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Effect of Mixed Powder Homogeneity on the UO_2-Gd_2O_3 Nuclear Fuel Sintering Behavior

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Abstract. Gadolinium oxide homogeneously mixed with uranium dioxide nuclear fuel is used as burnable poison in modern nuclear reactors. Direct incorporation of gadolinium to the fuel is important to provide longer fuel cycles and to optimize the fuel utilization by reactivity compensation and power distribution adjustment. According to the published data, the results on sintering UO_2-Gd_2O_3 compacts are contradictory and apparently very sensitive on the mixed powder production route. The incorporation of Gd_2O_3 powder to the UO_2 powder by the most attractive commercial method of dry mechanical blending leads to technological difficulties for attending to the specified density of sintered fuel pellets. Otherwise, good sintered densities are obtained when the co-precipitation route is adopted to prepare the mixed fuel powder. This work presents the results in sintering UO_2-Gd_2O_3 compacts prepared by mechanical dry blending of both ceramic powders and by two co-precipitation methods. The results showed that the final sintered density and the gadolinium distribution homogeneity observed in the sintered fuel pellets are directly related to the homogeneity of the initial powder mixture. The powders prepared by the different methods presented different sintering behavior. Possible mechanisms are proposed to explain the divergent sintering behaviour.

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 (^{235}U) in the reactor core has to be compensated by the introduction of additional neutron absorber material in the reactor core. 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). The use of UO_2-Gd_2O_3 poisoned fuel in PWR reactors in general requires Gd_2O_3 concentrations up to 10 wt%.

From the different industrial methods for the conversion of UF_6 to ceramic grade UO_2 powder [2,4], the AUC process [3] 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. All the other processes need additional milling, pressing aids addition (lubricant, binder), homogenization, pre-compacting and granulating steps [4]. In the AUC process the Gd_2O_3 powder is incorporated to the UO_2 powder by blending a master mix of UO_2/Gd_2O_3 with ratio 1:1, which is added to the bulk of the UO_2 powder and homogenized. Then, the mixed UO_2 and Gd_2O_3 powder is directly pressed into pellet form, without pre-pressing and granulating steps [4,5]. In the other processes the Gd_2O_3 powder is added to the UO_2 powder in the milling step, and the two powders are co-milled [4]. Another method to produce the UO_2-Gd_2O_3 fuel is based on the co-precipitation of the mixed uranium and gadolinium nitrates. This method is mostly used in laboratories to produce homogeneous pellets [6,7].

Several researchers report on the sintering UO_2-Gd_2O_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_2O_3 content into the fuel is evident in some sintering results, but it does not appear to be significant in the others.

Considering this apparent discrepant sintering behavior, this work was done to achieve additional information on the UO_2-Gd_2O_3 sintering behavior that can help to clarify the cause of this sintering data disagreement. This work is directed to study the sintering behavior of UO_2-Gd_2O_3 mixed powder produced by the commercially attractive AUC process, which is simpler than the available and has been studied at IPEN since 1985 [8]. This process was recently chosen to be installed in industrial scale.

Experimental

The samples were prepared by co-precipitation from ADU and AUC, starting from mixed nitrate solutions, and by mechanically dry mixing of both UO_2 and Gd_2O_3 powders. The UO_2-Gd_2O_3 pellets were fabricated with Gd_2O_3 content in the range of 0 to 10 wt%. The gadolinium oxide, purity 99.9 %, was supplied by Ventron Alfa Produkte. The UO_2 powder was obtained from uranium hexafluoride via AUC conversion [8].

In the co-precipitation method, the aqueous solutions of uranyl nitrate and gadolinium nitrate were prepared by dissolving UO_2 and Gd_2O_3 powders with 7N nitric acid solution. The uranyl and gadolinium nitrate solutions were thoroughly blended together in varying proportions up to 10 wt% Gd_2O_3. The ADU was precipitated by adding of a 13M NH_4OH solution to the $UO_2(NO_3)_2/Gd(NO_3)_3$ solutions at 60 °C (final pH=9). The AUC was precipitated from the mixed nitrate solutions by adding of a 3.2M NH_4HCO_3 solution at 60 °C (final pH=8.5). 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 in hydrogen atmosphere.

