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Journal of Nuclear Materials 257 (1998) 189–193

journal of nuclear materials

Letter to the Editors

A feasibility study of the preparation of $(U,Gd)_3O_8$ solid solutions by thermal decomposition of co-precipitated carbonate mixtures

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Received 5 May 1998; accepted 4 July 1998

Abstract

Co-precipitation from equimolar nitrate solutions of uranium (VI) and gadolinium has been used to obtain a mixture of $(NH_4)_4UO_2(CO_3)_3$ and $Gd_2(CO_3)_3 \cdot 3H_2O$ at a pre-determined composition. Simultaneous measurements by TG, DTA and evolved gas analysis (EGA) showed that a calcination temperature of 700°C was necessary to decompose the carbonate completely to oxides. X-ray diffraction data indicated that a solid solution of Gd_2O_3 in U_3O_8 cannot be obtained by heating the carbonate mixtures up to 800°C in inert atmospheres.

1. Introduction

Modern nuclear fuel design aims to achieve enhanced burn-up by using gadolinia additions as burnable poison to the uranium oxide fuel pellet [1]. Ammonium diuranate (ADU) and ammonium uranyl carbonate (AUC) are commonly used as precursors for the uranium dioxide powder employed in the fuel fabrication. Co-precipitation of gadolinium along with ADU or AUC, mixing the respective oxides in required amounts prior to sintering, etc. are possible methods for the preparation of fuel precursors containing gadolinium. Co-precipitation ensures a uniform distribution of gadolinium in the precipitate enhancing the possibility of solid solution formation at a lower temperature and hence is an attractive procedure [2]. In an earlier study [3] using ADU as the precursor it was concluded that co-precipitation of gadolinium with uranium enables the preparation of a solid solution of gadolinia in urania by calcination of the precipitate at 650°C. Since AUC powder has more attractive characteristics [4] such as better flowability and sinterability, better-defined composition, etc., a characterization of the AUC powder co-precipitated with gadolinium carbonate trihydrate is of interest in this context. Further, differences in solubilities, complexing nature of the metal ions, etc., may lead to a change in the composition (Gd/U) of the precipitate with respect to the initial composition of the nitrate mixture. Hence, a detailed study of the preparation and thermal decomposition of the co-precipitated carbonate mixture was undertaken in our laboratory and the results are presented in this paper.

2. Experimental

Ammonium uranyl carbonate and gadolinium carbonate trihydrate were co-precipitated from a mixture of the respective nitrate solutions (0.45 M each, prepared from nuclear grade U_3O_8 and Specpure Gd_2O_3) using ammonium carbonate as the precipitant by the method used earlier for the precipitation of ammonium uranyl carbonate [5]. The gadolinium content of the precipitate was adjusted to provide an oxide mixture containing 10% by weight of Gd_2O_3 and 90% UO_2 on reduction and sintering by ensuring an identical composition in the initial mixture of the nitrate solutions ($UO_2(NO_3)_2/Gd(NO_3)_3 = 6$ by volume). The effects of gadolinium

