

THE SINTERING BLOCKAGE MECHANISM IN THE $\text{UO}_2\text{-Gd}_2\text{O}_3$ SYSTEM

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ABSTRACT

The incorporation of gadolinium directly into nuclear power reactor fuel is important from the point of reactivity compensation and adjustment of power distribution enabling thus longer fuel cycles and optimized fuel utilization. The incorporation of Gd_2O_3 powder directly into the 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. This is due to blockages during the sintering process. There is little information in published literature about the possible mechanism for this blockage and this is restricted to the hypothesis based on formation of a low diffusivity Gd rich $(\text{U,Gd})\text{O}_2$ phase. The objective of this investigation has been to study the blockage mechanism in this system during the sintering process, contributing thus, to clarify the cause for the blockage. Experimentally it has been shown that the blocking mechanism is based on pore formation because of the Kirkendall effect, instead the formation of low diffusivity phases. The formation of a solid solution during the intermediate stage of sintering leads to formation of large pores, which are difficult to remove in the final stage of sintering. The phenomenon is better characterized as a concurrence between formation and elimination of pores during sintering than as a sintering blockage.

1. Introduction

The demand for extended fuel cycles and higher target burnups is a strong incentive to use Gd_2O_3 as a burnable poison in modern Pressurized Water Reactors. This type of fuel is being proposed to be implanted in Brazil according to the future requirements established for Angra II Nuclear Power Plant. The Brazilian Nuclear Industries (INB) has recently implanted a fuel pellets fabrication unit that adopts the ammonium uranyl carbonate (AUC) technology to produce the UO_2 fuel. Due to the good characteristics of the UO_2 powder derived from AUC [1], the fabrication process of the $\text{UO}_2\text{-Gd}_2\text{O}_3$ fuel adopts the dry mechanical blending method to prepare the mixed powders. In this process, the Gd_2O_3 powder is incorporated to the UO_2 powder and homogenized without additional milling, pre-pressing and granulating steps, which are necessary when the UO_2 powder is derived from other methods for the conversion of UF_6 [2].

Nevertheless, the incorporation of Gd_2O_3 powder to the AUC deriving UO_2 powder by the most attractive commercial method of dry mechanical blending leads to difficulties while obtaining sintered $\text{UO}_2\text{-Gd}_2\text{O}_3$ pellets with the minimum required density [3,4], due to the deleterious effect of the Gd_2O_3 on the traditional UO_2 sintering behavior. The initial sintering stage up to 1200 °C is identical for both UO_2 and $\text{UO}_2\text{-Gd}_2\text{O}_3$ fuels. Nevertheless, above 1200 °C the shrinkage of the $\text{UO}_2\text{-Gd}_2\text{O}_3$ pellets is delayed, the sintering rate is decreased and the densification is shifted to higher temperatures. As a consequence, the final sintered density is significantly lower than the traditional density obtained in sintering the pure UO_2

fuel [3]. This bad sintering behavior was confirmed experimentally in this work (see Figure 1), whose result is very similar to the one obtained by Manzel and Dörr [3]. As the AUC technology is already implanted at INB, the method to produce $\text{UO}_2\text{-Gd}_2\text{O}_3$ fuel pellets would be the dry mechanical blending. So, it was started an research program aiming at investigating the possible causes for explaining the bad sintering behavior of the $\text{UO}_2\text{-Gd}_2\text{O}_3$ fuel prepared by this method.