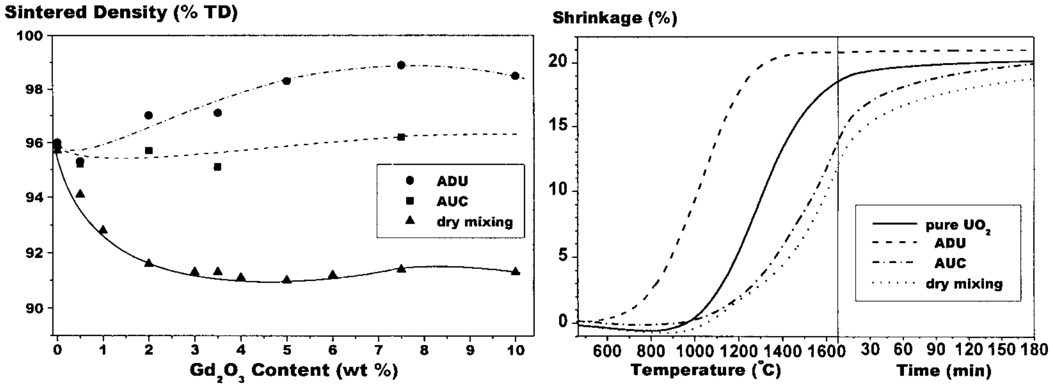
The mechanically blended samples were prepared by homogenizing a 1:1 UO_2 : Gd_2O_3 master mixture in a Turbula T2C shaker mixer. Then, additional UO_2 powder was added to the master mixture to adjust the required Gd_2O_3 composition. The total homogenization time was 40 minutes. No additives to the powders were used. The surface area of the UO_2 powder is around 5 m^2/g, typical for the UO_2 derived from AUC.

The different mixed oxide powders were pressed into pellets in the 2.5 to 4.0 tf/cm^2 range to obtain green densities around 50 % of the theoretical density. Before pressing, the powders produced from the ADU method were granulated to achieve the required green density. The green pellets were sintered in a hydrogen atmosphere at 1650 °C for 3 h. The sintering kinetics was also characterized by means of dilatometric analysis using the same sintering cycle. The heating rate was controlled to be 5 °C/min. The sintered densities were determined by measuring the weight of samples immersed in xylol (Archimedes principle).

The gadolinium distribution in the mixed powder was characterized by diffractometric analysis in the oxidized powders, since the most intense diffraction peaks for UO_2 and Gd_2O_3 are coincident. The gadolinium distribution in the sintered fuel pellets was characterized by electron probe microanalysis.

Results and Discussion

The influence of increasing concentrations of Gd_2O_3 on the sintering behavior of pellets obtained by the three methods investigated is shown in Fig. 1. As can be observed, three different sintering behaviors is evidenced, resulting in three levels of densification during the sintering, each of them apparently related to the UO_2-Gd_2O_3 powder production route.



(A) (B)

Figure 1 – Sintering behavior of UO_2-Gd_2O_3 fuel pellets prepared by the three methods studied. (A) – Effect of gadolinium content on the sintered density. (B) – Sintering curves.

As is shown in Fig. 1, in the mechanically dry mixing powders, the presence of Gd_2O_3 strongly inhibits the sinterability of the UO_2. These results are in a relatively good agreement to the obtained by Assmann et al [9] and Davis et al [10], who also used the mechanical blending route to prepare their samples. Similar to our case, these authors used the UO_2 powder derived from the AUC process. In the co-precipitated AUC derived mixed powders, the sintered densities appear to be less sensitive to the Gd_2O_3 additions. A slight tendency to increase the densification with higher Gd_2O_3 additions can be observed in Fig. 1a. This result agrees well with the ones obtained by Ho et al [11] and Littlechild et al [12]. The samples used by these authors were obtained by co-milling both the UO_2 and Gd_2O_3 powders. It seems to be clear from this presented data that a second typical sintering behavior occurred, which characterizes a second level of UO_2-Gd_2O_3 fuel densification during the sintering process. The sintering results obtained from the co-precipitated ADU derived mixed powders demonstrate that these powders have a high sinterability and the Gd_2O_3 addition enhances the fuel densification during the sintering process, as is shown in Fig. 1a. This result has also been observed by Fukushima et al [6] in sintering UO_2-Gd_2O_3 mixed powders that were derived from the ADU co-precipitation.

The low sintered densities observed for the mechanically blended powders can be explained by the sintering kinetics, as is shown in Fig. 1b for the mixed fuel containing 10 wt% Gd_2O_3. It can be observed that addition of Gd_2O_3 by this method has a pronounced effect on the sintering behavior of the fuel. Above 1100 °C the shrinkage of UO_2-Gd_2O_3 pellets is delayed, the sintering rate is decreased and the densification is shifted to higher temperatures. This behavior has also been observed by Manzel et al [5], who attribute it to the start of the formation of solid solution. On the other hand, the co-precipitate ADU mixed powder shows an inverse behavior. The shrinkage starts at lower temperature and a higher sintering rate is observed. The co-precipitated AUC mixed powder shows approximately the same behavior observed for UO_2-Gd_2O_3 fuel derived from the mechanical blending method.

