Studies on the Sintering Behaviour of UO2-Gd2O3 Nuclear Fuel

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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 Gd2O3 powder directly into the UO2 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 (U,Gd)O2 phase. Experimental evidences indicated the existence of phases in the (U,Gd)O2 system with structure different from the fluorite type structure of UO2. The apparition of these new phases coincides with the lowering of the density after sintering and with the lowering of the interdiffusion coefficient. However, it has been shown experimentally that the sintering blockage phenomena cannot be explained on the basis of the formation of low diffusivity Gd rich (U,Gd)O2 phases. The work was continued to investigate other possible blocking mechanism.

1 INTRODUCTION

The need to improve reactor performance through longer cycle lengths or improved fuel utilization has been apparent since the beginning of commercial nuclear power generation. Among several modifications introduced as a consequence, the fuel initial enrichment has been increased, which means that the additional amount of fissile material (235U) in the reactor core has to be compensated by the introduction of additional neutron absorber material in the reactor core. This compensation was initially achieved only by using neutron absorber materials assembled in control rods or/and by addition of soluble absorber (boric acid) in the reactor coolant.

In Boiling Water Reactors (BWR), the use of soluble absorber in the coolant/moderator was prohibited for technological reasons. In Pressurized Water Reactors (PWR), the use of boric acid as a soluble absorber added to the coolant/moderator has been routinely used, but the increase in initial fuel enrichment cannot be indefinitely compensated by increasing the boric acid concentration. Beyond a certain concentration, thermal expansion of water at start-up reduces the quantity of boron in the core, resulting ultimately in a positive moderator reactivity coefficient, which is an unacceptable situation regarding to the safe reactor operation. This is the reason why the introduction of solid burnable absorbers (or burnable poison) within the fuel rods was considered.

The use of a burnable poison in nuclear reactors provides the necessary negative moderator reactivity coefficient at the beginning of core life and help shape core power distributions [1]. The poison material should have a high neutron absorption cross section and form daughter products with low absorption cross sections. Then, as soon as the irradiation proceeds, the burnable poison burns up and the macroscopic absorption cross section decreases.
From a nuclear viewpoint, gadolinia is an excellent burnable poison, having a high neutron absorption cross section coupled to a burn up rate that, if properly designed, can match approximately the $^{235}$U depletion, minimizing the reactivity penalty at end-of-cycle (EOC) [2,3]. The UO$_2$-Gd$_2$O$_3$ poisoned fuel was first introduced in 1967 in the BWR type Dresden 2 reactor and has been universally used in all commercial BWR reactors since then. The maximum Gd$_2$O$_3$ concentration usually incorporated to the BWR fuel is about 4 wt%. Its use in PWR reactors is more recent and in general requires higher Gd$_2$O$_3$ concentrations (up to 10 wt%). This type of fuel is being proposed to be implanted in Brazil according to the future requirements established for Angra II nuclear power plant.

Four different methods for the conversion of UF$_6$ to ceramic grade UO$_2$ powder have been developed to an industrial scale [4]. Two of them, the ammonium diuranate (ADU) and ammonium uranyl carbonate (AUC) processes, are based upon precipitation of uranium compounds from aqueous solution. The other two follow a dry route in which UF$_6$ is decomposed and reduced by steam and hydrogen in either fluidized beds or rotating kilns.

From all these processes, the AUC process [5] is the most attractive due to the smallest number of process steps involved. The AUC process major advantage is the good flowability of the UO$_2$ powder produced, what allow the direct pelletizing process. In the AUC process the Gd$_2$O$_3$ is universally used in all commercial BWR reactors since then. The maximum Gd$_2$O$_3$ concentration usually incorporated to the BWR fuel is about 4 wt%. Its use in PWR reactors is more recent and in general requires higher Gd$_2$O$_3$ concentrations (up to 10 wt%). This type of fuel is being proposed to be implanted in Brazil according to the future requirements established for Angra II nuclear power plant.

Two of the ammonium diuranate (ADU) and ammonium uranyl carbonate (AUC) processes, are based upon precipitation of uranium compounds from aqueous solution. The other two follow a dry route in which UF$_6$ is decomposed and reduced by steam and hydrogen in either fluidized beds or rotating kilns.

From all these processes, the AUC process [5] is the most attractive due to the smallest number of process steps involved. The AUC process major advantage is the good flowability of the UO$_2$ powder produced, what allow the direct pelletizing process. In the AUC process the Gd$_2$O$_3$ is incorporated to the UO$_2$ powder by the dry mechanical blending method. Then, the mixed UO$_2$ and Gd$_2$O$_3$ powder is directly pressed into pellet form, without pre-pressing and granulating steps [6,7]. In the other industrial processes the Gd$_2$O$_3$ powder is added to the UO$_2$ powder in the milling step, and the two powders are co-milled. The mixed powder is pre-pressed and granulated [6].

Nevertheless, the incorporation of Gd$_2$O$_3$ powder to the AUC deriving UO$_2$ powder by the most attractive commercial method of dry mechanical blending leads to difficulties while obtaining sintered UO$_2$-Gd$_2$O$_3$ pellets with the minimum required density [7,8], due to the deleterious effect of the Gd$_2$O$_3$ on the traditional UO$_2$ sintering behaviour.

As the AUC technology is already implanted at INB (Brazilian Nuclear Industries), the method to produce UO$_2$-Gd$_2$O$_3$ fuel pellets would be the dry mechanical blending method. The purpose of this work is to investigate the possible causes for explaining the bad sintering behaviour of the UO$_2$-Gd$_2$O$_3$ fuel prepared by the dry mechanical blending method. Once elucidated the sintering blockage mechanism, the final objective of the investigation program is to propose possible actions to overcome the sintering blockage, in order to obtain pellets with good sintered densities.