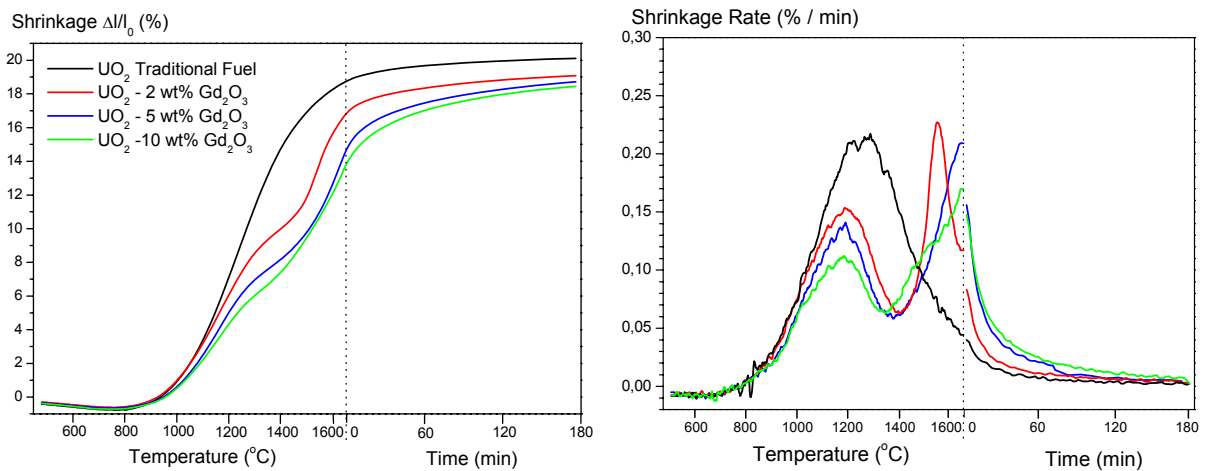


Fig 1. Effect of gadolinia content on the sintering behavior of $\text{UO}_2\text{-Gd}_2\text{O}_3$ fuel pellets

In the first part of this program, it was studied a sintering blockage mechanism based on the formation of low diffusivity Gd rich $(\text{U,Gd})\text{O}_2$ phases that could actuate as a diffusion barrier during the sintering process. Although low diffusivity phases with crystalline structure different from the fluorite were detected in our previous work (probable rhombohedral structure), this hypothesis was not supported by the experimental results. In the present work, the investigation program was continued and another hypothesis was investigated, which was based on the formation of stable pores during the formation of the solid solution simultaneously with the sintering process. This hypothesis was named the Pore Formation Hypothesis.

The formation of closed porosities during sintering the $\text{UO}_2\text{-Gd}_2\text{O}_3$ fuel has been reported in the literature [5,6,7]. In our previous work, the interdiffusion studies carried out in $\text{UO}_2/\text{Gd}_2\text{O}_3$ couples revealed that the penetration of the gadolinium into the UO_2 is considerably greater than the penetration of the uranium into the Gd_2O_3 . This result shows that an unbalancing in material transport during the solid solution formation occurs while sintering the $\text{UO}_2\text{-Gd}_2\text{O}_3$ fuel prepared by the dry mechanical blending method, where Gd_2O_3 agglomerates are dispersed in a UO_2 matrix before sintering. The gadolinium cations diffuse more quickly into the UO_2 phase than the opposite, and a greater flow of gadolinium deriving from the Gd_2O_3 agglomerates in direction to the UO_2 phase is established, when compared with the uranium flow in direction to the interior of the Gd_2O_3 agglomerates. In this situation is probable the occurrence of the Kirkendall effect. The UO_2 phase expands for receiving the extra gadolinium cations and a void is generated at the place of the original Gd_2O_3 agglomerate. This phenomenon is commonly observed in mixed powders systems where exists an unbalanced diffusivity or solubility between the powders [8]. As an example, in the $\text{UO}_2\text{-Y}_2\text{O}_3$ system the maximum solubility of uranium in the cubic Y_2O_3 (C form) is 7-8 mol% [9]. The maximum solubility of uranium in the B form Gd_2O_3 (monoclinic) is only 2 mol% [10,11]. On the other hand, gadolinium diffuses easily into the UO_2 fluorite structure, which shows a wide range of gadolinium concentration where solid solution is formed.

2. Testing the Pore Formation Hypothesis

If the Kirkendall effect is really occurring, it is expected a swelling in the $\text{UO}_2\text{-Gd}_2\text{O}_3$ fuel pellet when solubilizing the Gd_2O_3 agglomerates in the UO_2 matrix at same time when the pores are formed. According to the proposed hypothesis, it should happen two simultaneous

phenomena during the sintering of the $\text{UO}_2\text{-Gd}_2\text{O}_3$ system. One of them is the shrinkage of the pellet as a result of the sintering process. The other is the swelling that follows the solid solution formation, which generates pores in the places where originally existed Gd_2O_3 agglomerates as a result of the Kirkendall effect. In this case, the sintering blockage should not be understood as a blockage, but as a competition between two independent and opposite phenomena (shrinkage and dilatation) that happen simultaneously during the sintering process.