The X-ray diffractograms presented in Fig. 2 show that Gd_2O_3 is distributed in the three different mixed powders in different ways. In the mechanically blended powder, the Gd_2O_3 is present in the cubic form and no modifications can be observed in the X-ray diffraction pattern for the orthorhombic U_3O_8. The co-precipitated ADU powder shows an inverse behavior, with the suppression of the U_3O_8 doublets (at $2\theta = 26°$ and $34°$) and broader diffraction peaks. Only the 100% intense diffraction peak for the bcc Gd_2O_3 ($2\theta \cong 28°$) is slightly apparent. The X-ray diffractogram obtained for the co-precipitated AUC powder shows a similar appearance to the observed for the mechanically blended powder, but the broadening of the U_3O_8 peaks and the decrease in the diffraction peaks intensity for the bcc Gd_2O_3 are evident. In the ADU co-precipitated powder most the added gadolinium may be present as solid solution. In the mechanically blended powder all the gadolinium added seems to be present as free bcc Gd_2O_3. In the AUC co-precipitated powder an intermediary situation may be occurring, with some gadolinium present as solid solution and some as free bcc Gd_2O_3. Three levels of homogeneity in the Gd_2O_3 distribution within the powder can be inferred.

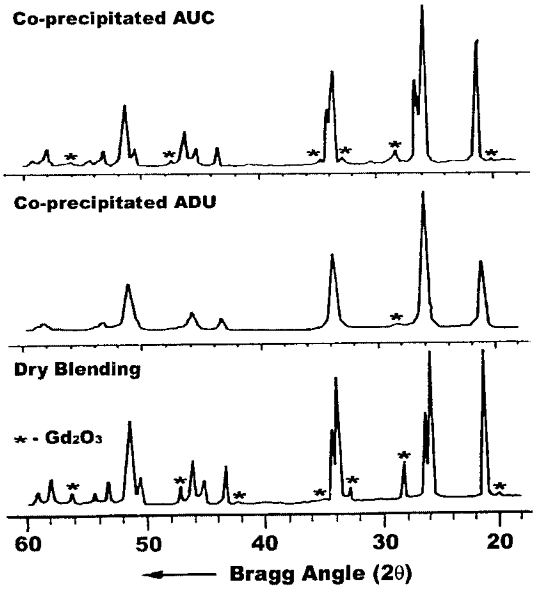
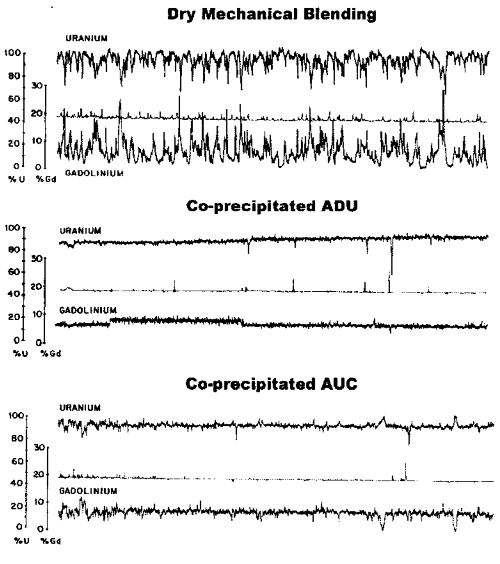


Figure 2 – X-ray diffractograms of UO_2-Gd_2O_3 oxidized at 800 °C for 3 hours.

Microprobe analysis was performed in sintered pellets prepared by the three different methods for mixed powder production. The gadolinium homogeneity distribution in the sintered mixed oxide fuel followed the same tendency observed by X-ray diffraction in the mixed powder. Also, three levels of homogeneity in the Gd_2O_3 distribution within the sintered fuel pellets were observed. The results are shown in Fig. 3.


Dry Mechanical Blending

Co-precipitated ADU

Co-precipitated AUC

Figure 3 – Electron microprobe diagrams of the UO_2-Gd_2O_3 sintered fuel pellets (7.5 wt% Gd_2O_3).

The obtained results indicate that the gadolinium distribution homogeneity, originally present in the reduced mixed fuel powder, determines the gadolinium distribution homogeneity in the sintered fuel pellets and, most importantly, the sintering behavior of the fuel. The sintering curves showed that the shrinkage is strongly influenced by the mixed powder homogeneity. The three levels of Gd_2O_3 homogeneity within the powder correspond directly to the three densification levels observed in sintering of the green pellets. The methods adopted to prepare the mixed powders give different levels of Gd_2O_3 distribution homogeneity within the powder, which can be described as following:

(a) ***Atomic Level*** – most of the Gd_2O_3 powder originally added to the UO_2 powder is present in the mixed powder as a solid solution. After the reduction, most of the gadolinium has already been incorporated in the UO_2 fcc lattice structure (fluorite type). The Gd_2O_3 is homogenized in an atomic level. This is the case of the ADU co-precipitation method.