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PII: S0022-3115(98)00472-3

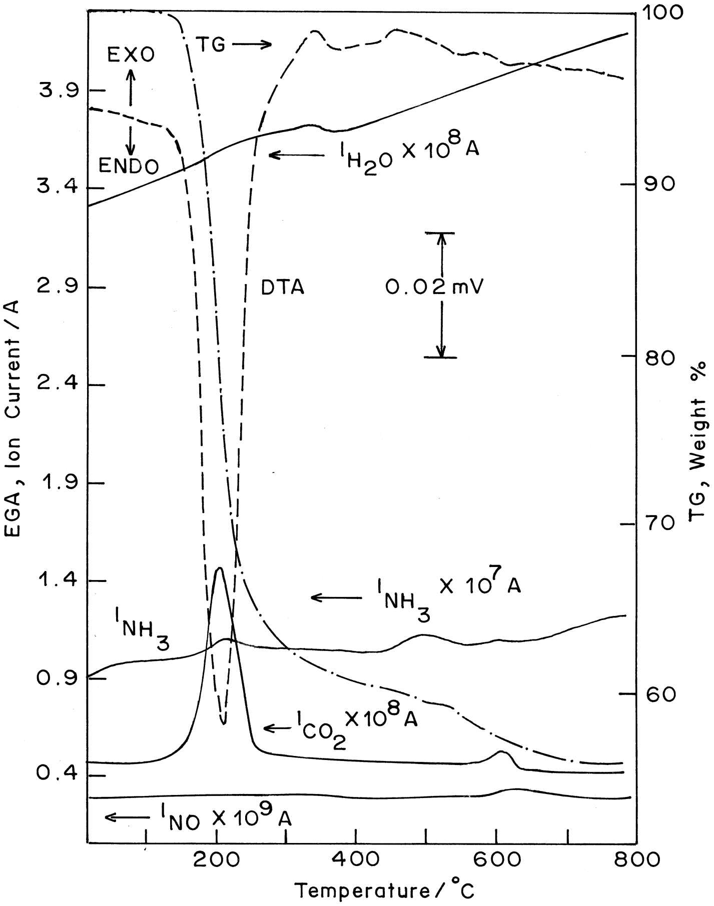

Fig. 1. TG–DTA–EGA curves for the decomposition of AUC co-precipitated with gadolinium carbonate at a heating rate of 10 K/min in argon flow.

addition to AUC were perceptible on TG–DTA–EGA curves for this composition. This is also close to the content of Gd_2O_3 added as burnable poison (5–10%) in the fuel for BWRs [6]. The uranium and gadolinium contents of the precipitate were determined by spectrophotometric and direct current plasma atomic emission spectroscopic (DCP-AES) methods, respectively. In the latter case, uranium was separated from gadolinium by extraction with 40% TBP and the aqueous phase was evaporated to dryness, the residue was dissolved in water acidified with a few drops of concentrated nitric acid and made up to known volume. An aliquot of this solution was used for DCP-AES measurements. No prior separation of gadolinium from uranium was attempted before the determination of the uranium content of the precipitate. However, the standard solutions used for calibration of spectrophotometric data were mixtures of uranyl nitrate and gadolinium nitrate solutions with a gadolinium to total metal ratio of 10% by weight. Alkaline hydrogen peroxide was used for complexing U (VI) in nitrate medium and the optical density was measured at a wavelength of 410 nm. The nitrate content of the precipitate was analysed using an ion chromatograph (Dionex, USA, Model 16) as described earlier [5]. X-ray diffraction data of the precipitate and the thermal decomposition residue at 800°C were recorded on a Philips X-ray diffractometer (Model PW1710) using Cu-Kα radiation (Ni-filtered, 30 kV, 20 mA).

TG–DTA–EGA measurements were carried out using a simultaneous thermal analyser described elsewhere [7]. Specimen holders made from recrystallized alumina and temperature and differential temperature sensors made from Pt/Pt–10%Rh thermocouples were used. The measurements were carried out at heating rates of 5, 10 and 20 K/min in dynamic argon (Indian Oxygen, IOLAR-2) atmosphere at a flow rate of 80 ml/min. Sample weights were in the range of 40–75 mg. Calcined alumina was used as the reference material.

3. Results and discussion

The results of chemical analysis of the precipitate showed a U content of 42.4% (93.0% AUC) and a Gd content of 6.0% (10.5% $Gd_2(CO_3)_3 \cdot 3H_2O$) against theoretical values of 41.53% (91.12% AUC) and 5.09% (8.9% $Gd_2(CO_3)_3 \cdot 3H_2O$), respectively, calculated on the basis of the composition of the initial mixture of uranyl nitrate and gadolinium nitrate. The nitrate ion present as occluded impurity in the sample was found to be only 0.93%. The fairly good agreement between the theoretical and experimental assay values for the carbonate mixture shows that the experimental conditions adopted favour the precipitation of carbonates of both uranium and gadolinium to the same extent. Hence, a mixture of pre-determined composition of the carbonates can be obtained by co-precipitation. X-ray diffraction data showed predominantly only peaks corresponding to ammonium uranyl carbonate [8] understandably because of low content of gadolinium carbonate trihydrate and overlap between diffraction patterns of the two carbonates.