This experimental evidence was obtained by separating the two opposed phenomena: the shrinkage due to the sintering process and the dilatation due to the pore formation due to the Kirkendall effect. A dilatometric test was conducted where the reducing H_2 atmosphere was substituted by inert argon atmosphere. As the O/U ratio of the original UO_2 powder was 2.15, the amount of U^{5+} cations present was considerable. If the sintering atmosphere is strongly reducing, these cations are reduced to U^{4+} under low temperatures (about $400\text{ }^\circ\text{C}$), before the beginning of the sintering process. On the other hand, if the atmosphere is inert the U^{5+} cations originally present in the $\text{UO}_{2.15}$ powder remain in this oxidation state during the sintering process. As the diffusivity of the U^{5+} cations is much larger than the one for the U^{4+} cations, the sintering process is benefited and begins at lower temperatures and also finishes at lower temperatures. In this way, the whole sintering curve is shifted to smaller temperatures. Following this argumentation, it was possible to obtain a result where the shrinkage due to the sintering process and the dilatation due to the Kirkendall effect was separated and evidenced. The result can be observed in the curve presented in Figure 2. In this figure, the sintering curve for a $\text{UO}_2\text{-Gd}_2\text{O}_3$ pellet sintered under reducing H_2 atmosphere is also presented for comparison.

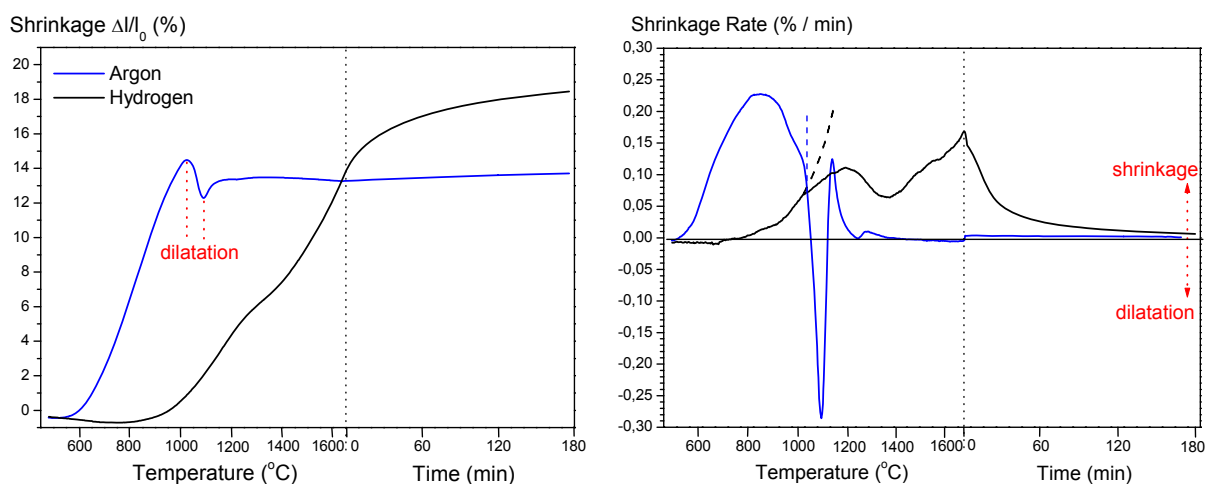


Fig 2. Sintering curves for $\text{UO}_2\text{-Gd}_2\text{O}_3$ pellets carried out under argon and hydrogen (10 wt% Gd_2O_3 , heating rate $5\text{ }^\circ\text{C}/\text{min}$)

It can be observed in Figure 2 that a dilatation process begins at temperatures above $1000\text{ }^\circ\text{C}$ in the pellet sintered under argon atmosphere. Under this atmosphere, as it was expected, the sintering begins at temperatures significantly inferior to the ones corresponding to the reducing H_2 atmosphere. That happens due to the presence of U^{5+} cations in the system. For the same reason, the whole sintering process is shifted to lower temperatures. When the solid solution formation is initiated, the shrinkage component due to the sintering process is smaller than the dilatation component due to the pore formation, which results in a dilatation that could be detected, as it is indicated in Figure 2. It can be noticed that when the pore formation due to the formation of the solid solution (Kirkendall effect) is finished, a further shrinkage is observed. This demonstrates that part of the pores formed due to the Kirkendall effect (probably the pores with smaller diameters) is eliminated together with the sintering of the UO_2 matrix, which has not been completed yet. This result demonstrates that the phenomenon is not a sintering blockage. The phenomenon is shown to be a competition between shrinkage and dilatation. Under reducing atmospheres, the dilatation component is