2 LITERATURE SURVEY ON SINTERING UO2-Gd2O3 FUEL

Several researchers report on the sintering UO$_2$-Gd$_2$O$_3$ mixed oxides, a number of them pointing to difficulties in sintering fuel pellets with the minimal specified density, of around 94 % of the theoretical density. Besides, a considerable disagreement between the published data can be observed. Despite the sintering conditions are not identical, the wide variation observed in the final densities of the sintered fuel pellets cannot be explained only based on this reason. The influence of the Gd$_2$O$_3$ content into the fuel is evident in some sintering results, but it does not appear to be significant in the others. Figure 1 summarizes the final densities achieved by different researchers in sintering UO$_2$-Gd$_2$O$_3$ pellets under reducing atmosphere. A wide range of sintered densities can be observed in this figure. Table 1 presents the main experimental conditions adopted in the sintering experiments.

The few sintering curves available in the literature show that the lower sintered densities are due to an abnormal sintering behaviour of the UO$_2$-Gd$_2$O$_3$ fuel, when compared with the sintering behaviour of the traditional UO$_2$ fuel. The dilatometric analyses show that at temperatures around 1100-1400 °C, the shrinkage of the UO$_2$-Gd$_2$O$_3$ pellets is delayed, the sintering rate is decreased and the densification is shifted to higher temperatures [7,17,18,20]. Yuda and Une [20] prepared the mixed powders by co-milling. The other researchers prepared the mixed powder by the dry mechanical blending method. The sintering atmosphere changed from very reducing to oxidizing. The sintering curves showed equivalent sintering behaviour in spite of the method for mixed powder preparation and sintering atmosphere. The sintering blockage was always evidenced.

Otherwise, sintering curves obtained in previous work [17] showed that the sintering blockage does not occur when the samples are prepared by the co-precipitation method through ADU. In this...
case, very high sintered densities are achieved under the same sintering conditions adopted in the case of dry mechanical blending samples. The co-precipitated UO$_2$-Gd$_2$O$_3$ powder is prepared by mixing uranium and gadolinium nitrates and adding a dilute ammonium hydroxide solution. The obtained material is decomposed by heating in air and reduced in a hydrogen atmosphere. The gadolinium distribution into the mixed powder is very homogeneous. This method is mostly used in laboratories to produce homogeneous pellets for measurement of cell constants and thermal properties of the (U,Gd)O$_2$ solid solutions [9,21,22].

![Graph](image)

**Figure 1:** Effect of gadolinia content on sintered density of UO$_2$-Gd$_2$O$_3$ fuel pellets.

**Table 1:** Main experimental conditions for the data presented in Figure 1

<table>
<thead>
<tr>
<th>Ref.</th>
<th>Sintering Cycle</th>
<th>UO$_2$ BET Surface (m$^2$/g)</th>
<th>Sintering Atmosphere</th>
<th>Method for Mixed Powder Preparation</th>
</tr>
</thead>
<tbody>
<tr>
<td>[9]</td>
<td>1750°C/4h</td>
<td>n.i.</td>
<td>Ar/8%H$_2$/H$_2$O</td>
<td>co-precip.</td>
</tr>
<tr>
<td>[10]</td>
<td>1650°C/4h</td>
<td>n.i.</td>
<td>N$_2$/8%H$_2$/H$_2$O</td>
<td>co-precip.</td>
</tr>
<tr>
<td>[11]</td>
<td>1750°C/4h</td>
<td>n.i.</td>
<td>25%N$_2$/75%H$_2$</td>
<td>co-milling</td>
</tr>
<tr>
<td>[12]</td>
<td>1750°C/6h</td>
<td>3.50</td>
<td>H$_2$/H$_2$O</td>
<td>co-milling</td>
</tr>
<tr>
<td>[13]</td>
<td>1620°C/3h</td>
<td>1.60</td>
<td>pure H$_2$</td>
<td>co-milling</td>
</tr>
<tr>
<td>[14]a</td>
<td>1700°C/2h</td>
<td>4.37</td>
<td>pure H$_2$</td>
<td>co-milling</td>
</tr>
<tr>
<td>[14]b</td>
<td>1700°C/2h</td>
<td>6.65</td>
<td>pure H$_2$</td>
<td>co-milling</td>
</tr>
<tr>
<td>[8]</td>
<td>1750°C/2h</td>
<td>n.i.</td>
<td>pure H$_2$</td>
<td>dry blend</td>
</tr>
<tr>
<td>[15]</td>
<td>1700°C/2h</td>
<td>3.10</td>
<td>pure H$_2$</td>
<td>dry blend</td>
</tr>
<tr>
<td>[16,17]</td>
<td>1650°C/3h</td>
<td>5.6</td>
<td>pure H$_2$</td>
<td>dry blend</td>
</tr>
<tr>
<td>[18]</td>
<td>1680°C/4h</td>
<td>5.0</td>
<td>pure H$_2$</td>
<td>dry blend</td>
</tr>
<tr>
<td>[19]</td>
<td>1650°C/4h</td>
<td>n.i.</td>
<td>N$_2$/6%H$_2$</td>
<td>dry blend</td>
</tr>
</tbody>
</table>

n.i. – not informed

114.3
As well as the densification results in sintering UO$_2$-Gd$_2$O$_3$ pellets are discrepant and contradictory, likewise are the mechanisms proposed to explain the sintering behavior.

Une and Oguma [15] rationalize the sintering behavior of the UO$_2$-Gd$_2$O$_3$ system by analogy to the UO$_2$-PuO$_2$ system. According to these investigators, when sintering UO$_2$-Gd$_2$O$_3$ fuel under reducing atmosphere, the system becomes hypostoichiometric to compensate electrically the incorporation of Gd$^{3+}$ ions in the cubic fluorite-type structure of UO$_2$. Anion vacancies are formed to balance the electrical charge. In this condition, as in the case of the UO$_2$-PuO$_2$ system, the cation diffusivity decreases under hypostoichiometric conditions that prevail during sintering, which would explain the low sintered densities achieved while sintering UO$_2$-Gd$_2$O$_3$ fuel pellets. Davis and Potter [19] also attribute the low densities achieved in sintering UO$_2$-Gd$_2$O$_3$ to the hypostoichiometric situation caused by the substitution of U$^{4+}$ ions by Gd$^{3+}$ ions, which would reduce the cation mobility and, consequently, the densification during sintering.

