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Technological Aspects Concerning the Production Procedures of UO_2-Gd_2O_3 Nuclear Fuel

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Abstract. The direct incorporation of Gd_2O_3 powder into UO_2 powder by dry mechanical blending is the most attractive process for producing UO_2-Gd_2O_3 nuclear fuel. However, previous experimental results by our group indicated that pore formation due to the Kirkendall effect delays densification and, consequently, diminishes the final density of this type of nuclear fuel. Considering this mechanism as responsible for the poor sintering behavior of UO_2-Gd_2O_3 fuel prepared by the mechanical blending method, it was possible to propose, discuss and, in certain cases, preliminarily test feasible adjustments in fabrication procedures that would minimize, or even totally compensate, the negative effects of pore formation due to the Kirkendall effect. This work presents these considerations.

Introduction

The demand for extended fuel cycles and higher target burnups is strong incentive for the use of Gd_2O_3 as a burnable poison in modern nuclear power reactors. This fuel has been proposed for implantation 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 ammonium uranyl carbonate (AUC) technology for UO_2 fuel production. Due to the good characteristics of UO_2 powder derived from AUC [1], the fabrication process of UO_2-Gd_2O_3 fuel adopts the dry mechanical blending method for preparing the mixed powders. In this process, Gd_2O_3 powder is incorporated into UO_2 powder and homogenized without additional milling, prepressing and granulating steps, which are required when UO_2 powder is derived from other methods for the conversion of UF_6 [2].

Nevertheless, the incorporation of Gd_2O_3 powder into AUC, deriving UO_2 powder by the most attractive commercial method of dry mechanical blending leads to difficulties in the acquisition of sintered UO_2-Gd_2O_3 pellets with the minimum required density [3,4], due to the deleterious effect of Gd_2O_3 on traditional UO_2 sintering behavior. This poor sintering behavior was confirmed experimentally in a previous work [5], as shown in the sintering curves of Figure 1. The initial sintering phase up to 1200ºC is identical for both UO_2 and UO_2-Gd_2O_3 fuels. However, above 1200ºC the shrinkage of the UO_2-Gd_2O_3 pellets is delayed, the sintering rate decreases and densification is shifted to higher temperatures. As a consequence, the final sintered density is significantly lower than the traditional density obtained when sintering pure UO_2 fuel [3].

As the AUC technology is already implanted at INB, the method of producing UO_2-Gd_2O_3 fuel pellets will be the dry mechanical blending method. Thus, a research program was initiated at IPEN aimed at investigating the possible causes of the poor sintering behavior of UO_2-Gd_2O_3 fuel prepared by the dry mechanical blending method.

In the first part of this program, a sintering blockage mechanism based on the formation of low diffusivity Gd rich $(U,Gd)O_2$ phases was studied, which could act as a diffusion barrier during the sintering process. This hypothesis was not supported by the experimental results. 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 confirmed experimentally.