significantly smaller than the shrinkage component. So, the resultant is shrinkage. Therefore, in reducing atmospheres, the Kirkendall effect (pore formation) does not result in dilation, but in a decrease in the shrinkage rate during the period in which the formation of solid solution occurs. This mechanism explains the shape of the sintering curves presented in Figure 1 and in the curve obtained by Manzel and Dörr [3]. When the formation of the solid solution is completed, the shrinkage rate increases again.

In order to confirm the hypothesis, $\text{UO}_2\text{-Gd}_2\text{O}_3$ pellets were prepared with Gd_2O_3 agglomerates of controlled size, which were added to the UO_2 powder by the mechanical blending method. The Gd_2O_3 agglomerates were obtained by compacting and granulating the original Gd_2O_3 powder. The granules were classified in the size ranges $<37\ \mu\text{m}$, between 37 and 45 μm , and between 45 and 53 μm . The Gd_2O_3 concentration was 10 wt%. The $\text{UO}_2\text{-Gd}_2\text{O}_3$ mixtures prepared with Gd_2O_3 granules of different size were compacted and sintered at 1650 °C for 3 hours under H_2 atmosphere. Polished sections of the sintered pellets were observed in optical microscope and the pore diameter distributions were determined. The micrographs presented in Figure 3 show pore structures with pore diameters superior to the range typically observed in the standard UO_2 fuel fabricated starting from AUC, which varies between 0.5 μm and about 10 μm [2,12]. In those micrographs it is possible to observe a consistent increase in the diameter of the big pores with the increase in the diameter of the Gd_2O_3 granules mixed to the UO_2 powder. In the micrographs corresponding to Gd_2O_3 granules superior to 45 μm , it is possible to observe that some granules were not totally solubilized in the UO_2 fluorite structure. A growing void around the granule perimeter can be observed.

This experimental observation demonstrates that the big pores observed in the micrographs of Figure 3 were really formed at places where initially existed Gd_2O_3 granules. Those pores are responsible for the bimodal form of the pore diameter distributions. Unlike the typical monomodal distribution, which is characteristic of the standard UO_2 fuel prepared starting from AUC, all the pore diameter distributions obtained are bimodal. It is also observed that the position of the second peak of the distributions is related to the size of the Gd_2O_3 granules added. As larger are the Gd_2O_3 granules present, larger are the pore diameter corresponding to the second peak of the bimodal distribution. If the size of the Gd_2O_3 agglomerate is sufficiently small, the diameter of the pore formed due to the Kirkendall effect is incorporated in the first peak of the bimodal distribution, which results in a monomodal distribution shifted in the direction of larger diameters. The correlation between the pore diameter in the second peak of the bimodal distribution and the presence of Gd_2O_3 inside pores in formation demonstrate that those pores of larger diameter are generated starting from Gd_2O_3 agglomerates by occasion of their dissolution in the crystal lattice of UO_2 during sintering, which is resulted from the Kirkendall effect. As the formation of solid solution occurs at elevated temperatures when the pore structure is probably already essentially closed, the pores formed cannot be eliminated, at least not entirely, resulting in a sintered body with larger residual porosity. The scanning electron micrographs presented in Figure 4 illustrate the formation of pores. Part of the gadolinium of the Gd_2O_3 agglomerate was already diffused into the UO_2 matrix, but the Gd_2O_3 is not completely solubilized. This figure shows Gd_2O_3 agglomerates inside pores in formation. This was confirmed by using microanalysis, as is also shown in Figure 4. The experimental results obtained in this work corroborate the mechanism based on the formation of stable pores for explaining the sintering behavior of the $\text{UO}_2\text{-Gd}_2\text{O}_3$ fuel. Moreover, the proposed mechanism explains the strong influence that the homogeneity of the Gd_2O_3 distribution in the mixed powder exercises in the final density obtained after sintering [13]. When the Gd_2O_3 is present in the mixed powder as agglomerates with large diameter (macroscopic level of homogeneity), pores are formed during the sintering due to the solid solution formation and the occurrence of the Kirkendall effect. When the Gd_2O_3 is present as solid solution (atomic level of homogeneity), the sintering is enhanced by the presence of Gd^{3+} , which causes the uranium oxidation to U^{5+} (charge compensation) and better sintering behavior, as can be seen when sintering $\text{UO}_2\text{-Gd}_2\text{O}_3$ pellets prepared by the co-precipitation method [13,14].