(b) ***Microscopic Level*** – some Gd_2O_3 powder originally added is present in the mixed powder as a solid solution and some of it remain as free bcc Gd_2O_3. Probably, the co-precipitation did not occur and a fractionating precipitation is probable to have been occurred. In this case the homogenization is done in the liquid phase and a good homogeneity is achieved, in a microscopic level. This is the case of the AUC co-precipitation method.

(c) ***Macroscopic Level*** – all the Gd_2O_3 powder originally added is present in the mixed powder as free bcc Gd_2O_3. In this case the worst homogeneity is achieved and the Gd_2O_3 is present as a dispersion of agglomerates within the UO_2 powder. The high tendency of the Gd_2O_3 powder to agglomerate was observed in the present work. This is the probable reason for Manzel et al [5] applying the master mixture procedure. In this case a poor homogenization is achieved, in a macroscopic level. This is the case of the dry mechanical blending method.

Based on the results presented in the references [11,12], a good homogeneity for the Gd_2O_3 distribution within the mixed UO_2-Gd_2O_3 powder apparently can be obtained by co-milling both the powders. The homogeneity achieved by this method approaches the microscopic level and results in a sufficient sintering behavior, as was already discussed.

The mechanism to explain the UO_2-Gd_2O_3 sintering behavior and the discrepancies observed is still an open question. Ho et al [11] attributed their high sintered densities to the formation of U^{5+} ions when Gd^{3+} ions substitute the U^{4+} ions originally present in the UO_2 lattice structure. The U^{5+} ion is formed to maintain the electrical charge balance of the lattice structure. These authors postulate that the smaller size of the U^{5+} ion formed causes the diffusivity is greatly enhanced and the sintered density is higher under the same sintering conditions of time and temperature. In contraposition, Une et al [13] explain their low sintered densities based on a oxygen vacancy model, where the incorporation of the Gd^{3+} ion to the UO_2 lattice structure causes the formation of oxygen vacancies, in order to balance the electrical charge. These authors rationalize the UO_2-Gd_2O_3 sintering behavior by analogy to the UO_2-PuO_2 system in which reduced cation diffusivities are found under hypostoichiometric conditions that prevail during sintering, and that can exist in the UO_2-Gd_2O_3 system.

Based on the results obtained in the present work, it can be concluded that the poor Gd_2O_3 distribution homogeneity is the primary cause to explain the low densities observed in sintered fuel pellets derived from the commercially adopted dry mechanical blending method to produce UO_2-Gd_2O_3 mixed powders. When the Gd_2O_3 is present at the atomic level within the powder, it enhances greatly the fuel pellet sintering, which sustains the model proposed by Ho et al [11]. On the other hand, if the Gd_2O_3 distribution into the mixed powder is not good, this proposed model is not valid and a poor sintering behavior is observed. The higher the homogeneity in the powder, the higher sintered density will be.

If the delay in the shrinkage coincide with the start of the solid solution formation (dry mechanical blending method), then a new model to explain the UO_2-Gd_2O_3 sintering behavior can be proposed, which is based on the formation of a rich gadolinium $(U,Gd)O_2$ phase which could have a low cation diffusivity. The formation of this phase near the Gd_2O_3 agglomerates, which would actuate as a diffusion barrier, should cause the sintering to be depressed caused by the low cation diffusivity. Assmann et al [9] suggest that there is a possibility of this model to be occurring in the UO_2-Gd_2O_3 sintering process. Based on this model, also could be explained the high densification observed in sintering mixed powders that were derived from the ADU co-precipitation. Once having the higher gadolinium homogeneity it does not allow the formation of regions with high gadolinium concentration and the formation of the diffusion barrier. No further discussion about this is feasible since very few data is available in the literature about the phases in the UO_2-Gd_2O_3 system.

Another possibility is that the phase transformation of the bcc Gd_2O_3 to the monoclinic form (around 1200 °C) could perturb the UO_2-Gd_2O_3 shrinkage during sintering. A model based in this phase transformation also can be proposed, since the gadolinium is present in the dry blended mixed oxide powder as free Gd_2O_3 agglomerates that should suffer the phase transformation during the sintering.

To fundament and develop both the hypothesis presented above, phase studies have been done in the UO_2-Gd_2O_3 system to verify the possible validation of the diffusion barrier model. The fully characterization of the phase transformation of the Gd_2O_3 from the form C to form B has already been started.

Conclusions

The sintering tests and the Gd_2O_3 distribution homogeneity analysis performed on mixed powders and sintered fuel pellets evidenced that the sintering behavior is directly related to the Gd_2O_3 homogeneity level present in the mixed oxide powders. According to the homogeneity level, different sintering behaviors can be expected.

Models have been proposed in order to explain the dependence of the sintering behavior on the Gd_2O_3 distribution homogeneity within the mixed oxide powders. They are based on the formation of a diffusion barrier or on the Gd_2O_3 phase transformation during the sintering process.

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