Sintering behavior of UO$_2$–Gd$_2$O$_3$ fuel: Pore formation mechanism

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Abstract

The incorporation of Gd$_2$O$_3$ has a harmful effect on traditional UO$_2$ sintering behavior. Above 1200 °C, the sintering rate decreases and the final sintered density is significantly lower. Some effort has been made to investigate the mechanism that could explain this abnormal sintering behavior of UO$_2$–Gd$_2$O$_3$ mixed fuel. A previous work concluded that the sintering difficulties of UO$_2$–Gd$_2$O$_3$ fuel cannot be explained by the formation of Gd-rich (U,Gd)O$_2$ phases with low diffusivity (diffusion barrier). This work investigates a new mechanism based on stable pore formation. Experimental observations show that gadolinium from Gd$_2$O$_3$ agglomerates preferentially diffuse into the UO$_2$ phase. The UO$_2$ matrix expands to receive extra gadolinium cations and a void is generated at the original Gd$_2$O$_3$ agglomerate site. Pores are generated when solid solution occurs in the intermediate sintering stage, making their removal more difficult in the final sintering stage. The new pores remain in the pellets after sintering.

1. Introduction

Demands for extended fuel cycles and higher target burnups are strong incentive to use Gd$_2$O$_3$ as a burnable poison in modern Pressurized Water Reactors. Due to the good characteristics of UO$_2$, the Gd$_2$O$_3$ powder is incorporated to UO$_2$ powder and homogenized with no additional milling, prepressing and granulating steps, which are necessary when UO$_2$ powder is derived from other methods for the conversion of UF$_6$ [2].

Nevertheless, the incorporation of Gd$_2$O$_3$ powder into the AUC derived UO$_2$ powder by dry mechanical blending involves some difficulties in obtaining sintered UO$_2$–Gd$_2$O$_3$ pellets with the minimum required density [3,4]. This is due to the harmful effect of Gd$_2$O$_3$ on traditional UO$_2$ sintering behavior. The initial sintering step up to 1200 °C is identical for both UO$_2$ and UO$_2$–Gd$_2$O$_3$ fuels. However, above 1200 °C, the shrinkage of the UO$_2$–Gd$_2$O$_3$ pellets is delayed, the sintering rate decreases and the densification is shifted to higher temperatures. As a consequence, the final sintered density is significantly lower than the traditional density obtained in pure UO$_2$ fuel sintering [3]. This phenomenon is denominated “sintering blockage” and was confirmed experimentally in the present work (Fig. 1). The results are very similar to those reported by Manzel and Dörr [3].

A program was initiated aimed at investigating the possible causes for this poor sintering behavior of UO$_2$–Gd$_2$O$_3$ fuel prepared by the dry mechanical blending method. In the first part of this program [5], our group studied a sintering blockage mechanism based on the formation of low diffusivity Gd-rich (U,Gd)O$_2$ phases that could actuate as a diffusion barrier during the sintering process. This hypothesis was not supported by the experimental results [6]. The investigation was continued and another hypothesis was proposed, which is based on the formation of stable pores during the formation of the solid solution simultaneously with the sintering process. This hypothesis is denominated the “Stable Pore Formation Hypothesis” and the purpose of the present work was to investigate this new mechanism in an attempt to explain the sintering behavior of UO$_2$–Gd$_2$O$_3$ fuel.

2. Experimental

All the UO$_2$–Gd$_2$O$_3$ samples used in this work were prepared according to the dry mechanical blending method [3,7]. The UO$_2$–Gd$_2$O$_3$ mixtures were prepared by mechanical blending a 1:1 UO$_2$:Gd$_2$O$_3$ master mixture in a Turbula T2C shaker mixer. Additional UO$_2$ powder was added to the master mixture to adjust the Gd$_2$O$_3$ content from 2 to 10 wt%. The UO$_2$ powder was obtained from uranium hexafluoride via AUC conversion [1,2]. The O/U ratio of UO$_2$ powder was 2.15. The Gd$_2$O$_3$ powder (99.9% pure) was supplied by Ventron Alfa Produkte. All powders were pressed into pellets with a green density of around 50% of the theoretical density.
The samples were sintered in a dilatometer up to 1650 °C, with isothermal treatment at this temperature for 180 min. The heating rate was 5 °C/min. The sintering atmosphere was pure hydrogen or inert argon. Argon atmosphere was used to anticipate the densification during sintering, as will be discussed further.