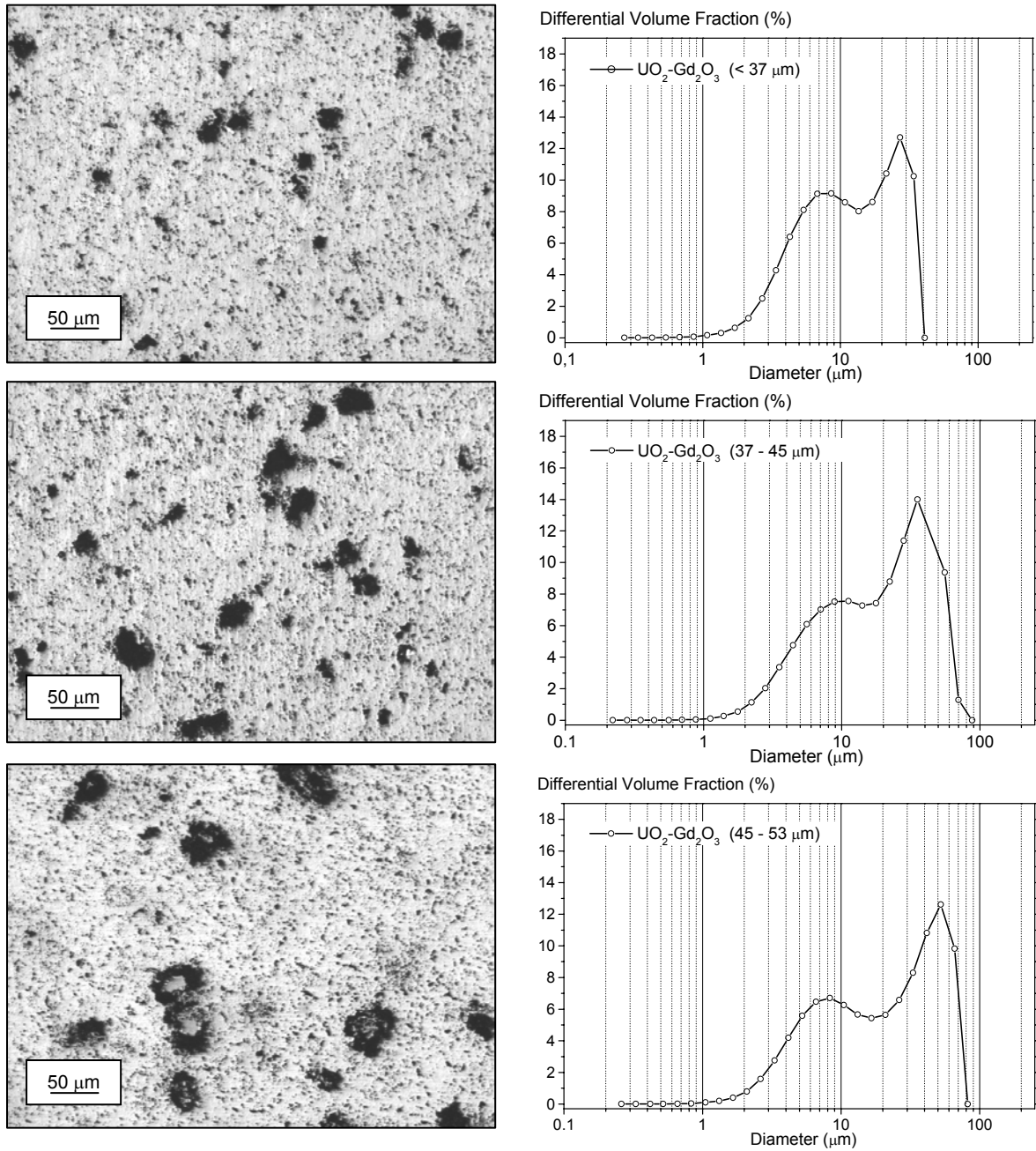


Fig 3. Pore structure of sintered $UO_2-Gd_2O_3$ pellets prepared with Gd_2O_3 granules of different sizes