In opposition to the above explanation, Ho and Radford [12] explain their high densities achieved in sintering UO$_2$-Gd$_2$O$_3$ fuel pellets with base in the formation of oxygen vacancies and oxidation of U$^{3+}$ ions. According to these investigators, the electrical charge compensation due to the Gd$^{3+}$ ions incorporation in the UO$_2$ fluorite structure is accomplished by the formation of oxygen vacancies and oxidation of U$^{3+}$ ions to U$^{5+}$ and/or U$^{6+}$ ions. When Gd$^{3+}$ ions are incorporated by the UO$_2$, the oxidation of U$^{4+}$ ions to U$^{5+}$ and U$^{6+}$ ions, which have smaller ionic radii, enhances the cation diffusion and leads to high sintered densities. Above a critical level of Gd$_2$O$_3$ addition (around 6 wt%) the diffusivity is inhibited due to the association of Gd$^{3+}$ ions with U$^{5+}$ or U$^{6+}$. In this case, the associated cations should moves only by cooperative transport, which reduces the sinterability of the system. According to Ho and Radford [9], the increase in the oxygen potential reduces the oxygen vacancies concentration and also allow the creation of oxygen interstitials, which would counterbalance the formation of the small size cations (U$^{5+}$ and U$^{6+}$), reducing the diffusivity and, therefore, the sinterability. The association of cations also would be favored.

Manzel and Dörr [7] attribute the low densities observed in sintering UO$_2$-Gd$_2$O$_3$ pellets to the formation of the solid solution simultaneously with the densification process. During sintering, the interdiffusion processes decrease not only to the densification but also to the formation of solid solutions. The interdiffusion processes decrease the sintering rate and shift the densification to higher temperatures. Assmann, Pehhs and Roepenack [8] complement this property by mentioning that the diffusion coefficients in the UO$_2$-Gd$_2$O$_3$ system depend in a complex manner on the relationship U:Gd:O relation in the generated oxide phases. Peehs, Dörr, Gradel and Maier [23] detected in sintered UO$_2$-Gd$_2$O$_3$ pellets the presence of a (U$_{0.8}$Gd$_{0.2}$)O$_2$ phase, without, however, discuss its possible participation in the sintering blockage mechanism. In all these studies, the samples were prepared by the dry mechanical blending method, which used UO$_2$ powder derived from AUC. Once considered that the sintering blockage occurs during the solid solution formation, that the diffusion coefficient depends on the oxide phases formed and the observation of the (U$_{0.8}$Gd$_{0.2}$)O$_2$ phase, it can inferred that the cause proposed for the sintering blockage in the UO$_2$-Gd$_2$O$_3$ system is related to the formation of low diffusivity phases during the sintering process, which reduces the densification and leads to low sintered densities.

Yuda and Une [20] proposed that the sinterability of the UO$_2$-Gd$_2$O$_3$ system could not just be evaluated from the viewpoint of cation diffusivity. According to these investigators the two peaks observed in their sintering rate curves correspond to the reaction between adjacent UO$_2$-UO$_2$ particles (first peak) and to the reaction between adjacent UO$_2$-Gd$_2$O$_3$ particles (second peak). They proposed the formation of large closed pores due to the difference in the sintering rates between UO$_2$-UO$_2$ particles and UO$_2$-Gd$_2$O$_3$ particles, which generates local and nonuniform volumetric changes. As the large pores are formed in high temperatures, when the pore structure is already partially closed, they are difficult to be eliminated in the posterior sintering treatment. This effect is more intense in oxidizing atmospheres because the pore structure is already essentially closed when the large pores are formed. This explains the lower density observed in UO$_2$-Gd$_2$O$_3$ pellets sintered under oxidizing atmospheres.

Nishida and Yuda [11] also explain the decrease in the density of samples sintered under higher oxygen potential atmosphere on the basis of closed porosities formation. Despite the diffusivity of U and Gd ions is enhanced corresponding with the oxygen potential, under oxidizing atmospheres the
effective diffusion length necessary to form solid solution is slightly elongated due to a barrier effect of closed porosities formation, which also results in sintered density decrease. Song et al. [18] concluded that the sintered density of UO$_2$-Gd$_2$O$_3$ pellets is decreased due to the formation of new pores in the regions with high Gd concentration as the oxygen potential of the sintering atmosphere increased. The delay of densification occurs together with the solid solution formation in the temperature range of 1300-1500 °C. While the formation of (U,Gd)O$_2$ progresses, new pores are produced at the original sites of Gd$_2$O$_3$ particles as a result of the directional diffusion of Gd ions into UO$_2$. The delay of densification is mainly attributed to the formation of new pores.

The sintering results in the Figure 1 and the experimental conditions presented in the Table 1 indicate that the method for the UO$_2$-Gd$_2$O$_3$ mixed powder preparation exerts an important influence in the densification during the sintering process. This influence was confirmed by experimental results previously published, presented in the Figure 2. The level of homogeneity of the gadolinium distribution in the UO$_2$ powder determines not only the final sintered density, as well as the form of the sintering curve, as presented in Figure 3. When the homogeneity of the gadolinium distribution is good, high densities are obtained during sintering and the sintering blockage is not apparent. On the other hand, when the homogeneity of the gadolinium distribution is bad, low densities are obtained after sintering and the sintering blockage is evidenced, which occurs in two stages [17]. The mechanism proposed by Une and Oguma [15] and Davis and Potter [19] to explain the sintering behaviour of the UO$_2$-Gd$_2$O$_3$ fuel is not consistent with the results presented in Figures 2 and 3. When the gadolinium distribution into the fuel is good, as a solid solution (ADU co-precipitation route), high densities are achieved and no blockage is evidenced (see Figure 3). So, the mechanism proposed by Ho and Redford [12] seems to be valid when the gadolinium distribution is homogeneous enough.