3. Results and discussion

3.1. Sustaining the hypothesis

The formation of closed porosities during the sintering of UO2–Gd2O3 fuel has been reported in the literature [8,9]. According to Yuda and Une [8], the two peaks observed in the shrinkage rate (see Fig. 1) correspond to the reaction between adjacent UO2–UO2 particles (the first peak) and to the reaction between UO2–Gd2O3 particles (the second peak). Due to the difference in sintering rates between UO2–UO2 particles and Gd2O3–UO2 particles, the researchers proposed the formation of large closed pores generated by local nonuniform volume variations caused by the difference in the densification rate resulting from reactions between UO2–UO2 particles and Gd2O3–UO2 particles. These large pores are formed at high temperatures by reacting UO2–Gd2O3 when the pore structure is already essentially closed and are therefore difficult to eliminate. The pores remain as closed pores following the sintering cycle and are the direct cause of the decreased final density of the system. In oxidizing atmospheres, sintering due to UO2–UO2 particles occurs more rapidly due to the presence of U5+ cations, which promotes higher sinterability in the system. This results in a more closed pore structure when the UO2–Gd2O3 reaction initiates, and the generation of large pores, which makes their removal more difficult. This explains the drastic decrease in the density of UO2–Gd2O3 pellets sintered under oxidizing atmosphere.

Song et al. [9] verified that the sintered density of the UO2–Gd2O3 mixed fuel decreased and new pores were formed in regions with a high Gd concentration as the oxygen potential of the sintering atmosphere increased. According to the authors, the densification delay occurs together with the formation of (U,Gd)O2 solid solution in the temperature range 1200–1450 °C. The mechanism they proposed for pore formation is based on the directional diffusion of Gd ions into the UO2 structure, which forms new pores (Kirkendall effect). Pore formation is similar under reducing and oxidizing sintering atmospheres, but the driving force for the densification of new pores is smaller under an oxidizing atmosphere, because the new pores are formed closer to the final sintering stage.

In a previous work [5], the interdiffusion studies conducted on UO2/Gd2O3 couples revealed that the penetration of gadolinium into UO2 is considerably higher than the penetration of uranium into Gd2O3. This observation confirms that the process of material transport is unbalanced during solid solution formation while sintering UO2–Gd2O3 fuel prepared by the dry mechanical blending method, where Gd2O3 agglomerates are dispersed in a UO2 matrix before sintering. The gadolinium cations diffuse more quickly into the UO2 phase than the opposite, and a higher flow of gadolinium derived from the Gd2O3 agglomerates in the direction of the UO2 phase is established, when compared with uranium flow in the direction of the interior of the Gd2O3 agglomerates. In this situation, the occurrence of the Kirkendall effect is probable. The UO2 rich phase expands to receive the extra gadolinium cations and a void is generated at the site of the original Gd2O3 agglomerate. This phenomenon is commonly observed in mixed powders systems where an unbalanced diffusivity or solubility between the powders exists [10].

According to the phase diagram of the UO2–Gd2O3 system [11], UO2 can dissolve Gd2O3 up to over 20 mol% GdO1.5. On the other hand, Gd2O3 can dissolve UO2 very slightly. The maximum solubility of uranium in the B-form Gd2O3 is about 2 mol% [11]. This fact suggests that the diffusion of Gd ions into UO2 is much more favorable than the diffusion of U ions into Gd2O3. Experimental results obtained by Song et al. [12] and by previous work [5] support the unbalanced diffusion situation.

Therefore, data from the literature [5,9,12] indicate that there is a considerable difference between the diffusion coefficients of gadolinium into UO2 and uranium into Gd2O3, which could cause an imbalance in material transport during solid solution formation when sintering UO2–Gd2O3 fuel prepared by the dry mechanical blending method.

The morphology of the Gd2O3 powder and the pore structure developed in sintered UO2–Gd2O3 pellets prepared by the dry mechanical blending method supports the pore formation hypothesis. The morphology of the Gd2O3 powder is illustrated in Fig. 2. The presence of Gd2O3 agglomerates with large diameters (>40 μm) can be verified. In sintered UO2–Gd2O3 pellets prepared by dry mechanical blending, pores are evident with diameters perceivably larger than those typically observed in pure UO2 pellets. The distribution of pore diameters is shifted toward larger diameters. This effect is illustrated in Fig. 3. In this figure, observation verifies that pore diameter distribution in pure UO2 fuel pellet is in agreement with the typical pore diameter distribution reported for UO2 fuel fabricated from AUC, which varies between 0.5 μm and 10 μm, with a mean between 3 and 4 μm [2,13]. In the sample containing 10 wt% Gd2O3, pores with diameters up to 25 μm can be observed, with the mean approximating 8 μm. This result supports...
the pore formation hypothesis, since the Gd₂O₃ agglomerates present in the system (Fig. 2) can lead to pores formation due to the Kirkendall effect during solid solution formation, which occurs simultaneously during the sintering process. Once they are formed at high temperatures, the pores cannot be totally eliminated during the sintering stage subsequent to their formation.