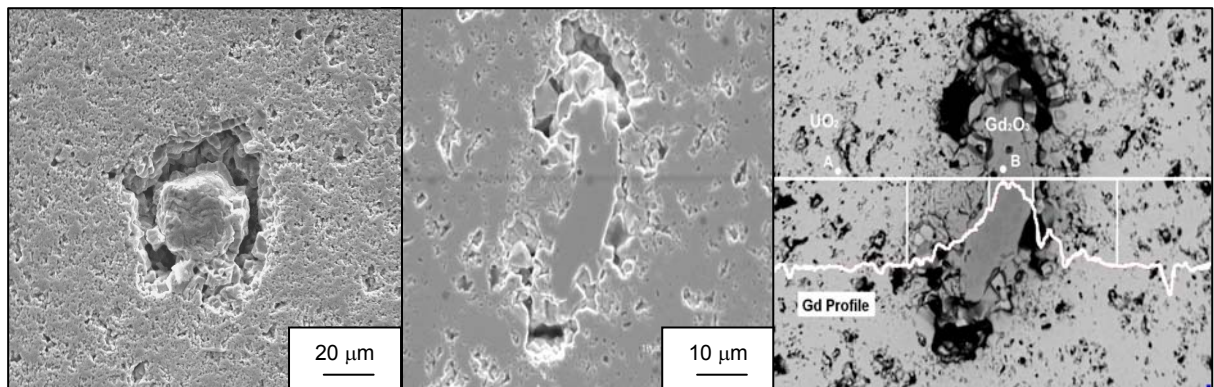


Fig 4. Scanning electron micrographs illustrating the pore formation at Gd_2O_3 original places

3. Conclusion

With base in the experimental evidences obtained in this work, the hypothesis based on the formation of stable pores can be considered demonstrated. The mechanism that explains the sintering behavior of the $\text{UO}_2\text{-Gd}_2\text{O}_3$ fuel prepared by the dry mechanical blending method and using UO_2 powder derived from the AUC technology is based on the occurrence of the Kirkendall effect. A significant difference in the interdiffusion coefficients of the gadolinium into UO_2 and of the uranium into Gd_2O_3 causes a misbalancing in the material transport during the formation of the solid solution. As a consequence of this phenomenon, the densification during sintering occurs simultaneously with the formation of pores in places where originally were present Gd_2O_3 agglomerates. The diameters of these pores are proportional to the initial diameter of the agglomerates originally present. The pores formed are stable, once they have been formed in high temperature in an essentially closed pore structure. Under this situation, it is not possible the elimination of these pores after their formation, in the subsequent sintering process. The pores remain in the sintered pellet and cause the low densities observed.

Adjustment actions in the fuel production procedures for minimizing the effects of this mechanism would probably optimize the final sintered density of $\text{UO}_2\text{-Gd}_2\text{O}_3$ fuel pellets fabricated according to the dry mechanical blending method, as following:

- a) adopt the heating rate in the sintering cycle as high as applicable technologically, to be defined with base in the resulting microstructure of the sintered pellet. A heating rate superior to $30\text{ }^\circ\text{C/minute}$ is recommended;
- b) adopt a UO_2 powder with activity adjusted in such a way that the beginning of the densification is delayed without compromising the densification in the final stages of the sintering process, or keeping a reserve of activity for sintering at elevated temperatures. The specific surface can be controlled by adjusting the conditions for reduction of the AUC powder.
- c) increase the duration of the isothermal stage of the sintering process for maximizing the densification in this stage in order to optimize the use of the activity reserve mentioned in the item b. The increase in the sintering temperature up to $1750\text{ }^\circ\text{C}$ should also be very beneficial.

Probably, a combination of the proposed adjustments in the activity of the UO_2 powder and in the sintering parameters will result in producing $\text{UO}_2\text{-Gd}_2\text{O}_3$ fuel pellets with the minimum density requested by the specification. However, a complementary work with that specific objective must still be accomplished.

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