The TG–DTA–EGA curves recorded at a heating rate of 10 K/min are presented in Fig. 1. The corresponding expanded DTA and TG curves for the decomposition in the temperature range of 300–700°C are shown in Fig. 2. It is evident from these data that unlike in the case of ammonium uranyl carbonate [5], the sample containing co-precipitated gadolinium carbonate trihydrate attains a constant weight plateau only at about 700°C. This is because gadolinium carbonate forms an intermediate oxycarbonate which is completely decomposed to gadolinium oxide only at about 700°C. The EGA curves show an evolution of carbon dioxide in the temperature ranges of 150–350°C and 550–700°C, the latter one being due to the decomposition of the oxycarbonate of gadolinium. Hence, the formation of solid solution reported during the decomposition of ADU with co-precipitated gadolinium hydroxide [3] seems not to take place in the case of decomposition of AUC with co-precipitated gadolinium carbonate. The EGA curves also indicate evolution of small amounts of nitric oxide in the temperature ranges of 250–500°C and 550–700°C. It has also been shown earlier [5] that uranyl

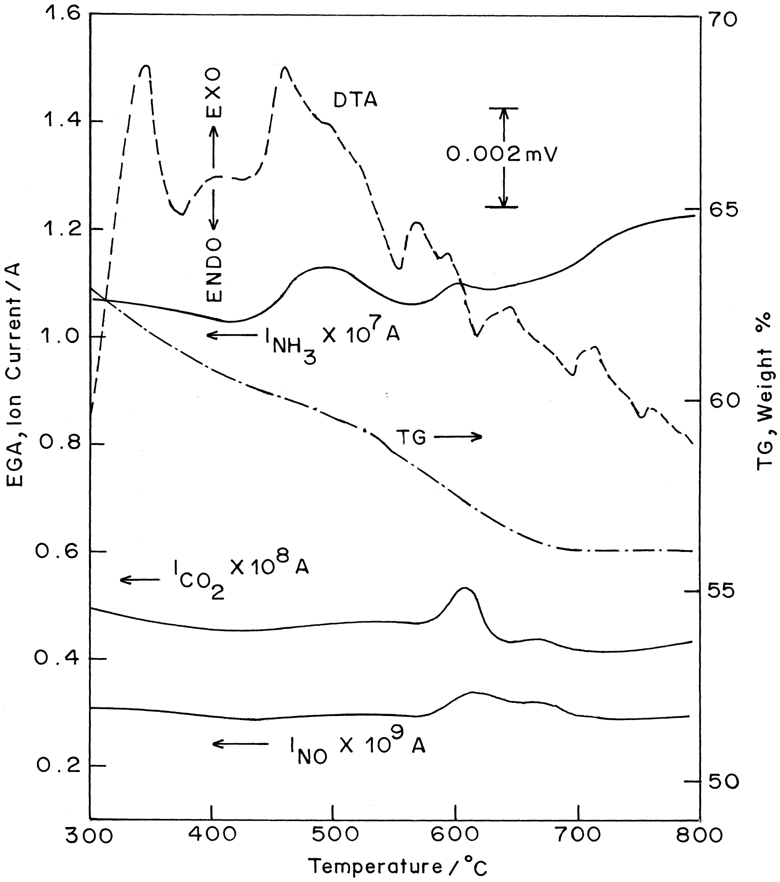

Fig. 2. Expanded TG–DTA–EGA curves showing thermal effects above 300°C in AUC co-precipitated with gadolinium carbonate.

nitrate occluded in the precipitate of AUC gives two peaks for NO evolution in the temperature ranges of 150–400°C and 400–500°C. The NO evolution peak in the temperature range of 550–700°C shows that the occluded nitrate is completely eliminated from the carbonate mixture only when the lattice of gadolinium carbonate is destroyed possibly because part of the occluded nitrate is in the form of gadolinium nitrate trapped in gadolinium carbonate. Our results show that complete destruction of carbonate and nitrate moieties in the precipitate is possible only when it is calcined at 700°C rather than at 650°C generally recommended [2]. The average value of total weight loss for the formation of the oxide mixture determined from several TG measurements is 44.7% which is in close agreement with the expected value of 45.12% for a mixture of the carbonates containing 8.88% gadolinium carbonate trihydrate and 91.12% AUC calculated from the composition of the mixture of nitrate solutions used for co-precipitation.