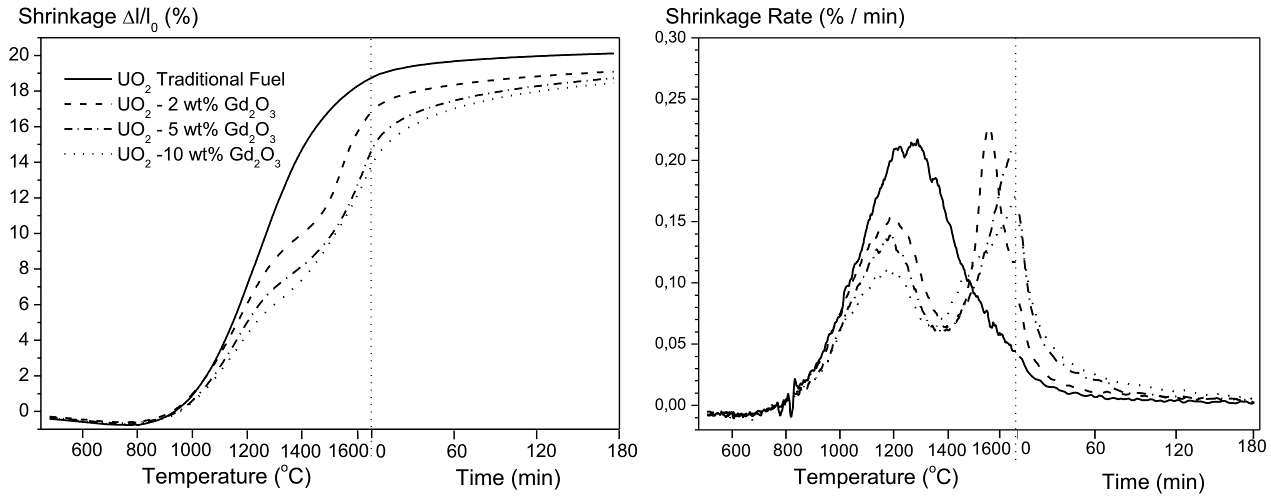

Fig. 1 - Effect of gadolinia content on the sintering behavior of UO_2-Gd_2O_3 fuel pellets.

The mechanism that explains the sintering behavior of UO_2-Gd_2O_3 fuel prepared by the dry mechanical blending method 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 misbalance in material transport during the formation of the solid solution. As a consequence, the densification during sintering occurs simultaneously with the formation of pores in locations where Gd_2O_3 agglomerates were originally present. The diameters of these pores are proportional to the initial diameter of these agglomerates. The pores formed are stable, since they are formed at high temperature in an essentially closed pore structure. Given this situation, the elimination of these pores after their formation is not possible in the subsequent sintering process. The pores remain in the sintered pellet and are the cause of the low densities observed.

The technological solution adopted industrially for this problem was the incorporation of aluminum into the UO_2 powder in the form of $Al(OH)_3$. Aluminum is incorporated in the homogenization step in concentrations varying from 5 to 500 ppm, which depends on the gadolinium concentration in the fuel [4].

Given that the mechanism that explains the insufficient densification of the UO_2-Gd_2O_3 fuel during the sintering process is known, it is possible to propose actions that could minimize or eliminate the problem. These are based on changing certain fabrication procedures, as follows:

a) activity optimization of the UO_2 powder used in the preparation of UO_2-Gd_2O_3 mixed powder, which can be achieved by adjusting the conditions for AUC reduction;
b) sintering cycle optimization by adjusting the heating rate, temperature and duration of the isothermal sintering step;
c) adjustment in the homogenization procedure of the UO_2 and Gd_2O_3 powders aimed at obtaining a mixture presenting a high level of homogeneity.

Activity optimization of the UO_2 powder

According to the results presented in Figure 1, the formation of pores due to solid solution formation began to occur at temperatures above 1000°C, during the second stage of sintering, and ended around 1350°C. Thus, when pore formation began, the densification process of the UO_2

matrix had already initiated and when pore formation was concluded, the densification process of the UO_2 matrix was at an advanced stage and the densification rate was already in decline. Under these conditions, the pores formed are difficult to eliminate, especially when the homogeneity level in Gd_2O_3 distribution is macroscopic, i.e., where large sized Gd_2O_3 agglomerates are present.

One possibility for acting on this process would be to delay the sintering process. In other words, to act on the sintering kinetics in order to determine that it occurs at higher temperatures, after the formation of the solid solution and, consequently, after pore formation. This would ensure that the pores derived from the Kirkendall effect would be formed in a more open pore structure and they could be more easily eliminated. The delay in the sintering process could be compensated in the isothermal stage of the sintering cycle. One way to achieve this objective is to reduce the activity of the UO_2 powder used to prepare the mixed powder.

This possibility was tested using UO_2 powder derived from AUC with different areas of specific surface when preparing the UO_2-Gd_2O_3 mixed powder. Controlling the activity of UO_2 powder was possible through controlling the parameters for AUC reduction. The results are presented in Figure 2.

