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DILATOMETRIC ANALYSIS OF THE GADOLINIA PHASE TRANSITION

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Abstract

Gadolinium has been added to the nuclear fuel to enable longer fuel cycles. The UO_2-Gd_2O_3 mixed fuel shows a bad sintering behavior, which is hindered at temperatures around 1200 ^{o}C. A possible proposed cause is the formation of large closed pores during sintering in Gd_2O_3 rich regions. The cause proposed in the literature could be deriving from the Gd_2O_3 phase transition. The objective of this investigation was to study the Gd_2O_3 phase transition to verify the consistence of this mechanism. The results showed that the phase transition results in volume reduction and occurs at temperatures consistent with the proposition.

Key-words: Gd_2O_3, phase transition, nuclear fuel.

1. INTRODUCTION

The inclusion of gadolinium into nuclear fuel is important regarding reactivity compensation, which enables longer fuel cycles, since it roles as neutron poison managing fuel wasting. The incorporation in the fuel is made as gadolinia (Gd_2O_3) powder directly added into UO_2 powder by dry mechanical blending. This is the most attractive process, because of its operational simplicity. Nevertheless, processing by this method leads to difficulties while obtaining sintered pellets with the minimum required density. This is due to the bad sintering behavior of the UO_2-Gd_2O_3 mixed fuel, which shows a blockage during sintering process that hinders the densification [1,2]. Sintering curves obtained in previous work [3,4] showed that the lower sintered densities are due to the abnormal sintering behavior of the UO_2-Gd_2O_3 fuel, compared to the sintering behavior of traditional UO_2 fuel. Dilatometric analyses show that at temperatures around 1200°C, the shrinkage of the UO_2-Gd_2O_3 pellets is delayed, the sintering rate decreases and densification shifts to higher temperatures [1,3].

Considering that sintering blockage occurs during the $(U,Gd)O_2$ solid solution formation [2], some authors proposed a mechanism to explain the abnormal sintering behavior of the UO_2-Gd_2O_3 fuel, which is based on the formation of low diffusivity oxide phases during the sintering process. The formation of low diffusivity phases reduces densification and lead to low sintered densities [2,5]. Although the existence of low diffusivity phases in UO_2-Gd_2O_3 system was experimentally observed [3], this mechanism was not supported by experimental observations [6].

Another possible mechanism to explain the UO_2-Gd_2O_3 sintering behavior was proposed by Yuda and Une [7], which is based on the formation of large closed pores in the UO_2-Gd_2O_3 mixed fuel, which are generated by local and non-uniform volumetric changes resulting from the different densification rate obtained from the reaction of UO_2-UO_2 and UO_2-Gd_2O_3 particles. These large pores were also reported by Song and co-workers [8] when sintering UO_2-Gd_2O_3 fuel pellets in oxidizing atmospheres.

Goldschmidt and co-workers recognized three crystallographic structures of rare earth oxides [9]. As temperature increases, C cubic transforms into B monoclinic, and finally into A hexagonal. Gschneider and Eyring [10] reported that the C to B transition occurs at approximately 1250°C or, according to El-Houte and El-Sayed Ali, at approximately 1200°C [11]. Thus, it could be concluded that at fuel fabrication temperatures gadolinia oxide could exist either in C cubic form (below 1200-1250°C) or in B monoclinic form (above 1250°C).

The reported density for the C-form is 7.62 g/cm^3 and for the B-form is 8.33 g/cm^3 [12]. Then, the C→B phase transition of gadolinia occurs with a decrease in volume of about 10%. If the volume reduction resulting from the Gd_2O_3 C→B phase transition occurs simultaneously with the sintering blockage (1200-1250°C), the pores reported in the literature [7,8] could be originated by the phase transition. The objective of this work is to investigate that possibility by characterizing the Gd_2O_3 C→B phase transition in realistic conditions of fuel fabrication.

2. METHODS AND MATERIALS

The Gd_2O_3 samples were prepared from powder (purity 99.9%) supplied by Ventron Alfa Produkte. The powder (cubic C-form) was pressed into pellets with green density around 50% of the theoretical density. Samples of UO_2-Gd_2O_3 were also prepared by the mechanical blending a method [1,4] The UO_2 powder was obtained from uranium hexafluoride via AUC conversion [13]. All samples were sintered under pure hydrogen reducing atmosphere in a dilatometer. The samples were heated from ambient to 1650°C, with isothermal treatment at this temperature during 180 min. The heating rate was 5 °C/min. The UO_2-Gd_2O_3 samples were sintered in order to compare the sintering curves resulting from Gd_2O_3 and the mixed fuel under the exactly same conditions. X-ray diffraction was used to characterize Gd_2O_3 phase transition.

3. RESULTS AND DISCUSSION

The Gd_2O_3 C→B phase transition was detected as an abrupt shrinkage starting at 1266°C, as showed in figure 1. The transition ends at around 1372 °C. Before the phase transition, the shrinkage rate increases smoothly almost linearly up to 1266°C, reaching the value of 0.015 %/°C at this temperature. When the phase transition starts the shrinkage rate increases sharply due to the volume reduction that accompanies the phase transition. A maximum shrinkage rate (0.082 %/°C) was observed at 1312°C. After the transition takes place, the shrinkage rate decreases to a value much smaller than the one observed before the transition (0.001 %/°C).