On the other hand, when the gadolinium distribution into the fuel is not homogeneous (dry mechanical blending route), the sintering blockage is evidenced (see Figure 3) and the diffusion barrier formation mechanism (formation of Gd rich phases with low diffusivity) seems to be possible. Also, the mechanism based on the pore formation during sintering [11,18,20] must be considered possible.

In this work, it is studied the 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.
Figure 3: Effect of the mixed powder preparation method on the sintering behaviour of UO$_2$-Gd$_2$O$_3$ fuel pellets.

3 PHASES IN THE UO$_2$-Gd$_2$O$_3$ SYSTEM

Once the ADU co-precipitation method for UO$_2$-Gd$_2$O$_3$ powder and pellets preparation demonstrated to result in samples with a high gadolinium homogeneity degree (solid solution) [17], this method was selected for preparation of samples containing concentrations of Gd$_2$O$_3$ from 0 to 100 wt%. These samples made possible the accomplishment of an investigation for verifying the existence of phases with low cation diffusivity in the (U,Gd)O$_2$ system, which could base the diffusion barrier hypothesis.
3.1 Experimental

The samples were prepared by co-precipitation from ADU, starting from mixed nitrate solutions. The \( \text{UO}_2 \cdot \text{Gd}_2 \text{O}_3 \) mixed powders were fabricated with \( \text{Gd}_2 \text{O}_3 \) content in the range of 0 to 100 wt%. The gadolinium oxide, purity 99.9%, was supplied by Ventron Alfa Produkte. The \( \text{UO}_2 \) powder was obtained from uranium hexafluoride via AUC conversion. The aqueous solutions of uranyl nitrate and gadolinium nitrate were prepared by dissolving \( \text{UO}_2 \) and \( \text{Gd}_2 \text{O}_3 \) powder with 7N nitric acid solution. The uranyl and gadolinium nitrate solutions were thoroughly blended together in varying proportions up to 100 wt% \( \text{Gd}_2 \text{O}_3 \). The ADU was precipitated by adding of a 13 M \( \text{NH}_4 \text{OH} \) solution (4 ml/min) to the \( \text{UO}_2(\text{NO}_3)_2 / \text{Gd(NO}_3)_3 \) solutions at 60 °C. The final pH value was adjusted to reach pH=9. Stirring was applied with a glass rod during the addition of the solution. The precipitates were vacuum filtered and dried in an oven at 80 °C during 24 h. The dried precipitates were reduced to uranium-gadolinium oxide in a tubular furnace at 650 °C under hydrogen atmosphere.

The mixed oxide powders were pressed into pellets in the range of 2.5 to 4.0 tf/cm\(^2\) in order to obtain green densities of around 50 % of the theoretical density. Before pressing, the powders were granulated to achieve the required green density. The green pellets were sintered in a hydrogen atmosphere at 1650 °C for 3 h. The sintered densities were determined by measuring the weight of samples immersed in xylol (Archimedes principle).

3.2 Results and Discussion

The variation of the sintered densities as function of the molar fraction of gadolinium present in the sample demonstrates that exist ranges of gadolinium concentration for which the sintered densities are unequivocally decreased, as can be observed in Figure 4. An increase of the sintered density with the increase in the \( \text{Gd}_2 \text{O}_3 \) concentration occurs up to 10 wt%, as presented in the Figure 2. This increase reaches a saturation starting from the composition \( \text{(U}_{0.9}\text{Gd}_{0.1})\text{O}_2 \), when a high densification level is maintained up to the composition \( \text{(U}_{0.5}\text{Gd}_{0.5})\text{O}_2 \). In this gadolinium concentration range the sintered densities remain very high, varying in the range from 98 to 99 % of the theoretical density. These high sintered densities can be explained according to the model proposed by Ho and Radford [12], in which the presence of \( \text{Gd}^{3+} \) ions causes an increase in the cation diffusivity and, therefore, an increase in the sinterability of the \( \text{UO}_2 \).

![Figure 4: Effect of the gadolinium concentration on the sintered density of \((\text{U},\text{Gd})\text{O}_2\) pellets prepared by co-precipitation (solid solution).](image-url)
When the number of Gd atoms outreaches the number of U atoms (Gd>0.5), the sintered densities decrease drastically and reach a minimum value for the composition (U_{0.3}Gd_{0.7})O_2. The further increase in the molar fraction of gadolinium elevates the sinterability of the (U,Gd)O_2 system again, until reaching a maximum for the composition (U_{0.2}Gd_{0.8})O_2, when densities of about 93 % of the theoretical density are obtained. After this densification peak, a new decrease in the sinterability is observed. Another minimum is observed in the composition (U_{0.18}Gd_{0.82})O_2, when the densification level rises to the typical density reached in sintering pure Gd_2O_3 pellets (94 % of the theoretical density).

It is interesting to notice the behaviour of the curve presented in Figure 4 between the compositions (U_{0.3}Gd_{0.7})O_2 and (U_{0.18}Gd_{0.82})O_2, where it can be observed a peak in the sintered densities. This behaviour was confirmed through repetitions in sintering tests for the composition (U_{0.2}Gd_{0.8})O_2 and by sintering the intermediate compositions between Gd=0.7 and Gd=0.9.

The UO_2-Gd_2O_3 sintered pellets were milled and analyzed by x-ray diffraction. The lattice parameters of (U,Gd)O_2 were determined with base on the diffractograms. Figure 5 presents the variation of the lattice parameter in function of the molar fraction of gadolinium in the sample. A linear decrease on the lattice parameter occurs for compositions up to (U_{0.5}Gd_{0.5})O_2, according Vegard’s law.

This observation indicates the presence of a single phase with fluorite type structure, with Gd^{3+} ions substituting U^{4+} (solid solution). A good adjustment was obtained in a linear regression from the experimental data. The straight line can be expressed by the equation:

\[ a = 0.54636 - 0.01592 \cdot x \]  

where: \( a \) is the lattice parameter (nm) and \( x \) is the molar fraction of gadolinium.