According to the proposed pore formation hypothesis, two simultaneous phenomena occur during the sintering of the UO₂–Gd₂O₃ system. One is pellet shrinkage resulting from the sintering process, the other is the swelling that follows solid solution formation, generating pores at sites where Gd₂O₃ agglomerates originally existed as a result of the Kirkendall effect. In this case, the sintering blockage should not be considered a blockage, but as a competition between two independent and opposite phenomena (shrinkage and dilatation) that happen simultaneously during the sintering process.

Experimental evidence to support the above proposition was obtained by separating the two opposing phenomena. That was achieved by a dilatometric test, in which the reducing H₂ atmosphere was substituted by an inert argon atmosphere. Since the O/U ratio of the original UO₂ powder used in the UO₂–Gd₂O₃ pellets preparation was 2.15, the amount of U⁵⁺ cations present was considerable. When the sintering atmosphere is strongly reducing, these cations are reduced to U⁴⁺ under low temperatures (about 400 °C), before the onset of the sintering process. In contrast, when the atmosphere is inert, the U⁵⁺ cations originally present in the UO₂.15 powder remain in this oxidation state during the sintering process. Since the diffusivity of U⁵⁺ cations is much greater than that of U⁴⁺ cations, the sintering process is benefited [14,8] and initiates at lower temperatures; it also terminates at lower temperatures. Thus, the maximum density occurs at lower temperatures.

Following this argument, it was possible to obtain results in which shrinkage due to the sintering process and dilatation due to pore formation were separated and emphasized. The results are presented in the curve shown in Fig. 4. The sintering curve for a UO₂–Gd₂O₃ pellet sintered under reducing H₂ atmosphere is also presented for comparison.

A dilatation process begins at temperatures above 1000 °C in the pellet sintered under argon atmosphere (Fig. 4). As expected, under the inert atmosphere, the sintering begins at significantly lower temperatures than those corresponding to the reducing H₂ atmosphere. Moreover, the entire sintering process shifted to lower temperatures. When solid solution formation is initiated, the shrinkage component due to sintering is smaller than the dilatation component due to pore formation (Kirkendall effect), which results in detectable dilatation (Fig. 4). When pore formation due to the formation of the solid solution is complete, further shrinkage of approximately 1% is observed. This demonstrates that some of the pores formed (probably those with smaller diameters) are eliminated together with the sintering of the UO₂ matrix, which at this point, is not yet complete.

Fig. 4 indicates that the onset of dilatation caused by pore formation corresponds to the start of the decrease in shrinkage rate observed in the sintering curve obtained for the pellet sintered under H₂ atmosphere.

This result demonstrates that the phenomenon is not a true sintering blockage. The phenomenon is better characterized as a competition between shrinkage and dilatation. Under reducing atmospheres, the dilatation component is significantly smaller than the shrinkage component, which is very significant in the temperature range in which the pore formation occurs. The overall result is shrinkage. Thus, under reducing atmospheres, pore formation does not result in dilatation, but in a decrease in the shrinkage
rate. When the formation of the solid solution is completed, the shrinkage rate increases again. This mechanism explains the shape of the sintering curves presented in Fig. 1 and that reported by Manzel and Dörr [3].

To complement verification of the hypothesis, experimental evidence revealed that the pore formation observed in the system (or dilatation) originated from the solid solution formation, when the Kirkendall effect occurs. Differential thermal analysis (DTA) was performed, in which fragments of a UO₂–Gd₂O₃ green pellet that was prepared according to the dry mechanical blending method were analyzed. The composition was 10 wt% Gd₂O₃. The experiment was conducted under argon atmosphere. Due to the low energies involved in the reaction to achieve solid solution formation, the heating rate could not be 5 °C/min, which was used in the dilatometric test. The heating rate chosen for the DTA experiment was 15 °C/min, which resulted in visible endothermic peaks.