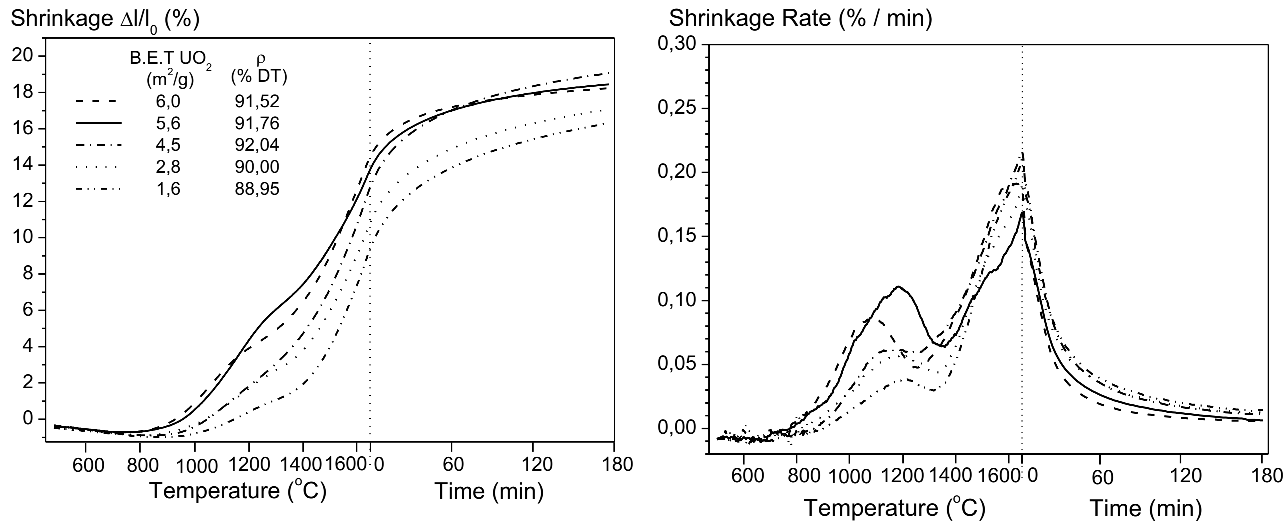

Fig. 2 - Effect of specific surface area (BET) on the sintering process of UO_2-Gd_2O_3 fuel.

Since UO_2 powders with high specific surface begin to sinter at lower temperatures, the formation of the solid solution and the consequent pore formation, due to the Kirkendall effect, occur in an essentially closed pore structure, during an advanced stage of the sintering process. For this reason, the elimination of the formed pores is difficult. In contrast, when the specific surface of the UO_2 powder is too low, although the pore formation process occurs in a more open pore structure, insufficient activity is available in the system after pore formation to promote good densification, which results in very low densities. Thus, it would seem that an optimal specific surface for UO_2 powder exists, which is not so high that it excessively closes the pore structure prior to solid solution formation and is not so low that it prejudices the sintering process of the system as a whole. The optimal specific surface would be that which provides the UO_2 powder a reserve of activity in order to guarantee that sufficient sinterability exists for densification at high temperatures, after solid solution formation. This reserve of activity for sintering at high temperatures would promote the efficient elimination of the pores formed due to the Kirkendall effect and optimize densification. In this context, densification is reinforced at temperatures above the temperature at which pore formation occurs, approximately 1350 °C, by means of a reserve of activity for sintering at elevated temperatures. In this work, the best result was obtained using UO_2 powder with a specific surface of 4.5 m^2/g. Figure 2 shows that densification during the isothermal cycle of sintering using low specific surface UO_2 powder is considerably larger than the densification observed in the case of UO_2 powder with high specific surfaces. This finding explains the results obtained by Agueda et al [6], who obtained sensibly superior densities after sintering using UO_2 powder with a smaller specific surface area.

The use of higher sintering temperatures, normally used to sinter the fuel UO_2-Gd_2O_3 (1700 to 1750°C), certainly would lead to more positive results, since the improvement observed in the sintering behavior of UO_2-Gd_2O_3 fuel in function of the control of UO_2 specific surface, by itself, did not achieve the minimum density specified for this fuel. As shown in Figure 2, the densification that occurred in the isothermal part of the sintering cycle is considerable, so an increase in isothermal sintering time should lead to higher densities in the sintered pellets. This observation was confirmed by previous results [7], which demonstrated that the additional elimination of approximately 2 vol% in the residual porosity was possible when the isothermal sintering time was increased from 3 to 6 hours.