When the molar fraction of gadolinium outreaches the value 0.5, the behaviour of the lattice parameter of the fluorite structure is not linear anymore, which indicates the end of the single-phase field. For compositions between (U_{0.25}Gd_{0.75})O_2 and (U_{0.10}Gd_{0.90})O_2, the diffractograms indicate only the presence of the body centered cubic structure, when a tendency to linear decrease on the lattice parameter with the molar fraction of gadolinium can also be observed. However, in this case, it is not possible to affirm that the Vegard’s law is obeyed, once a bad adjustment was obtained in a linear regression from the experimental data. This observation may indicate the existence of two or more...
phases in that composition range. An attempt to fit a straight line to the data is illustrated in Figure 5. The straight line can be expressed by the equation:

\[ a = 0.54809 - 0.00773 \cdot x \]  

(2)

In the intermediate range of composition between \((U_{0.5}Gd_{0.5})O_2\) and \((U_{0.25}Gd_{0.75})O_2\) it cannot be affirmed that occur the simple coexistence between the FCC and BCC phases, once the lattice parameter is not constant for none of the two structures. For compositions between \((U_{0.25}Gd_{0.75})O_2\) and \((U_{0.1}Gd_{0.9})O_2\) it also cannot be affirmed that the system is single-phase with BCC structure, once cannot be affirmed that the Vegard’s law is obeyed. Therefore, in that extensive composition range, where the molar fraction of gadolinium varies from 0.5 to 0.9, the results presented in Figure 5 indicate the existence of one or more phases different from the FCC fluorite structure of \(UO_2\) and BCC of \(Gd_2O_3\). For compositions over \((U_{0.15}Gd_{0.85})O_2\) the coexistence between the forms C and B of \(Gd_2O_3\) was evidenced, with structures BCC and monoclinic, respectively.

Aitken, Bartran and Juenke [24] observed a phase with rhombohedral structure in the U-Y-O system, with composition varying in a wide range of yttrium concentration, from 51 to 86 mol%. This phase was designated RI. A second phase was observed in this system, also with rhombohedral structure, designated RII, with composition varying between 68 and 75 mol% yttrium. These two rhombohedral phases were also observed in the U-La-O system and a third rhombohedral phase, designated RIII, was detected in the concentration range varying from 55 to 67 mol% of lanthanum [25].

These rhombohedral phases were also observed in the compounds U-R-O (R=Nd, Sm, Eu, Ho, Er, Yb and Lu) and in the rare earth R-O system, where R=Ce, Pr and Tb, which can present valences +3 and +4. Kang and Eyring [26] observed that these rare earths exhibit a family of binary oxides where coexist the valences +3 and +4, resulting in oxygen deficient fluorite related structures. Among them, the composition \(R_2O_{12}\) has the same rhombohedral structure observed in the U-Y-O system. In that and in subsequent reports [27], these researchers propose the construction of crystalline structures of a group of compounds in the R-O system by assembling modules, which are unitary cells of the fluorite structure with oxygen vacancies in different positions in the unitary cell. With base in that mechanism, these researchers established and characterized 14 different phases in the R-O system. The \(R_7O_{12}\) phase is isostructural to the rhombohedral \(UGd_2O_{12}\) phase.

The experimental observation of the phases built with base in the methodology proposed by Kang and Eyring indicates that an extensive series of phases with structure based on the fluorite structure may exist, where oxygen vacancies are distributed in different ways. This is an important conclusion; once phases that are isostructural to the phases observed by Kang and Eyring in the R-O system may probably also exist in the system U-Gd-O. The \(U^{4+}\) cation can be present in these structures substituting the \(R^{4+}\) cation. Besides, with the possibility for occurrence also of the \(U^{5+}\) and \(U^{6+}\) cations, the possibility for occurrence of phases more complex than the identified ones cannot be discarded.

Many researchers agree that the stoichiometry in the \((U,Gd)O_2\) system stays close to 2 up to the concentration of 40 mol% \(Gd_2O_3\) [9,28,29,30]. It is also noticed the occurrence of a slight hypostoichiometry in this system for this \(Gd_2O_3\) concentration range. Starting from 40 mol% \(Gd_2O_3\), Beals and Handwerk [28] observed a consistent decrease in the O/M ratio with the increase in the molar fraction of gadolinium, until the value of 1.5 is reached in the case of pure \(Gd_2O_3\). With base in the literature, it can be considered that when \(Gd^{3+}\) cations are incorporate in the fluorite structure, \(U^{4+}\) cations may be oxidized for load compensation. According to Ohmich et al [30], the formation of a small proportion of oxygen vacancies may also occurs, probably randomly distributed in the crystal lattice of the solid solution, which is evidenced by the hypostoichiometry. This mechanism, which would be the model 3 proposed by Ho and Radford [12], could be considered valid for \(Gd_2O_3\) concentrations up to 50 mol%.

Above 50 mol% in \(Gd_2O_3\), it is started a systematic formation of oxygen vacancies for load compensation. When the number of oxygen vacancies reaches a critical value, the oxygen vacancies rearranges to form new phases that would be isostructural to the ones observed and modelled by Kang and Eyring in the R-O system, as discussed previously. The rhombohedral phase would
probably be one of them. In that way, the variation on the lattice parameter as function of the molar fraction of gadolinium stops satisfying the Vegard’s law. With the continuous increase in the number of oxygen vacancies, the crystalline structure develops until obtaining the BCC structure of Gd$_2$O$_3$, where 16 oxygen vacancies are present. If the straight line that represents the variation of the lattice parameter in the composition range of $x = 0.75$ to 0.9 is extrapolated, it intercepts the ordinate axis at the value 0.5404 nm for $x = 1$ (GdO$_{1.5}$), which is very close to the x-ray diffraction standard value of 1.0813 nm for the Gd$_2$O$_3$ unitary cell, or 0.5407 nm for the pseudo fluorite cell of the GdO$_{1.5}$.

