, the values increased with dopants addition till 29.3 μm (niobia) and 14.1μm (alumina). When U₃O₈ were added (B.E.T.=0.8 m²/g), the average values diminished because the lower sinterability of the mix powder with U₃O₈ (lower specific surface area).

Key-words: U₃O₈, doping technology, grain growth, niobia, alumina.

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 ceramic 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, 5, 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 both 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 UO₂ powder used to manufacture the pellets was obtained at INB Reconversion Plant by commercial Ammonium Uranyl Carbonate (AUC) route.

In this work, INB has made various experiments in laboratory scale so as to know the influence of U₃O₈ on sintered density and average grain size of UO₂-doped and undoped sintered pellets. Additionally, the influence of both dopants was also analyzed in this paper.

**MATERIALS AND METHODS**

**Preparation of U₃O₈ powder**

The U₃O₈ powder was obtained by the oxidation of a mix of defected UO₂ pellets and grinding sludge (mass ratio: 0.6/0.4, respectively), during 20 hours at 380°C in air atmosphere. The orthorhombic U₃O₈ phase has an about 30% larger lattice volume than the cubic UO₂ phase, so UO₂ defected pellets are spontaneously pulverized by the stress involved in the oxidation process (8). Later than the oxidation process, the U₃O₈ formed was then sieved in a sieve of 350 μm.

**Preparation of the Blends**

In order to analyze the effects of U₃O₈ and dopants on UO₂ pellets microstructure and sintered density, two background experiments were made. The first one was called “Z”, in which only UO₂ and aluminum distearate (ADS), a solid lubricant, were used (UO₂ + 0.2 wt% ADS). The second one was named as “M”, in which 12 wt% of U₃O₈ was added to the mixture Z to obtain another blend with the following composition: 89.8 wt% UO₂ + 0.2 wt% ADS + 12.0 wt% U₃O₈. This blend is identical to the large scale production of INB Pelletizing Process.
The blends were prepared using Al₂O₃ (> 99.5%, ALCOA calcined alumina – APC G) and Nb₂O₅ (> 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. Tab. 1 shows the samples and their identifications.

<table>
<thead>
<tr>
<th>Dopants wt % (g Metal/g U)</th>
<th>Z*</th>
<th>M*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃</td>
<td>Nb₂O₅</td>
<td>Al₂O₃</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.

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 H₂O to H₂ gas corresponded to 5.0 x 10⁻⁴). Afterwards, samples of UO₂ pellets were sent to the Physical Characterization Laboratory to quantify the sintered density and the average grain sizes. The first one was performed by water immersion method. Sintered pellets were sectioned longitudinally and then polished. So as 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.

RESULTS AND DISCUSSIONS

Sintering density

The UO₂ pellets were manufactured and identified according to the Tab. 1. The average results for sintered density were calculated and are plotted in Fig. 1.
Figure 1: Variation of sintered density with both dopants and U₃O₈ additions.

Without any addition of U₃O₈, the sintered density obtained was 10.58 g/cm³ for Z test (0% of additive). This value was reduced to 10.51 g/cm³ owing to the U₃O₈ addition.

It is clear that the U₃O₈ addition decreases the sintered density. Previous authors (14) have studied the U₃O₈ 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 U₃O₈ wt%, the density of UO₂ 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 U₃O₈, the sintered density will decrease more when the oxidizing temperature is higher.

Regarding the U₃O₈ and dopants additions, it is clear that the densities decreased in both M(Al) and M(Nb) tests. As mentioned above, 12 wt% of U₃O₈ decreased the density from 10.58 (Z test) to 10.51g/cm³ (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/cm³ for each 0.1 wt% of dopants added. In other words, the U₃O₈ addition decreased the sintered densities of both samples in a factor of about 0.20 g/cm³. This reduction is associated to the fact that the specific surface area of U₃O₈ powder is much lower than UO₂ powder (6.1 times lower in this study), resulting in a powder with lower sinterability (10).
Average Grain Size

The average grain sizes of UO₂ sintered pellets were obtained in order to evaluate the influence of U₃O₈ and both dopants on grain growth. Fig. 2 shows the evolution of the average grain sizes as a function of dopants content (wt%).

![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).

Fig. 3 portrays a comparison between the undoped and alumina doped UO₂ pellets microstructures for Z and M samples.

![Microstructures of Z and M samples for alumina doped pellets.](image)
The microstructures presented before 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 content. 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. 4 presents these data.

Figure 4: Microstructures of Z and M samples for niobia doped pellets.

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. Considering 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 UO$_2$ doped pellets (7, 15). The stable form of niobium oxides, with dew point of -30°C ($\text{H}_2\text{O}/\text{H}_2 = 5.0 \times 10^{-4}$), is Nb$_2$O$_5$ below 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 process. Yet, the substitution of Nb$^{4+}$ ion for the U$^{4+}$ ion does not cause the creation of any extrinsic defects in UO$_2$ structure. This way, the enhancement in grain growth cannot be explained by this mechanism. So, it is supposed that the Nb$^{4+}$ ions enter interstitially in the UO$_2$ 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.

**CONCLUSIONS**

UO$_2$-doped pellets were successfully manufactured at INB in a laboratory scale. The U$_3$O$_8$ addition decreased the sintered densities of both samples in a factor of about 0.20 g/cm$^3$, because the specific surface area of the U$_3$O$_8$ powder is much lower (6.1 times) than UO$_2$ powder, resulting in a powder with lower sinterability. The alumina addition decreased the sintered density in a rate of 0.03 g/cm$^3$ 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/cm$^3$ in Z(Nb)5 sample.

Comparing with those undoped UO$_2$ 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 Nb$^{4+}$ ion in UO$_2$ 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 U$_3$O$_8$ addition.

**ACKNOWLEDGMENTS**

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REFERENCES

11. OHÅI, D. Large grain size UO₂ sintered pellets obtaining used for burn up extension. *Transactions of the 17th International Conference on Structural Mechanics in Reactor Technology (SMiRT 17)*, Prague, Czech Republic, August 17-22, Paper # C02-3 2003.