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Letter to the Editor

Remarks on the sintering behavior of UO_2–Gd_2O_3 fuel

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ABSTRACT

The previous work by our group showed experimental evidence that supports the idea that a diffusion barrier is formed around Gd_2O_3 agglomerates due to the formation of gadolinium-rich $(U,Gd)O_2$ phases with low diffusivity. This would be the reason for the bad sintering behavior of the UO_2–Gd_2O_3 fuel. The objective of this investigation was to confirm that hypothesis by direct experimental evidence. Analysis of the results showed that the diffusion barrier hypothesis is not applicable.

1. Introduction

The incorporation of gadolinium directly into nuclear fuel is important for reactivity compensation, which enables longer fuel cycles. The implementation of UO_2–Gd_2O_3 poisoned fuel in Brazil has been proposed according to the future requirements established for the Angra II and Angra III nuclear power plants. The reconversion process adopted the Ammonium Uranyl Carbonate (AUC) route [1]. Following this route, Gd_2O_3 powder is incorporated into UO_2 powder using the dry mechanical blending method. Then, the UO_2–Gd_2O_3 mixed powders are directly pressed into pellet form, following sintering under reducing hydrogen atmosphere.

Various studies [2,3] have verified that the incorporation of Gd_2O_3 powder into AUC-derived UO_2 powder by dry mechanical blending leads to difficulties in preparing sintered UO_2–Gd_2O_3 pellets with the minimum required density, due to the deleterious effect of Gd_2O_3 on the traditional UO_2 sintering behavior. The sintering curves show that the lower sintered densities are due to the abnormal sintering behavior of UO_2–Gd_2O_3 fuel, compared to the sintering behavior of traditional UO_2 fuel. Dilatometric analyses show that at temperatures around 1100–1400 °C, the shrinkage of the UO_2–Gd_2O_3 pellets is delayed, the sintering rate decreases and densification shifts to higher temperatures [2,4,5]. This behavior was confirmed in a previous work by our group [6], when Gd_2O_3 powder was added to AUC-derived UO_2 powder using the dry mechanical blending route.

In recent studies concerning phase formation in the UO_2–Gd_2O_3 system [7], this phenomenon was denominated "sintering blockage" and a possible mechanism was proposed to explain the bad sintering behavior of the system. The results provided some basis for the proposition of the "diffusion barrier hypothesis". The sinterability of the system is drastically diminished for concentrations higher than 50 mol% Gd_2O_3. The cause of sinterability decrease seems to be the sudden decrease in the interdiffusion coefficient for concentrations higher than 50 mol% Gd_2O_3, as was unequivocally demonstrated by the results of the studies [7]. In compositions ranging from 0 to 100 mol% Gd_2O_3, the variation of the lattice parameter of the fluorite phase revealed the presence of other unidentified phases with different crystalline structure for concentrations higher than 50 mol% Gd_2O_3. This experimental evidence supports the proposition of a hypothesis that a diffusion barrier is formed around Gd_2O_3 agglomerates due to the formation of gadolinium-rich $(U,Gd)O_2$ phases with low diffusivity, the diffusion barrier hypothesis. The formation of such phases would be one mechanism for explaining the sintering blockage in the system. The objective of this investigation was to confirm this hypothesis by direct experimental evidence. This was achieved by performing a very simple and effective test that is described below.

2. Experimental procedure

The methodology adopted for testing the hypothesis is based on performing a sintering test in pellets prepared from mixed powders, where the Gd_2O_3 is incorporated into the UO_2 in such a way that guarantees that the diffusion barrier is not formed. In other words, the method guarantees that the Gd_2O_3 concentration never surpasses the critical value of 50 mol%. Since the formation of low sinterability phases different from fluorite begins for Gd_2O_3 concentrations higher than 50 mol%, as verified in a previous work by our group [7] and presented in Fig. 1, mixed powders were prepared by dry mechanical blending, in which pure Gd_2O_3 powder was substituted by powders prepared by coprecipitation containing Gd_2O_3 concentrations inferior to 50 mol%. Thus, the formation of phases during gadolinium solubilization with gadolinium concentrations above 50 mol% is not possible; consequently,