X-ray diffractions confirmed that the abrupt shrinkage was due to the Gd_2O_3 phase transition. As shown in figure 2, at temperatures below the phase transition (indicated as D1 in figure 1 at 1200°C) the diffractogram shows only the presence of the C-form of Gd_2O_3 (cubic). At the point D2 in figure 1 (1290°C), the reflections in figure 2 starts to show the presence of the B-form of Gd_2O_3 (monoclinic). At the point D3 (1330°C), the cubic form is almost transformed to monoclinic. At the point D4 (1400°C) only the presence of the B-form is observed.

By overlapping the sintering curve of the UO_2-Gd_2O_3 fuel with the curve of the Gd_2O_3 phase transition it can be noted that the sintering blockage in the fuel (regardless the Gd_2O_3 concentration) occurs almost simultaneously

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with the Gd_2O_3 phase transition. This observation supports the hypothesis that the Gd_2O_3 phase transition may be negatively influencing the sintering of the mixed fuel due to pore formation caused by volume reduction of Gd_2O_3 agglomerates. Figure 3 illustrates this proposition.
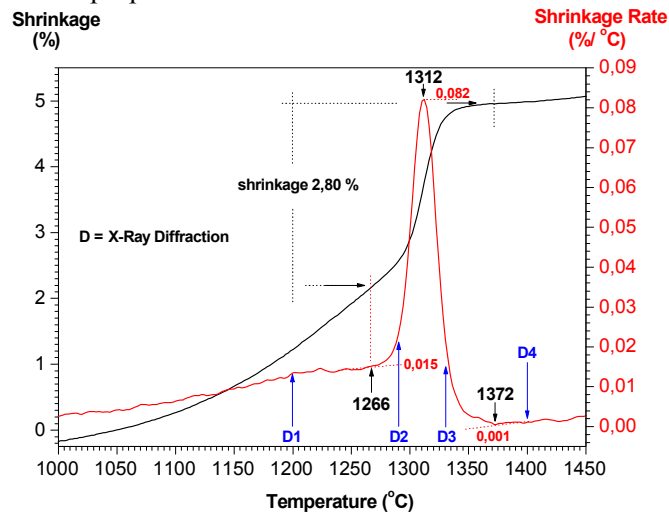

Fig. 1. Gd_2O_3 phase transition (C-form → B-form) detected by dilatometry
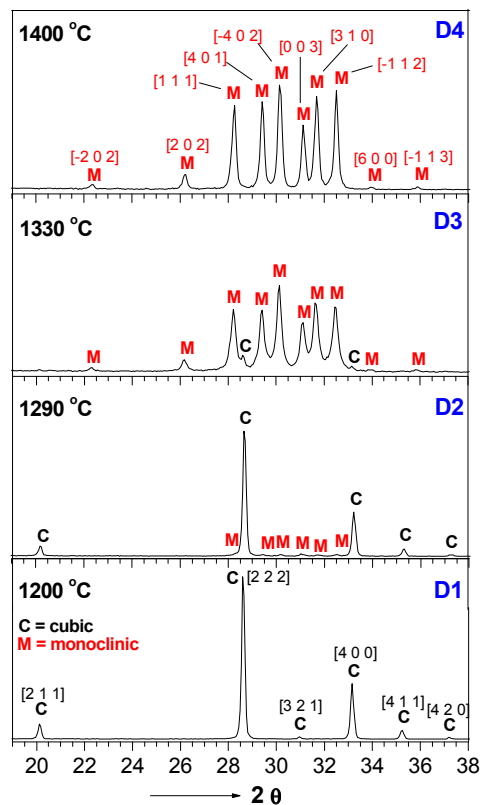

Fig. 2. Gd_2O_3 phase transition detected by x-ray diffraction (see D points in figure 1)

4. CONCLUSION

The phase transition of Gd_2O_3 from the cubic C-form to the monoclinic B-form occurs in the temperature range of 1266^oC and 1372^oC. This result agrees with the results reported by Gschneider and Eyring [10]. This temperature range is compatible with the temperature range related to the UO_2-Gd_2O_3 sintering blockage.

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The C→B phase transition of gadolinia occurs with a decrease in volume at temperatures when also occurs the Gd_2O_3 incorporation by UO_2 fluorite lattice to form a solid solution. The volume reduction due to phase transition in Gd_2O_3 agglomerates can be the mechanism to explain the large pore formation reported in the literature [7,8]. This pore formation mechanism could explain the bad sintering behavior of the UO_2-Gd_2O_3 mixed fuel.
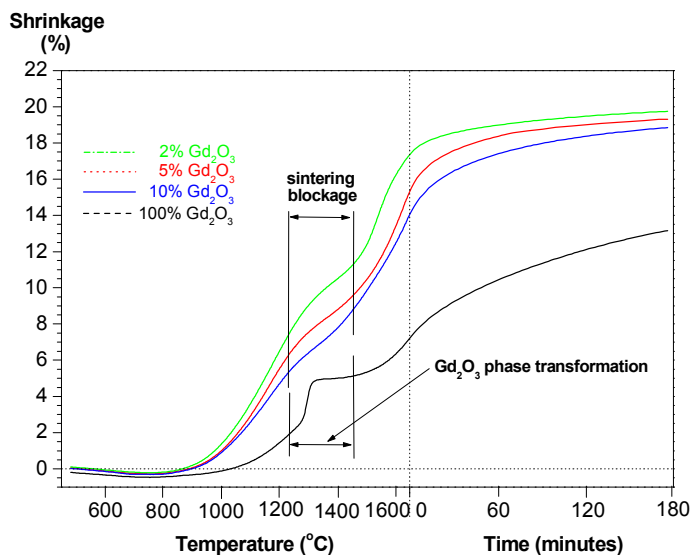

Fig. 3. **Experimental evidence supporting the hypothesis**

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