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Study on thermal decomposition and sintering behaviour of internally gelated simulated inert matrix fuel

K. Suresh Kumar[a], Tom Mathews[b,*], N.P. Bhat[c]

[a] Kalpakkam Reprocessing Plant, BARC (F), Kalpakkam 603102, India
[b] Reprocessing Research and Development Division, Indira Gandhi Centre for Atomic Research, Kalpakkam 603102, India
[c] Materials Characterization Group, Indira Gandhi Centre for Atomic Research, Kalpakkam 603102, India

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Abstract

Simulated inert matrix fuels corresponding to the compositions $Zr_{0.75}Y_{0.10}Er_{0.05}Ce_{0.10}O_{1.925}$ and $Zr_{0.70}Y_{0.10}Er_{0.05}Ce_{0.15}O_{1.925}$ were synthesized through the ammonia internal gelation process. The thermal decomposition behaviour of the gel was investigated using thermogravimetry/differential thermal analysis (TG/DTA) and powder X-ray diffraction (XRD). The gel decomposes in two stages. The first step involves evolution of water and ammonia at around 200 °C and in the second step at around 600 °C the decomposition of trapped formaldehyde (HCHO) occurs simultaneously with crystallization of zirconia. The crystallite size of the decomposed powder was found to be smaller than 10 nm. The decomposed powder could be sintered to around 90% of theoretical density using microwave energy source in 60 min.

Keywords: Inert matrix fuels; Differential thermal analysis; X-ray diffraction

1. Introduction

An important scientific and political challenge of our era is the safe disposal of Pu from reactors and nuclear weapons no longer needed for defense purposes. Out of two options for Pu disposal, one is the incorporation of Pu in a suitable glass via vitrification and burying the mixture in a geologic repository and the other is burning the Pu in an existing nuclear reactor. An alternative to the utilization of Pu in reactors as mixed oxide fuel ($(U,Pu)O_2$) is the incorporation of Pu in a non-fertile (inert) matrix and burn it in existing light water nuclear reactors, followed by burial in a geologic repository without further reprocessing. These types of fuels are known as inert matrix fuel (IMF) [1–3]. This cradle-to-grave fuel cycle represents a new paradigm for global sustainable nuclear power and is termed as burn and bury options for Pu [4]. Burning Pu in a non-fertile matrix produces spent fuel with less Pu in contrast to burning it in a conventional UO_2 fuel where large amount of new actinides are formed. Moreover, the isotopic composition of the Pu in irradiated IMF is degraded to the extent that the spent fuel is of little use as a nuclear explosive material.

One of the best inert matrices identified for the incorporation of Pu is yttria stabilized zirconia (YSZ) [5–7]. Cubic stabilized zirconia (ZrO_2) is an actinide host phase in which actinides have high solubility (over 10% for U and Pu). In fact, cubic ZrO_2 is isostructural with actinide oxides such as UO_2, PuO_2 and ThO_2; this implies that single-phase fuels, similar to existing UO_2 nuclear fuels, can be fabricated readily. Addition of the cubic stabilizer, Y_2O_3 in ZrO_2 can enhance actinide solubility in a cubic fluorite host phase. In fact ∼3% yttria stabilizes the cubic phase and they increase the melting point of the compound, thereby further enhancing the chemical stability of ZrO_2. Addition of burnable poisons makes it possible to use the IMF with higher initial concentrations of fissile nuclides and extended fuel burnups. For instance, addition of the rare earth element Er to ZrO_2–PuO_2 fuel makes

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[*] Corresponding author. Tel.: +91 4114 280 399; fax: +91 4114 280 207.
E-mail address: tom@igcar.ernet.in (T. Mathews).

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it feasible to incorporate high plutonium mass loading in the fuel [5–7].