The DTA curve obtained is presented in Fig. 5. The sintering curve is also presented in order to facilitate visualization of the direct correspondence between pore formation (dilatation) and solid solution formation.

The results presented in Fig. 5 confirm that solid solution formation, indicated by the endothermic peaks in the DTA curve, occurs at the same temperature range for which pore formation is observed. The small displacement between the start of the endothermic peak in the DTA curve and the onset of the pore formation (dilatation) in the sintering curve could be attributed to the higher heating rate adopted for the DTA experiment, which causes a small displacement of the reaction in the direction of higher temperatures.

3.2. Testing the hypothesis

Testing the hypothesis was accomplished by preparing UO₂–Gd₂O₃ pellets, in which Gd₂O₃ agglomerates of a controlled size were added to the UO₂ powder using the mechanical blending method. The Gd₂O₃ agglomerates were obtained by compacting and granulating the original Gd₂O₃ powder. The granules were classified in the size ranges <37 μm, 37–45 μm, 45–53 μm and 53–62 μm. The concentration of Gd₂O₃ was 10 wt%. The UO₂–Gd₂O₃ mixtures prepared with Gd₂O₃ granules of different sizes were compacted and sintered at 1650 °C for 3 h under H₂ atmosphere. Polished sections of the sintered pellets were examined under an optical microscope and the pore diameter distributions were determined.

The micrographs presented in Fig. 6 show pore structures with diameters greater than the range of diameters typically observed in standard UO₂ fuel fabricated from AUC, which varies from 0.5 μm to 10 μm [2,13]. A consistent increase in large pore diameter is observed with a corresponding increase in the diameter of the Gd₂O₃ granules mixed with UO₂ powder. In mixtures containing Gd₂O₃ granules greater than 45 μm, some Gd₂O₃ granules were not totally solubilized in the UO₂ matrix. A growing void around the granule perimeter can be observed.

This experimental observation verifies that the large pores observed in the micrographs of Fig. 6 were actually formed at sites where Gd₂O₃ granules initially existed. These pores are responsible for the bimodal form of pore diameter distributions presented in the respective micrographs (Fig. 6). Unlike the typical monomodal distribution, which is characteristic of the standard UO₂ fuel prepared from AUC, observation verified that all the pore diameter distributions were bimodal. Observation also confirmed that the position of the second peak in pore diameter distributions is related to the granulometry of the Gd₂O₃ granules added. The larger the Gd₂O₃ granule, the larger is the pore diameter corresponding to the second peak of bimodal distribution. If the size of the Gd₂O₃ agglomerate is sufficiently small, the diameter of the pore formed due to the Kirkendall effect is incorporated into the first peak of the bimodal distribution, resulting in a monomodal distribution shifted toward larger diameters.

![Fig. 4. Sintering curves for UO₂–Gd₂O₃ pellets under argon and hydrogen (10 wt% Gd₂O₃, 5 °C/min).](image1)

![Fig. 5. DTA curve verifying (U,Gd)O₂ solid solution formation (10 wt% Gd₂O₃, 15 °C/min, argon atmosphere).](image2)
The scanning electron micrographs presented in Fig. 7 illustrate the formation of pores due to the Kirkendall effect. Part of the gadolinium of the Gd₂O₃ agglomerate was already diffused into the UO₂ matrix, but solubilization was incomplete. This figure shows Gd₂O₃ agglomerates inside pores in formation, an observation confirmed by microanalysis (Fig. 8). The Gd concentration profile was determined through qualitative microanalysis (energy dispersive X-ray spectroscopy – EDS) over the line indicated in Fig. 8. The Gd concentration profile confirms previously reported results [5]. Gadolinium diffusion into the UO₂ matrix is notably greater than uranium penetration into the Gd₂O₃ phase. This is direct evidence that the Kirkendall effect is the cause of pore formation.

The correlation between pore diameter in the second peak of the bimodal distribution and the size of Gd₂O₃ granules, as well as the presence of Gd₂O₃ inside pores in formation, demonstrates that pores of larger diameter are generated from Gd₂O₃ agglomerates due to their dissolution in the crystal structure of UO₂ during sintering. Since the formation of solid solution occurs at elevated temperatures when the pore structure is probably essentially closed, during the second stage of sintering, the pores formed cannot be eliminated, at least not entirely, resulting in a sintered body with greater residual porosity.