Sintering cycle optimization

Other possibility of acting on the sintering kinetics by delaying the sintering process in order to determine that it occurs after pore formation by the Kirkendall effect, would be to increase the heating rate of the sintering cycle. If the kinetics for solid solution formation, or for pore formation due to the Kirkendall effect, occurs faster than sintering kinetics, the effect of increasing the heating rate would be beneficial in terms of residual porosity, since a larger fraction of pores formed could be eliminated in the sintering process subsequent to pore formation. A delay in the sintering process could be compensated in the isothermal stage of the sintering cycle. In order to test this possibility, UO_2-Gd_2O_3 pellets containing 10 wt% Gd_2O_3, prepared according to the dry mechanical blending method, were sintered under H_2 atmosphere using different heating rates. The heating rates varied from 1°C/min up to 90°C/min. The sintering curves obtained are presented in Figure 3. The shrinkage rates are also presented in this figure.

The positive effect of increasing the heating rate can be verified in the final sintered density, as illustrated in Figure 3. Elevation of the heating rate from 5°C/min to 30°C/min led to an increase in the final sintered density of almost 1.5 vol%. When the heating rate was very low (1°C/min), pore formation during the formation of the solid solution was very clearly observed and densification in the isothermal period was very low. In contrast, when the heating rate was superior to 10°C/min, the decrease in the shrinkage rate due to pore formation was smaller and densification at the onset of isothermal treatment was pronounced, resulting in a beneficial effect in eliminating porosity, which led to higher densities in sintered fuel pellets.

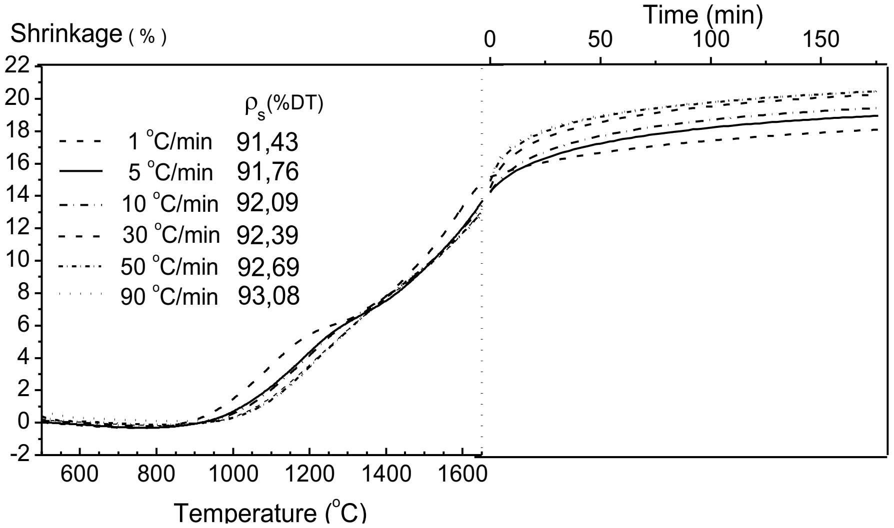

Fig. 3 - Effect of the heating rate on the sintering process of UO_2-Gd_2O_3 fuel.

Adjustment in the homogenization procedure

Previous experimental results [5] demonstrated that homogeneity in the Gd_2O_3 distribution within the mixed powder exerted a decisive influence on the sintering process of UO_2-Gd_2O_3 fuel. In other words, the better the homogeneity in the mixed UO_2-Gd_2O_3 powder, the higher the final sintered density. This behavior is explained based on the Kirkendall effect mechanism. The development of an alternative method for UO_2 and Gd_2O_3 powder homogenization, which permits good homogeneity at a microscopic level, is another possible action that could improve the sintering behavior of UO_2-Gd_2O_3 fuel.

The homogenization method should preserve the original morphology of the particles of the AUC powder, which gives good flowability to the UO_2 produced and the desirable direct pressing procedure. The use of comilling, in spite of resulting in good sintered densities (microscopic level of homogeneity), is not technologically interesting, because this procedure destroys the original morphology of the UO_2 powder, which implies the incorporation of a granulation procedure.

