

INFLUENCE OF UO_2 STOICHIOMETRY ON THE DENSIFICATION OF $\text{UO}_2\text{-Gd}_2\text{O}_3$ NUCLEAR FUEL

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Abstract

The incorporation of gadolinium directly into nuclear power reactor fuel is important regarding reactivity compensation for optimized fuel utilization. Dry mechanical blending of both UO_2 and Gd_2O_3 powders is the most attractive process because of its simplicity. Nevertheless, fuel pellets processed by this method shows an abnormal sintering behavior. Pore formation when sintering the mixed fuel has been pointed as the cause to explain the bad sintering behavior, mainly if an oxidizing atmosphere is used. This paper investigates the pore formation as the possible mechanism and the role of UO_2 powder stoichiometry in the $\text{UO}_2\text{-Gd}_2\text{O}_3$ sintering behavior.

Key-words: urania-gadolinia, nuclear fuel, sintering.

1. INTRODUCTION

Improving reactor performance through longer cycle lengths is a goal pursued since the beginning of commercial nuclear power generation. Among several modifications introduced as a consequence, the use of a burnable poison homogeneously mixed to the nuclear reactor fuel has been adopted. Gadolinium is an excellent burnable poison and is incorporated as Gd_2O_3 into the UO_2 standard fuel by dry mechanical blending of both powders. The mixed powder is directly pressed into pellet form, with no co-milling, prepressing and granulating steps [1].

Nevertheless, the incorporation of Gd_2O_3 powder into the UO_2 powder by dry mechanical blending leads to difficulties while obtaining sintered $\text{UO}_2\text{-Gd}_2\text{O}_3$ pellets with the minimum required density. This is due to the deleterious effect of the Gd_2O_3 on the traditional UO_2 sintering behavior. Dilatometric analyses show that at temperatures around 1100-1400°C, the shrinkage of the $\text{UO}_2\text{-Gd}_2\text{O}_3$ pellets is delayed, the sintering rate decreases and densification shifts to higher temperatures [2,3]. Two peaks in the shrinkage rate curves were observed [2].

Usually both the traditional UO_2 fuel and $\text{UO}_2\text{-Gd}_2\text{O}_3$ mixed fuel are sintered under H_2 reducing atmosphere. It is known from literature [4] that the sintering of pure UO_2 fuel in an oxidizing atmosphere (CO/CO_2 mixture) is enhanced by the presence of U^{5+} cations due to its lower ionic radius, resulting in increased cation diffusivity. However, the literature reports that the bad sintering behavior of $\text{UO}_2\text{-Gd}_2\text{O}_3$ mixed fuel is substantially worse when sintering under oxidizing atmosphere [5,6].

The formation of closed porosities during the sintering of the $\text{UO}_2\text{-Gd}_2\text{O}_3$ fuel has been reported in the literature [5,6]. According Yuda and Une [5] the two peaks observed in the shrinkage rate correspond to the reaction between adjacent $\text{UO}_2\text{-UO}_2$ particles (the first peak) and to the reaction between $\text{UO}_2\text{-Gd}_2\text{O}_3$ particles (the second peak). Due to the difference in sintering rates between $\text{UO}_2\text{-UO}_2$ particles and $\text{Gd}_2\text{O}_3\text{-UO}_2$ particles,

these researchers proposed the formation of large pores generated by local non-uniform volume variations caused by the difference in densification rates resulted from reactions between UO_2 - UO_2 particles and UO_2 - Gd_2O_3 particles. These large pores are formed at high temperatures by reacting UO_2 with Gd_2O_3 when the pore structure is already essentially closed and, therefore, are difficult to eliminate. The pores remain closed after the sintering cycle and decrease the final density of the system. In oxidizing atmospheres, the sintering between UO_2 - UO_2 particles occurs more rapidly owing to the presence of U^{5+} cations, which gives higher sinterability to the system. When starting with UO_2 - Gd_2O_3 reaction, generating large pores, they are formed in a closed pore structure, which makes their removal more difficult. This explains the drastic decrease in the density of UO_2 - Gd_2O_3 pellets sintered under oxidizing atmosphere.

Song and co-workers [6] found that, as the oxygen potential of the sintering atmosphere increased, the sintered density of the UO_2 - Gd_2O_3 mixed fuel decreased and new pores are formed in regions with high Gd concentration. The densification delay occurs together with the formation of $(\text{U,Gd})\text{O}_2$ solid solution in the temperature range of 1200-1450°C. The mechanism for pore formation proposed by these authors is based on the directional diffusion of Gd ions into UO_2 , forming new pores. This pore formation occurs similarly in reducing and oxidizing sintering atmospheres, but the driving force for the densification of new pores is smaller under oxidizing atmosphere because the new pores are formed near the final sintering stage.