The beginning in the sinterability decrease in the UO$_2$-Gd$_2$O$_3$ system corresponds to the end of the monophase area in the system, with fluorite structure, for the composition (U$_{0.5}$Gd$_{0.5}$)$_2$O$_2$ (see Figures 4 and 5). This also corresponds to the beginning of the systematic formation of oxygen vacancies, evidenced by the decrease in the O/M ratio, which was almost constant until approximately this composition, according to the literature [28]. Although the new (U,Gd)O$_2$ phases have not been observed directly in this work, the obtained results support the proposition that the beginning of the systematic oxygen vacancies formation makes possible the formation of new (U,Gd)O$_2$ phases in the system, which are different from the fluorite phase. One very probably phase is the rhombohedral phase observed in the U-Y-O system, which should be isostructural to the one observed in the rare earth oxides CeO$_{2-x}$, PrO$_{2-x}$ and TbO$_{2-x}$. This complex phase structure would be responsible for the decrease in the cation diffusivity of the system, leading to the decrease in the sinterability. The presence of some phase with good diffusivity (not detected directly in this work) could be responsible for the form of the curve presented in Figure 4, which revealed good sinterability for the composition (U$_{0.2}$Gd$_{0.8}$)$_2$O$_2$.

The experimental results presented in the Figure 4 give base for the proposed diffusion barrier hypothesis, once molar fractions of gadolinium higher than 0.5 results in very low sintered densities. The occurrence of phases different from fluorite for molar fractions of gadolinium higher than 0.5 was also observed, what could explain the decrease in the sinterability. However, nothing can be affirmed about the dependence of the interdiffusion coefficient in the UO$_2$-Gd$_2$O$_3$ system on the gadolinium concentration, which ultimately is what determines the sinterability of the system. Aiming at complementing the hypothesis basement, an interdiffusion study in the system UO$_2$-Gd$_2$O$_3$ was accomplish, whose results are presented and discussed in the next item.

4 INTERDIFFUSION STUDIES

The interdiffusion studies were accomplished by determining the gadolinium profile concentration (penetration curves) in a couple of sintered UO$_2$/Gd$_2$O$_3$. The interdiffusion coefficient was determined in function of the molar fraction of gadolinium by applying the Matano-Boltzman method.

4.1 Experimental

The UO$_2$/Gd$_2$O$_3$ couple was prepared by compacting simultaneously both the UO$_2$ and Gd$_2$O$_3$ powders. Initially, the die cavity was filled out with Gd$_2$O$_3$ powder, which was pre-compacted at low pressure. After that, the UO$_2$ powder was introduced in the die cavity and the couple was compacted to form a solid body with density of approximately 50 % of the theoretical density, which was calculated considering the average between the UO$_2$ and Gd$_2$O$_3$ theoretical densities. The pressure for pre-compacting the Gd$_2$O$_3$ powder was very low, below the detection limit of the press. High pre-compacting pressures led invariably to a low mechanical resistance in the UO$_2$/Gd$_2$O$_3$ interface. The couple was sintered at 1650 °C for 3 hours. The heating rate was 5 °C/min. and the sintering atmosphere was pure H$_2$. The couple obtained after sintering presented good mechanical resistance in the interface, which makes possible its longitudinal cut perpendicular to the interface. The surface of the sample was prepared through conventional metallographic techniques.

Initially, a qualitative analysis was accomplished in the polished surface, where the appearance of the UO$_2$/Gd$_2$O$_3$ interface was revealed through scanning electron microscopy and the general form of the concentration profile was determined through qualitative analysis (EDS) of the gadolinium concentration over a line perpendicular to the interface. Once accomplished the observation of the
interface, three areas were selected where it was observed continuity between the pure UO$_2$ and pure Gd$_2$O$_3$ phases. In that areas, it was accomplished a quantitative analyses for the gadolinium concentration through WDS in points spaced by 0.5 µm. The precision in the determination of the gadolinium concentration was esteemed to be 0.1 %. From the penetration curves, the interdiffusion coefficient was determined through graphic integration applying the Matano-Boltzmann method.

4.2 Results and Discussion

The Figure 6 presents an electronic micrography illustrating the UO$_2$/Gd$_2$O$_3$ interface. In general, it was observed the presence of a void between the phases, with width between 1 and 3 µm. The uranium (red) and gadolinium (green) concentrations were determined along the line indicated in the Figure 6. The concentration profiles indicate interpenetration of approximately 16 µm after sintering for 3 hours at 1650 °C. The gadolinium penetration into the UO$_2$ phase is sensibly higher than the uranium penetration into Gd$_2$O$_3$ phase (higher than 2/3 of the total interpenetration distance).

An inspection was accomplished along the interface with aiming at selecting areas with good continuity between the UO$_2$ and Gd$_2$O$_3$ phases, where the width of the void was minimum. Three areas were selected, which presented a good continuity between the phases. In those areas quantitative analyses were performed for gadolinium concentration determination in points spaced 0.5 µm along a line normal to the UO$_2$/Gd$_2$O$_3$ interface line. The experimental points are presented in Figure 7. Once constructed the penetration curve, the interdiffusion coefficient in the UO$_2$-Gd$_2$O$_3$ system was calculated in function of the molar fraction of gadolinium by applying the data analysis method proposed by Matano [31].

The Matano’s method is a graphic method for the solution of the second Fick’s law, give by the differential equation:

\[
\frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left( D \frac{\partial c}{\partial x} \right)
\]

were: $c$ is concentration, $t$ is time and $x$ is position.

![Figure 6: Scanning electron micrograph illustrating the UO$_2$/Gd$_2$O$_3$ interface.](image-url)
This method was applied by using the experimental penetration curve, which was derived from the experimental data presented in Figure 7. The Figure 8 illustrates the applied methodology. As a first step, the areas bellow and above the penetration curve were integrated from \( x = 0.25 \) µm distance elements, totalizing 56 elements in the total interpenetration distance of 14 µm. The intersection between the curves of cumulative area bellow and above the penetration curve determines the position of the plane of Matano, which divides the integral of concentration in two equal parts. This position is taken as the new position zero, as it is indicated in Figure 8. That construction satisfies the condition imposed by the method: 

\[
\int_0^x \hat{c}c \, dx = 0 \tag{4}
\]

After that, it is graphically determined the integral of concentration from zero to the concentration for which it will be determined the interdiffusion coefficient, as well as the tangent of the penetration curve for that concentration. In Figure 8, the methodology is indicated for a generic concentration \( C \).