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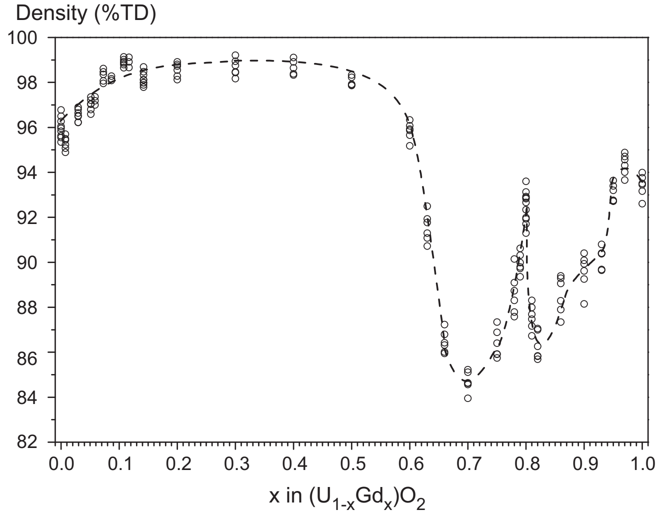

Fig. 1. Effect of gadolinium concentration on the sintered density of $(U,Gd)O_2$ pellets prepared by coprecipitation (solid solution) [7].

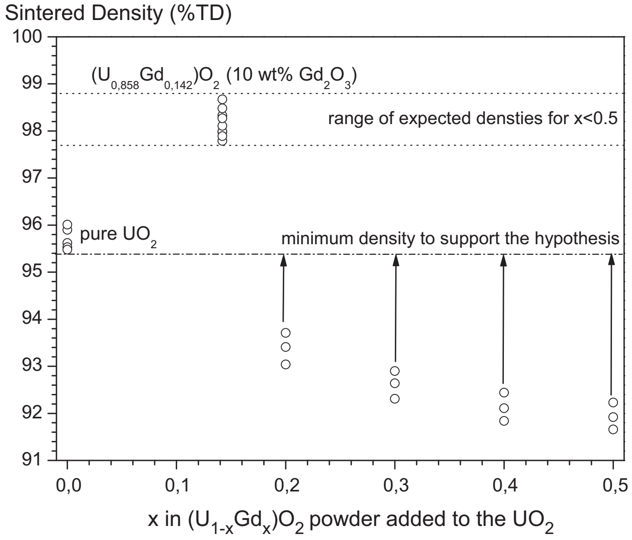

Fig. 2. Densification levels observed when sintering UO_2–Gd_2O_3 pellets prepared by mechanical blending using $(U_{1-x}Gd_x)O_2$ coprecipitated mixed powders.

the formation of the diffusion barrier also is not possible. If we have at one side mixed powders with Gd_2O_3 concentration lower than 50 mol%, which are bellow the critical value to start the formation of low diffusivity phases, and we have at the other side pure UO_2, the formation of the diffusion barrier will not be possible, and very good sintered densities are expected (≅98% TD), even better than the ones observed for pure UO_2, since the presence of gadolinium in the fluorite structure favors the sintering process, as shown in Fig. 1.

To apply this idea for testing the diffusion barrier hypothesis, powders prepared by coprecipitation via ADU, which presents good homogeneity and good sinterability, were mechanically blended with UO_2 powder by homogenizing the mixture in a shaker mixer. Powders prepared by coprecipitation with compositions of 20, 30, 40 and 50 mol% of Gd_2O_3 were added to the UO_2 powder in order to obtain the equivalent concentration of 10 wt% Gd_2O_3 (or 14.2 mol%) in each sample. The samples were pressed into pellets and sintered under the same conditions used previously (1650 °C for 3 h under H_2 atmosphere) [7]. After sintering, the densities were determined by measuring the weight of the samples immersed in xylol (the Archimedes principle). Table 1 show the scheme of sample preparation.

3. Results and discussion

Fig. 2 presents the densification levels observed in sintering UO_2–10 wt% Gd_2O_3 pellets prepared by mechanical blending using $(U_{1-x}Gd_x)O_2$ coprecipitated mixed powders.

Table 1
Scheme of sample preparation for testing the diffusion barrier hypothesis.