The objective of this study is to investigate the pore formation during sintering as a mechanism responsible for the abnormal sintering behavior of the UO_2 - Gd_2O_3 fuel as well as the influence of sintering atmosphere in that mechanism.

2. METHODS AND MATERIALS

The UO_2 - Gd_2O_3 samples were prepared by mechanical blending method [7]. The Gd_2O_3 content was 10 wt%. The UO_2 powder was obtained via AUC conversion [8]. The O/U ratio of UO_2 powder was 2.15. The Gd_2O_3 powder (purity 99.9%) was supplied by Ventron Alfa Produkte. All powders were pressed into pellets and sintered in a dilatometer up to 1650°C, with isothermal treatment at this temperature during 180 min. The heating rate was 5°C/min. To verify the influence of the presence of U^{5+} cations, the sintering was conducted under reducing pure H_2 atmosphere and inert argon atmosphere. As the original O/U ratio of UO_2 is 2.15, the UO_{2+x} hyperstoichiometry ensures the presence of U^{5+} cations when sintering in inert atmosphere. Under reducing atmosphere all U^{5+} cations are reduced to U^{4+} (O/U=2.00). In this way, sintering under inert atmosphere simulates the sintering under oxidizing atmosphere.

3. RESULTS AND DISCUSSION

If pores are formed during sintering, two simultaneous phenomena may be occurring. One of them is the shrinkage of the pellet as a result of the sintering process. The other is the swelling that follows the solid solution formation, which generates pores in the places where originally existed Gd_2O_3 regions, as proposed in the literature [5,6]. Direct experimental evidence of this mechanism was obtained by separating the two opposed

phenomena, the shrinkage due to the sintering process and the dilatation due to the pore formation. This was accomplished by substituting the reducing H_2 atmosphere by inert argon atmosphere in the dilatometric test. The U^{5+} cations originally present in the $UO_{2.15}$ powder remains under inert argon atmosphere. As the diffusivity of U^{5+} cations is much larger than for U^{4+} cations, sintering process is benefited and begins at lower temperatures and also finishes at lower temperatures.

Following this argumentation, it was possible to obtain a result where the separation of shrinkage from dilatation was done. So, the pore formation was separated and evidenced. The result can be observed in the curve presented in figure 1. In this figure, the sintering curve for a UO_2 - Gd_2O_3 pellet sintered under reducing H_2 atmosphere is also presented for comparison. It can be observed that a dilatation process begins at temperatures above $1000^\circ C$ in the pellet sintered under argon atmosphere and the whole sintering process is shifted to lower temperatures. When the solid solution formation is initiated, the shrinkage component due to the sintering process is smaller than the dilatation component due to pore formation, which results in a dilatation that could be detected, as indicated in figure 1. It can be noticed that when pore formation owing to formation of the solid solution is finished, a further shrinkage of approximately 1% is observed. This demonstrates that part of the formed pores (probably pores with smaller diameters) is eliminated together with sintering of the UO_2 matrix, which has not been completed yet.