Different fabrication processes explored for IMF fabrication are sol–gel, gel supported precipitation and ceramic processes [8,9]. As limited literature is available on the feasibility of internal gelation for the preparation and the gel characterization of IMF and even for simulated IMF, the present study is aimed on the detailed characterization of the internally gelated product of simulated IMF by using thermogravimetry/differential thermal analysis (TG/DTA) and X-ray diffraction (XRD). Moreover, the feasibility of using microwave energy source for sintering of the decomposed powder also has been attempted. In the present investigation CeO_2 is used as a surrogate for PuO_2 [10].

2. Experimental

Simulated IMF corresponding to the compositions $Zr_{0.75}Y_{0.10}Er_{0.05}Ce_{0.10}O_{1.925}$ and $Zr_{0.70}Y_{0.10}Er_{0.05}Ce_{0.15}O_{1.925}$ were prepared from the metal nitrate solutions through the ammonia internal gelation process [11]. The gel thus prepared was dried at 120 °C in an air oven prior to thermal decomposition. A horizontal thermal analysis system (Model Seiko 320), with platinum crucibles and alumina as reference was employed for recording TG/DTA. The X-ray powder patterns were obtained within the 5 mass% threshold for the detection of impurity phases, by using Philips X-ray diffractometer (XPERT MPD system obtained from Philips, The Netherlands). The microwave source used for the sintering purpose is a domestic microwave oven, M/s. BPL, India, and 2450 MHz with a power rating of 800 W. The density measurements of the pellets were carried out by liquid immersion technique employing dibutyl phthalate as the immersion liquid using a Precisa instruments AG device. High resolution electron micrograph (HREM) images were taken by using an electron microscope (JEOL 2000 EX I).

3. Results and discussion

The dried gel samples corresponding to the compositions $Zr_{0.75}Y_{0.10}Er_{0.05}Ce_{0.10}O_{1.925}$ and $Zr_{0.70}Y_{0.10}Er_{0.05}Ce_{0.15}O_{1.925}$ were subjected to TG/DTA experiments in a dynamic O_2 atmosphere with a heating rate of 5 °C/min up to 400 °C and of 10 °C/min from 400 to 1200 °C. Since the thermal decomposition behaviour of both samples was found to be identical, the TG/DTA curves obtained for the composition with high Ce content, which is more relevant in nuclear fuel cycle, are presented in Fig. 1. The total weight loss observed by heating the gel till 1200 °C is 41%. The thermal decomposition of the gel occurs in two steps as illustrated by the TG curve where the initial major weight loss is (33.4%) observed in the range of 194–360 °C and the second weight loss is at around 600 °C. Corresponding to the weight loss steps in TG, exothermic peaks are observed in the DTA spectrum. The initial weight loss and the two exothermic peaks at around 226 and 262 °C can be attributed to the loss of water and ammonia from the gel. The second exothermic reaction accompanied by the weight loss is probably the decomposition of HCHO trapped in the gel associated with crystallization of zirconia [12,13]. The presence of high amount of carbon in the gel was confirmed by the disappearance of black color of the gel when it was heated at 700 °C in air for 10 min. In our earlier study [14] for the thermal decomposition of zirconia and zirconia-ceria gel, the TG/DTA results showed an exothermic peak at around 500 °C without a weight loss corresponding to the crystallization of zirconia. To understand the crystallization behaviour of the simulated IMF gel during its thermal decomposition, high temperature XRD was performed on the gel from 400 to 800 °C in vacuum environment. The XRD pattern indicates that the crystallization starts when the gel is heated at 700 °C. The slow kinetic of the reaction may be due to the vacuum environment which is a restriction of the high temperature experimental set up. Hence room temperature XRD patterns for the gel heated in air at various temperatures and quenched to room temperature were recorded and are given in Fig. 2. The result shows that the amorphous gel is completely converted to cubic fluorite structure when heated at 600 °C in air. The average crystallite size of the product obtained by heating the gel at 700 °C in air was calculated from the XRD pattern by using Scherrer formula and found to be 14.7 nm. The grain size of the decomposed powder was measured using HREM and is found to be less than 10 nm (Fig. 3).