Value of *X* in the $(U_{1-x}Gd_x)O_2$ powder added to the UO_2 powder	Mass fraction of Gd in the $(U_{1-x}Gd_x)O_2$ powder added to the UO_2 powder	Mass percentage (wt%) of $(U_{1-x}Gd_x)O_2$ powder added to the UO_2 powder to get the final equivalent concentration of 10 wt% Gd_2O_3
0 (pure UO_2)	0	0
0.142 (UO_2–10 wt% Gd_2O_3)	0.10	100
0.2	0.144	69.59
0.3	0.224	44.76
0.4	0.309	32.34
0.5	0.402	24.89

As discussed in a previous work [7] by our group, the sinterability decrease in the UO_2–Gd_2O_3 system, or the interdiffusion coefficient decrease, is due to the formation of phases different from the fluorite structure of UO_2 (according to the diffusion barrier hypothesis), which only occurs for Gd_2O_3 concentrations above 50 mol%. Below this concentration, the only phase present is a solid solution where Gd^{3+} cations substitute U^{4+} cations in the fluorite structure, which is beneficial in terms of the sinterability of the system due to the formation of U^{5+} cations with a smaller ionic radius and higher diffusivity [8], as demonstrated by previous results reported by our group (Fig. 1). Therefore, the formation of the diffusion barrier cannot occur when pure Gd_2O_3 powder is substituted by coprecipitated powders containing Gd_2O_3 concentrations smaller than 50 mol% when preparing the mixed oxides by mechanical blending. In this case, the occurrence of areas where the gadolinium concentration exceeds 50 mol% becomes improbable and, therefore, the formation of low diffusivity phases that could act as a diffusion barrier is also improbable. Under these conditions, the presence of gadolinium should necessarily increase the sinterability of the system, even when it is added through the mechanical blending method. The sintered density expected should be that observed in sintering coprecipitated powder containing 10 wt% Gd_2O_3 (or 14.2 mol%). Based on the diffusion barrier hypothesis, the minimum acceptable sintered density is one which corresponds to that of pure UO_2 (indicated in Fig. 2), assuming that the presence of gadolinium does not affect UO_2 sinterability. The results presented in Fig. 2 show behavior that does not support the diffusion barrier hypothesis.

When the nominal Gd_2O_3 concentration in all the sintered pellets is 10 wt% (or 14.2 mol%), the formation of areas where the Gd_2O_3 concentration is superior to 50 mol% in sintering samples which are prepared with coprecipitated mixed powders with composition inferior to $(U_{0.5}Gd_{0.5})O_2$ is not possible. Since the interdiffusion coefficients remain constant between the molar fractions of gadolinium varying from 0.2 to 0.5 [7], in the range from 6 to 8×10^{-16} m^2/s, the final density expected after sintering mechanically blended mixed powders prepared with coprecipitated powders with compositions of gadolinium inferior to 50 mol% should necessarily be compatible with the density level observed in sintering pellets containing 10 wt% Gd_2O_3 prepared by coprecipitation (approximately 98% TD). Even adopting an extreme hypothesis, which would include considering that no gadolinium redistribution occurs during sintering, the minimum acceptable density that would support the diffusion barrier hypothesis is the typical density obtained when sintering pure UO_2 (approximately 95.5% TD), which did not occur. Therefore, experimental evidence supporting the hypothesis should include high sintered densities resulting from the samples prepared with mixtures UO_2–$(U_{1-x}Gd_x)O_2$, with $X \leqslant 0.5$.

Consequently, based on the experimental results obtained in testing the hypothesis, the formation of a diffusion barrier as an explanation for the sintering behavior of UO_2–Gd_2O_3 fuel pellets must be rejected as a possible mechanism.

4. Conclusion

The experimental evidence resulting from this work does not support the diffusion barrier hypothesis as an explanation for the abnormal sintering behavior of the UO_2–Gd_2O_3 system. This hypothesis was proposed in a previous work and is based on the formation of a diffusion barrier surrounding the Gd_2O_3 agglomerates due to the formation of the gadolinium-rich phases with low diffusivity. Blockage in the sintering process continues to occur even when the molar fraction of gadolinium added as $(U,Gd)O_2$ solid solution is smaller than 0.5, when the system is monophase with fluorite type crystal structure and, consequently, presents high diffusivity and high sinterability.

Another hypothesis is under investigation, based on the formation of stable pores during sintering due to the significant difference in the interdiffusion coefficients of gadolinium into UO_2 and uranium into Gd_2O_3 (the Kirkendall effect).

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