According to previous results [5], the coprecipitation process via AUC permitted the acquisition of good homogeneity, at a microscopic level, in the distribution of Gd_2O_3 in the UO_2-Gd_2O_3 mixed powder, which resulted in an adequate densification level during sintering. In fact, coprecipitation does not occur in the AUC case. Probably, simultaneous precipitation occurs and homogenization is achieved in the liquid phase. Ravindran et al [8] was also unable to acquire solid solution by coprecipitation via AUC. Although this method for Gd_2O_3 incorporation during the precipitation stage resulted in a homogeneity level that was adequate for obtaining sufficiently good sintered densities, this method has the disadvantage of contaminating the precipitation reactor, which would demand exclusive equipment. To avoid duplication of the precipitation installation, an alternative would be the incorporation of the Gd_2O_3 powder into the AUC suspension prior to filtration. Thus, homogenization would be achieved in a liquid media, which is much more efficient at allowing the desegregation of Gd_2O_3 powder and would permit its dispersion in individual particles among the AUC crystals. In this case, after AUC precipitation in the traditional reactor, the suspension would be pumped towards a homogenizing tank and then towards a second filter, different from that used in the process for producing the standard UO_2 fuel. In this case, the duplication of the filtration system and the installation of an additional tank for homogenization would only be required.

This proposed solution was tested in the present work at laboratory scale. However, the results were unsatisfactory, since a strong tendency for segregation of the Gd_2O_3 powder in the AUC suspension was observed, as well as an accentuated tendency for agglomeration of the Gd_2O_3 powder during filtration. Additional work is required, aimed at determining ways that guarantee good homogeneity in the suspension and filtration processes, possibly by using some type of dispersant.

The more common methods for Gd_2O_3 synthesis are based on the thermal decomposition of carbonates and hydroxides. However, using such methods, the minimum particle size obtained is limited by the sensitive tendency for agglomeration during thermal decomposition. Mazdiyani and Brown [9] developed a technique based on dynamic calcination that prevented aggregation during thermal decomposition, which made the acquisition of fine particles of Gd_2O_3 of approximately 28 nm possible. Moreover, as new applications for Gd_2O_3 have been investigated recently, mainly as an additive and dopant, new methods for its preparation have also been investigated. Ultra fine Gd_2O_3 powder was obtained by mechanochemical synthesis, resulting in particles of 0.1 μm [10,11]. The use of ultrafine Gd_2O_3 powders presenting low tendency to agglomerate could result in a good homogeneity level by adopting the technique of Gd_2O_3 incorporation into AUC, or even using the dry mechanical blending method. This action would probably minimize the sintering problems, due the decrease in the diameter of the pores formed due to the Kirkendall effect, which would lead to good sintered densities.

Conclusion

Observation revealed that a decrease in UO_2 powder activity and an increase in the heating rate of the sintering cycle exerted a positive influence on the densification process experimentally. This behavior is in agreement with the mechanism based on the Kirkendall effect. The results presented address possible adjustment actions in the fuel production procedures capable of minimizing the effects of this mechanism in order to optimize the final sintered density of UO_2-Gd_2O_3 fuel pellets fabricated according to the dry mechanical blending method, as follows:

a) adopting a heating rate in the sintering cycle as high as technologically applicable and defined based on the resulting microstructure of the sintered pellet. A heating rate of approximately 30°C/minute is recommended;

b) adopting a UO_2 powder with activity adjusted in such a manner that the onset of densification is delayed without compromising densification in the final stages of the sintering process. The specific surface can be controlled by adjusting the conditions for reduction of the AUC powder. The ideal specific surface was not precisely determined in this work, but it should be within the range of 4 to 5 m^2/g;

c) increasing the duration of the isothermal stage of the sintering process in order to maximize densification in this stage. An increase in the sintering temperature up to 1750 ºC should also be very beneficial.

It is likely that a combination of the proposed adjustments in the activity of UO_2 powder and in the sintering parameters will result in good density UO_2-Gd_2O_3 fuel pellets. However, a complementary work with that specific objective is still required.

Finally, the development of alternative techniques for homogenizing the powders, together with the use of Gd_2O_3 powder with special characteristics (low tendency to agglomerate), would probably permit the acquisition of UO_2-Gd_2O_3 fuel pellets presenting the minimum specified density. A specific work in that area is yet to be conducted.

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