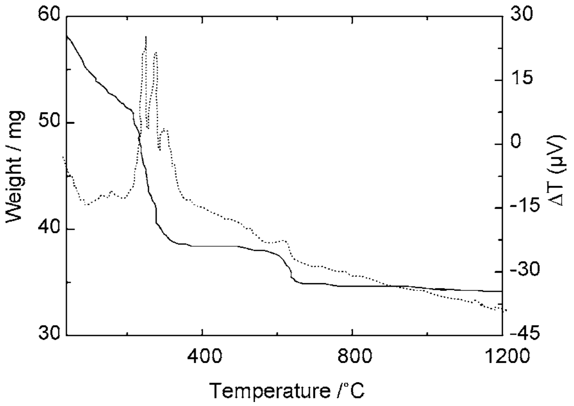

Fig. 1. TG/DTA curves of the $Zr_{0.70}Y_{0.10}Er_{0.05}Ce_{0.15}O_{1.925}$ gel in dynamic O_2 environment.

Recently it was reported that the sodium beta alumina family compounds are very good absorbers of microwaves and that sodium beta alumina could be used as a microwave susceptor to heat ceramics that do not directly couple with microwaves [15,16]. The decomposed powder of $Zr_{0.70}Y_{0.10}Er_{0.05}Ce_{0.15}O_{1.925}$ was pelletized at a pressure of 300 MPa and sintered by using conventional furnace at 1200 °C for 24 h as well as microwave energy source for 15, 30 and 60 min. The sample temperature during the microwave heating could not be measured exactly as the set up used is

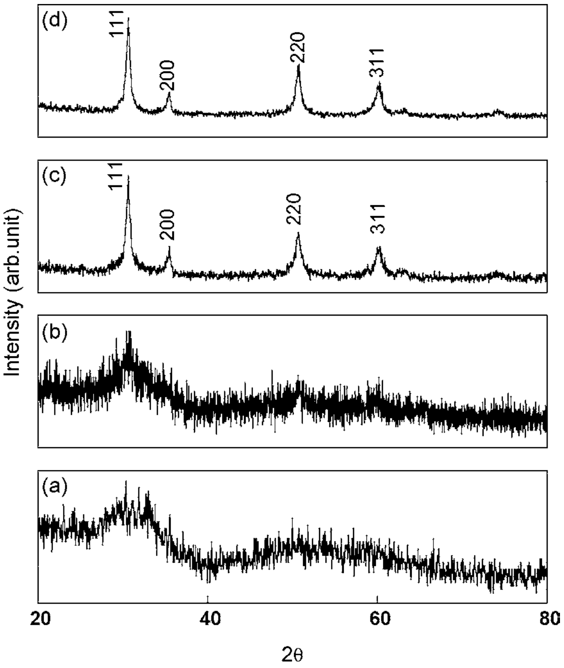

Fig. 2. XRD patterns of the $Zr_{0.70}Y_{0.10}Er_{0.05}Ce_{0.15}O_{1.925}$ gel heated in air at (a) 400 °C, (b) 500 °C, (c) 600 °C, and (d) 700 °C.

based on a domestic oven which does not has the facility. The XRD patterns obtained for the conventionally as well as microwave heated samples showed the sintered product to be a single cubic phase and the lattice parameter for the samples was calculated to be 516.73 ± 0.5 pm. The densities obtained for the microwave assisted sintered samples corresponding to the compositions $Zr_{0.75}Y_{0.10}Er_{0.05}Ce_{0.10}O_{1.925}$ and $Zr_{0.70}Y_{0.10}Er_{0.05}Ce_{0.15}O_{1.925}$ for different duration are summarized in Table 1. The densities obtained for the two samples are comparable. The result indicates that the simulated IMF could be sintered to around 90% of theoretical density by using microwave energy source for 60 min and which is comparable to the results reported by Lee et al. [17] wherein conventional heating at 1600 °C was used. The ceramographs obtained for the conventionally as well as microwave heated samples are shown in Figs. 4 and 5, respectively. The micrographs show that even though both the sintered samples contain pores on the polished surface, the pore fraction in the microwave sintered sample is comparatively less than that of the conventionally sintered material. Moreover, the grains in the microwave sintered sample are amoeba shaped whereas those of conventionally sintered sample have sharp edges. This indicates a high sinterability for the microwave sintered sample.