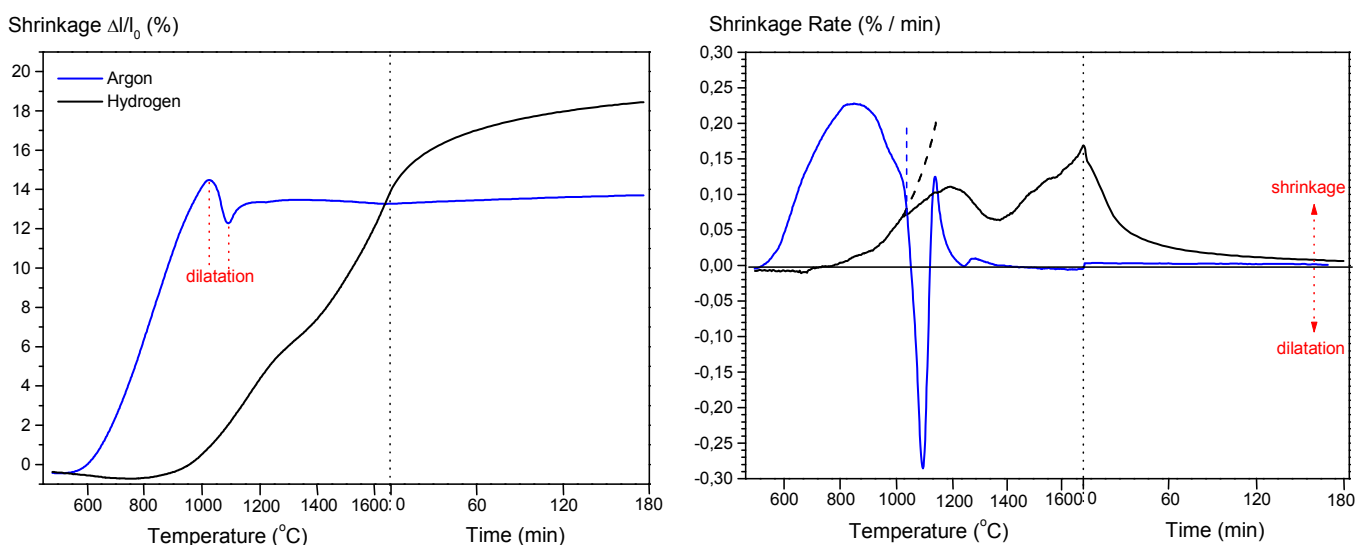


Fig. 1. Sintering curves for UO_2 - Gd_2O_3 pellets carried out under argon and hydrogen. (10 wt% Gd_2O_3 , heating rate $5^\circ C/min$)

A DSC experiment evidenced that the pore formation observed in the system (or dilatation) is originated from the formation of the solid solution, when the pore formation happens. Fragments of a UO_2 - Gd_2O_3 green pellet were analyzed. The experiment was conducted under argon atmosphere. Due to the low energies, which is involved during the reaction for solid solution formation, the heating rate was adjusted to $15^\circ C/min$, which gave a good result.

The DSC curve is presented in figure 3. In this figure, the sintering curve is also presented, which facilitates the visualization of the existence of a direct correspondence between the pore formation (dilatation) and the solid solution formation. The solid solution formation is evidenced by the endothermic peaks in the DSC curve. The

small displacement between the beginning of the endothermic peak in the DSC curve and the beginning of the pore formation (dilatation) in the sintering curve could be attributed to the higher heating rate adopted for the DSC test, which causes a small displacement to detect the reaction towards higher temperatures.

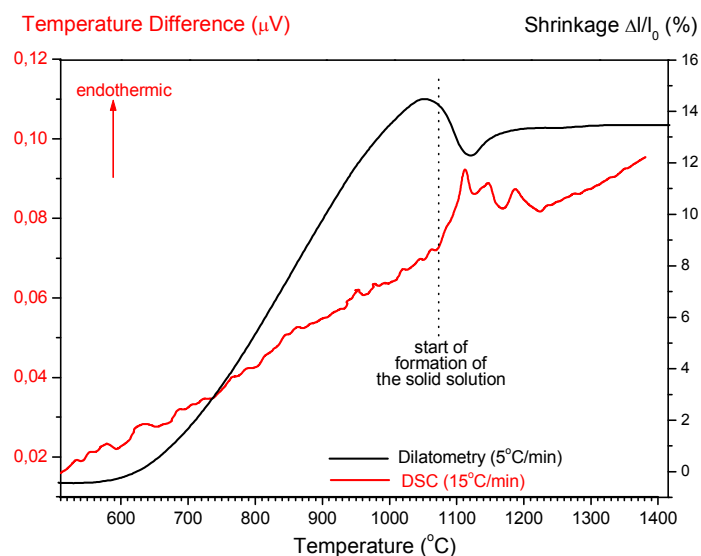


Fig. 3. DSC curve evidencing the (U,Gd)O₂ solid solution formation. (10 wt% Gd₂O₃, heating rate 15 °C/min, argon atmosphere)

4. CONCLUSION

Experimental evidence obtained in this work supports the formation of stable pores as the mechanism to explain the bad sintering behavior of the UO₂-Gd₂O₃ fuel. Contrary to traditional UO₂ fuel, sintering the UO₂-Gd₂O₃ fuel under oxidizing atmosphere disturbs considerably the densification. Due to the presence of U⁵⁺ cations, there is an anticipation of UO₂-Gd₂O₃ system densification. Elimination of pores is more difficult, when the solid solution takes place inside a more closed pore structure.

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