In that way, the differential equation:

\[
D = \frac{1}{2} \frac{\partial^2 c}{\partial x^2} \left[ \int_0^c x \, \partial c \right] \tag{5}
\]

is solved by knowing the area indicated in Figure 8 and the value of the tangent of the curve for the concentration \( C \):

\[
D = \frac{1}{2} \frac{1}{t} \left( \frac{1}{\text{tangent at } c} \right) \left( \text{area from } c_1 = 0 \text{ to } c \right) \tag{6}
\]

In this work, the diffusion time was considered 3 hours. The heating period up to the temperature test (1650 °C) was despised.
The interdiffusion coefficient was calculated for 0 to 100 mol% of gadolinium. The results are presented in Figure 9. The most important characteristic in this figure is the sudden decrease in the interdiffusion coefficient for gadolinium concentrations above 50 mol%. It is also interesting to observe the increase in the interdiffusion coefficient value for gadolinium concentrations of about 80 mol%. These results are in good agreement with the results presented in Figure 4, and confirm in a direct way that the interdiffusion coefficient in the $\text{UO}_2$-$\text{Gd}_2\text{O}_3$ system decreases abruptly when the molar fraction of gadolinium is higher than 0.5, or when more than half of the cations presents are $\text{Gd}^{3+}$. Although the imprecision of the applied method, which is evidenced by the considerable dispersion in the experimental data presented in Figure 7, it is conclusive that the $\text{UO}_2$-$\text{Gd}_2\text{O}_3$ sinterability decreases drastically starting from the composition $(\text{U}_0.5\text{Gd}_0.5)\text{O}_2$ due to a sudden decrease in the interdiffusion coefficient of the system starting from that composition.

The results presented in Figure 9 agree in many aspects with the results obtained by other researchers. Loose et al. [32] studied the interdiffusion in the $\text{UO}_2$-$\text{Gd}_2\text{O}_3$ system through pairs prepared starting from a pre-compacted $\text{Gd}_2\text{O}_3$ pellet positioned inside $\text{UO}_2$ powder, which were pressed simultaneously. The sintering was carried out under temperatures in the range varying from 1600 to 1900 °C during 4, 16 and 64 hours. The penetration curves were obtained starting from autoradiographies impressed by alpha particles emitted by the samples. Nishida and Yuda [11] also studied the interdiffusion in the $\text{UO}_2$-$\text{Gd}_2\text{O}_3$ system through pairs prepared in a similar way to the one adopted by Loose et al. In that case the sintering was carried out at 1700 °C and 1800 °C during 100 hours and the concentrations were determined by EDS.

These researchers also obtained complex penetration curves as the ones obtained in this work. The penetration curve obtained by Loose et al [32] in their sample sintered at 1900 °C for 64 hours has a form very similar to the form of the penetration curve obtained in this work, presented in Figure 7. With base in the form of the penetration curve, those authors concluded that it occurs other phases different from the fluorite. On the other hand, the penetration curves obtained by Nishida and Yuda [11] are considerably different from the curve obtained in this work. The reason for this discrepancy can be related to the big void observed by these researchers in the interface $\text{UO}_2$/Gd$_2$O$_3$, which had a width of about 50 µm.

Unfortunately, in these two published works, the authors despised the form of the penetration curves and they assumed that the interdiffusion coefficient was independent of the gadolinium
concentration. So, they determined the effective interdiffusion coefficient. According their results, the interdiffusion coefficient in the \( \text{UO}_2\)-\( \text{Gd}_2\text{O}_3 \) system can be calculated from the expressions:

\[
D = 3.3 \times 10^{-3} \exp(-2000000/RT) \quad (\text{cm}^2/\text{s}) \quad \text{(ref. 32)} \tag{7}
\]

\[
D = 1.0 \times 10^{-5} \exp(-2600000/RT) \quad (\text{cm}^2/\text{s}) \quad \text{(ref. 11)} \tag{8}
\]

Starting from those expressions, the interdiffusion coefficients can be calculated considering the conditions adopted in this work, or 1650 °C and 3 hours. The values \( 3.6 \times 10^{-12} \text{ cm}^2/\text{s} \) [32] and \( 0.9 \times 10^{-12} \text{ cm}^2/\text{s} \) [11] would be obtained. It can be noticed that the value obtained considering the expression formulated by Loose et al agrees reasonably well with the results obtained in this work, and is located approximately in the center of the variation range presented in Figure 9. On the other hand, the value obtained by adopting the expression determined by Nishida and Yuda can be considered low when compared with the experimental results presented in Figure 9. This conclusion can be inferred by the small interpenetration observed in the results obtained by these researchers when compared with the ones obtained in this work. Nishida and Yuda obtained an interpenetration of 25 \( \mu \text{m} \) while sintering at 1700 °C for 100 hours. In this work, under sintering conditions much less severe (3 hours at 1650 °C), it was obtained an interpenetration of 14 \( \mu \text{m} \). This discrepancy could be explained with base in the big void developed at the \( \text{UO}_2/\text{Gd}_2\text{O}_3 \) interface in the samples prepared for Nishida and Yuda (about 50 \( \mu \text{m} \)), as previously commented.