Fig. 3. HREM micrograph of $Zr_{0.70}Y_{0.10}Er_{0.05}Ce_{0.15}O_{1.925}$ gel powder decomposed at 700 °C for 30 min.

Table 1
Densities obtained for different compositions of simulated IMF after sintering at various duration in microwave energy

Time (min)	Density (g/cm^3)	
	$Zr_{0.75}Y_{0.10}Er_{0.05}Ce_{0.10}O_{1.925}$ (TD = 6.218 g/cm^3)	$Zr_{0.70}Y_{0.10}Er_{0.05}Ce_{0.15}O_{1.925}$ (TD = 6.234 g/cm^3)
15	4.971	4.979
30	5.374	5.369
60	5.612	5.601

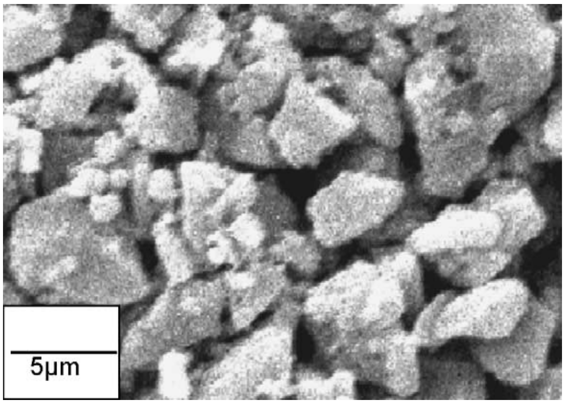

Fig. 4. Ceramograph of pellet of $Zr_{0.70}Y_{0.10}Er_{0.05}Ce_{0.15}O_{1.925}$ sample sintered by conventional heating at 1200 °C for 24 h (absolute density = 5.182 g/cm^3; 83.12% of theoretical density).

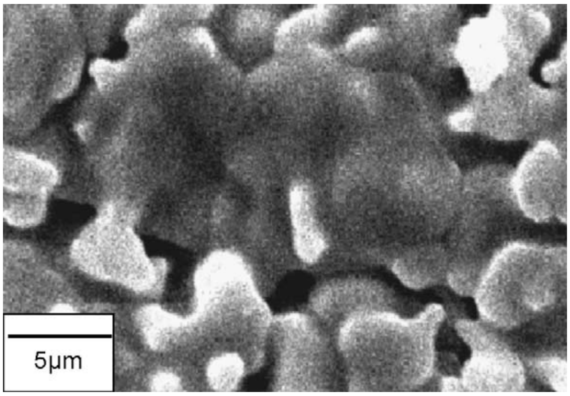

Fig. 5. Ceramograph of pellet of $Zr_{0.70}Y_{0.10}Er_{0.05}Ce_{0.15}O_{1.925}$ sample sintered by microwave heating for 1 h.

4. Conclusion

Single-phase nanosized simulated inert matrix fuels corresponding to the compositions $Zr_{0.75}Y_{0.10}Er_{0.05}Ce_{0.10}O_{1.925}$

and $Zr_{0.70}Y_{0.10}Er_{0.05}Ce_{0.15}O_{1.925}$ had been synthesized via ammonia internal gelation technique at temperatures as low as 700 °C. The decomposed powder could be sintered to around 90% of theoretical density using microwave energy source with sodium beta alumina as susceptor in 60 min.

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