The experimental results obtained in this work corroborate the mechanism of stable pore formation that explains the sintering.
behavior of the UO₂–Gd₂O₃ fuel. The proposed mechanism also explains the strong influence that the homogeneity of Gd₂O₃ distribution in the mixed powder exerts on the final density obtained after sintering [7,5].

When the Gd₂O₃ is present in the mixed powder as large diameter agglomerates (macroscopic level of homogeneity), the pores formed during the sintering process due to the Kirkendall effect are small in diameter, which makes their elimination during the subsequent sintering process possible. In addition, a larger fraction solid solution is formed in the UO₂ matrix that has high diffusivity and results in good sinterability, all of which should aid the process of eliminating the pores formed, according to the proposed mechanism.

When the Gd₂O₃ is present in the atomic level of homogeneity, gadolinium is already present as solid solution in the mixed powder, which presents high cation diffusivity, according to the model proposed by Ho and Radford [14]. This was confirmed by experimental results obtained in previous work [7,5]. Since the powder is totally homogeneous, the occurrence of the Kirkendall effect is not possible. Due to the high sinterability, high sintered densities are obtained in the sintered pellets and the sintering curve shows only one stage.

The pore formation mechanism also explains the decrease in the sintered densities with a corresponding increase in the oxygen potential of the sintering atmosphere [8,9]. In this case, since the sintering process is favored and proceeds at lower temperatures, pore formation due to the Kirkendall effect occurs in an almost totally closed pore structure, which essentially impedes their elimination, because the sintering process is essentially finished when the pores are formed. Under an oxidizing atmosphere, the phenomenon is more evident and the final sintered density obtained is even more impaired.

The pore formation mechanism also explains the influence of the specific surface of the UO₂ powder on the sintered densities of UO₂–Gd₂O₃ pellets, as reported by Agueda et al. [15]. Their results revealed that the sintered density is significantly increased when the specific surface of the UO₂ powder used to prepare the UO₂–Gd₂O₃ mixed powder by the dry mechanical blending method is decreased from 6.5 to 4.4 m²/g. When the specific surface of UO₂ powder is high, the sintering process is favored and the pore structure closes at lower temperatures, making elimination of the pores formed due to the Kirkendall effect more difficult. On the other hand, when the specific surface of UO₂ powder is low enough, the sintering process is sufficiently delayed to allow the formation of pores in a pore structure open enough to assist further elimination. Technologically, this observation indicates that an optimal activity of UO₂ powder could be used to fabricate UO₂–Gd₂O₃ fuel using the dry mechanical blending method.

Other important experimental evidence that supports the proposed mechanism, based on the formation of stable pores, was observed by Manzel and Dörr [3]. During the irradiation of UO₂–Gd₂O₃ fuel fabricated with UO₂ powder from AUC and adopting the dry mechanical blending method, the researchers observed large diameter pore formation in areas where a high concentration of Gd₂O₃ initially existed. Since the specification for fuel manufactured according to this process permits the existence of pure Gd₂O₃ in areas up to 220 μm [4], the formation of the solid solution occurs in these areas during irradiation and large pores are formed according to the stable pore formation mechanism. The formation of these pores ceases after a certain level of burnup, after solid solution formation is completed, as observed experimentally. Therefore, the mechanism demonstrated in this work also explains the formation of large pores during the irradiation of UO₂–Gd₂O₃ fuel manufactured by the dry mechanical blending method.

![Fig. 7. Scanning electron micrographs illustrating pore formation at the original sites of Gd₂O₃ agglomerates (secondary electrons).](image1)

![Fig. 8. Gadolinium concentration profile confirming the presence of Gd₂O₃ inside the pore in formation (backscattered electrons).](image2)
4. Conclusion

Based on experimental evidence presented, the hypothesis concerning stable pore formation in the UO$_2$–Gd$_2$O$_3$ system is considered proven. The mechanism that explains the sintering behavior of UO$_2$–Gd$_2$O$_3$ fuel prepared by the dry mechanical blending method and using UO$_2$ powder derived from 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$_2$O$_3$ causes an imbalance in material interdiffusion transport during the formation of a solid solution. As a consequence of this phenomenon, densification during sintering occurs simultaneously with the formation of pores at sites where Gd$_2$O$_3$ agglomerates were originally present. The diameters of these pores are proportional to the initial diameter of the agglomerates originally present. The pores formed are stable, since they are formed at high temperature with an essentially closed pore structure. Under these conditions, it is difficult to eliminate these pores after their formation, in the subsequent sintering process. The pores remain in the sintered pellet and cause the low densities observed.

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