5 TESTING THE HYPOTHESIS

The presented results give base for the barrier diffusion hypothesis. The sinterability of the system is drastically decreased for concentrations higher than 50 mol% \( \text{Gd}_2\text{O}_3 \), as is unequivocally shown in Figure 4. The cause for the sinterability decrease seems to be the sudden decrease on the interdiffusion coefficient for concentrations higher than 50 mol% \( \text{Gd}_2\text{O}_3 \), is shown in Figure 9. Although they have not been detected directly, other unidentified phases with crystalline structure different from the fluorite probably exist for concentrations higher than 50 mol% \( \text{Gd}_2\text{O}_3 \), as is indicated by the variation of the lattice parameter presented in Figure 5. This observation is reinforced by the identification of a series of phases in the systems (Ce, Pr, Tb)-O, which probably have the same
crystalline structure of the phases still not identified in the system U-Gd-O, once the model for construction of these phases in the rare earth oxides is entirely applicable for the UO₂-Gd₂O₃ system.

The methodology adopted for testing the hypothesis is based on performing a sintering test in mixed powders where the Gd₂O₃ is incorporated to the UO₂ in such a way that guarantees that the diffusion barrier is not formed. In other words, it is guaranteed that the Gd₂O₃ concentration never surpasses the value of 50 mol%. As the formation of low sinterability phases different from the fluorite just begins for Gd₂O₃ concentrations higher than 50 mol%, as previously discussed, mixed powders were prepared where the pure Gd₂O₃ powder was substituted by powders prepared by coprecipitation containing Gd₂O₃ concentrations inferior to 50 mol%. In that case, the formation of phases with gadolinium concentration above 50 mol% is not possible during the gadolinium solubilisation, and the formation of the diffusion barrier also is not possible. According to the results presented in Figure 4, this new mixed powder presents sinterability higher than pure UO₂, once the presence of gadolinium in the fluorite structure favours the sintering process.

Powders obtained by coprecipitation via ADU, which presents good homogeneity, were mechanically blended with UO₂ powder by homogenizing the mixture in a shaker mixer. Powders prepared by coprecipitation with compositions of 20, 30, 40, 50, 60, 70, 80 and 90 mol% of Gd₂O₃ were added to the UO₂ powder in order to always obtain the equivalent concentration of 10 wt% Gd₂O₃ (or 14,2 mol%) in the sample. The samples were compacted and sintered under the same conditions used previously (1650 °C for 3 hours under H₂ atmosphere). After sintering, the densities were determined by measuring the weight of samples immersed in xylol (Archimedes principle). The results are presented in Figure 10.

As previously mentioned, the sinterability decrease in the UO₂-Gd₂O₃ system, or the interdiffusion coefficient decrease, is due to the formation of phases different from the fluorite structure of UO₂ (according the diffusion barrier hypothesis) and it only happens for Gd₂O₃ concentrations above 50 mol%. Below that concentration the only one phase present is a solid solution where Gd³⁺ cations substitute U⁴⁺ cations in the fluorite structure, which is beneficial in terms of sinterability of the system, as it is illustrated in Figure 4. Therefore, the formation of the diffusion barrier is unable to

![Figure 10](image-url)
happen when pure Gd₂O₃ powder is substituted by coprecipitated powders containing Gd₂O₃ concentrations smaller than 50 mol% in preparing the mixed oxides by mechanical blending. In this case, it becomes impossible the occurrence of areas where the gadolinium concentration exceeds 50 mol% in mol and, therefore, it becomes impossible the formation of low diffusivity phases that could act as a diffusion barrier. In that condition, 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 would be the one observed in sintering coprecipitated powder containing 10 wt% Gd₂O₃ (or 14.2 mol%). With base in the diffusion barrier hypothesis, the minimum acceptable sintered density would be the one correspondent to pure UO₂ (indicated in Figure 10), supposing that the presence of gadolinium does not affect the UO₂ sinterability. The results presented in Figure 10 show a behaviour that does not support the diffusion barrier hypothesis.

If the nominal Gd₂O₃ concentration in all the sintered pellets is 10 wt% (or 14.2 mol%), it is not possible the formation of areas where the Gd₂O₃ concentration is superior to 50 mol% during sintering samples which are prepared with coprecipitated mixed powders with composition inferior to \((U_{0.5}Gd_{0.5})O₂\). As the interdiffusion coefficients stay in a constant level between the molar fractions of gadolinium varying from 0.2 to 0.5 (see Figure 9), in the range from 6 to 8×10⁻¹² cm²/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% Gd₂O₃ prepared by coprecipitation (approximately 98 %TD). Even so adopting an extreme hypothesis, which would consider that does not happen any gadolinium redistribution during sintering, the minimum acceptable density that would support the diffusion barrier hypothesis would be the typical density obtained in sintering pure UO₂ (approximately 95.5 %TD), which did not also happen. Therefore, the experimental evidence that would support the hypothesis would be an abrupt increase in the sintered density obtained in the samples prepared with mixtures UO₂· (U₁₋ₓGdx)O₂, with \(x = 0.5\). Low densities should be observed only for values of \(x\) superior to 0.5 in the formula, once, in that case, the formation of low diffusivity phases is possible.

Consequently, with base in the experimental results obtained in testing the hypothesis, the formation of a diffusion barrier to explain the sintering behaviour of UO₂·Gd₂O₃ fuel pellets must be rejected as a possible mechanism.

6 CONCLUSIONS

The presence of phases different from the fluorite structure of UO₂ was indirectly detected. These phases have low diffusivity and occur when the molar fraction of gadolinium surpasses the value of 0.5. These phases could not be identified in this work, but they should be isostructural to the series of phases recently identified in the systems Ce-O, Pr-O and Tb-O. Despite this experimental evidence, the hypothesis more frequently proposed to explain the sintering behaviour of the UO₂·Gd₂O₃ fuel was not proven experimentally in this work. The hypothesis is based on the formation of a diffusion barrier around the Gd₂O₃ agglomerates due to the formation of the gadolinium rich phases with low diffusivity. The blockage in the sintering does happen even when the molar fraction of gadolinium added as \((U,Gd)O₂\) solid solution is smaller than 0.5, when the system is monophase with fluorite type crystal structure and has high diffusivity.

Another hypothesis is under investigation, which is based on the formation of stable pores during sintering due to the significant difference in the interdiffusion coefficients of the gadolinium into UO₂ and of the uranium into Gd₂O₃ (Kirkendall effect).

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