X-ray diffraction data recorded for the residue obtained at 800°C (Fig. 3) showed predominantly the diffraction peaks for α-U_3O_8 (orthorhombic) [9]. The presence of gadolinium oxide could be inferred from the diffraction peak corresponding to the *d*-spacing of 0.312 nm. It is also possible that this diffraction peak was due to the presence of a uranate of gadolinium, Gd_6UO_{12} [10,11]. The other diffraction peaks for Gd_2O_3 or Gd_6UO_{12} could not be identified because of the low level of gadolinium in the mixture and overlap of diffraction data for U_3O_8, Gd_2O_3 and Gd_6UO_{12}. The results of analysis of the diffraction data (excluding the peak at 0.312 nm) are presented in Table 1. Diffraction peaks with a relative intensity (I/I_0) better than 10% only have been considered for the analysis. It is seen from these data that the residue obtained by heating the co-precipitated carbonate mixture up to 800°C is predominantly α-U_3O_8 with orthorhombic structure [9]. The fact that the diffraction pattern for U_3O_8 was unaffected in the present study indicated that solid solution formation had not occurred even at 800°C. This result is in conformity with the observation of Beals and Handwerk [12] who reported only very small amounts of a cubic solid solution in U_3O_8–Gd_2O_3 mixtures sintered in air even at a temperature of 1700°C. Hence the validity of the conclusion by earlier workers [3] that decomposition of ADU containing co-precipitated gadolinium hydroxide results in the formation of a solid solution of Gd_2O_3 in U_3O_8 at about 600°C seems to be doubtful. The decrease in intensity of the peak for self-reduction of UO_3 observed in presence of Gd by these authors might have been due to other factors such as formation of small amounts of a stable uranate of gadolinium

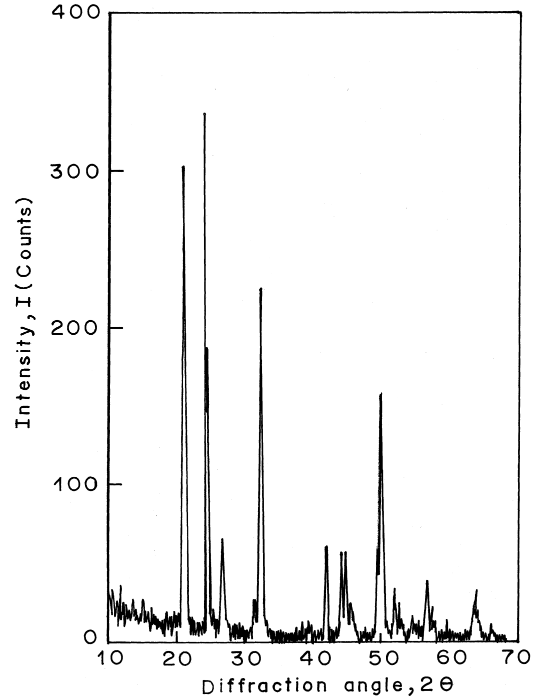

Fig. 3. X-ray diffraction pattern of the residue from TG–DTA–EGA measurements up to 800°C.

Table 1
Results of analysis of X-ray diffraction data for the residue obtained at 800°C

h	*k*	*l*	*d* (obs.) (×10^{10} m)	*d* (calc.) (×10^{10} m)	I/I_0 (obs.) (%)	Unit cell parameters (nm)			Volume (nm^3)
						a	*b*	*c*	
0	0	1	4.142	4.147	90.27	0.6715	1.1914	0.4147	0.33178
1	3	0	3.408	3.418	100.00	α	β	γ	
2	0	0	3.368	3.358	56.05	**90.00**	**90.00**	**90.00**	
1	3	1	2.637	2.638	67.26				
0	0	2	2.072	2.074	18.88				
0	6	0	1.977	1.986	17.40				
3	3	0	1.956	1.950	17.40				
1	3	2	1.773	1.773	35.69				
2	6	0	1.707	1.709	11.21				
2	6	1	1.579	1.580	12.98				

which also would account for the decrease in weight loss observed for the reduction step. Part of the UO_3 formed from ADU might have reacted with Gd_2O_3 to form Gd_6UO_{12}. The fact that these authors did not provide any X-ray diffraction data for the residue at 650°C further complicates the interpretation of their data. In the present study, UO_3 decomposed to U_3O_8 prior to the complete decomposition of gadolinium carbonate as evident from the TG–DTA–EGA data and the formation of gadolinium uranate, if any, would have occurred only above 700°C by the reaction of U_3O_8 with Gd_2O_3.

4. Conclusions

The present study shows that co-precipitation can be used as a suitable method for ensuring precipitation of a mixture of gadolinium carbonate and ammonium uranyl carbonate of a pre-determined composition. It is also concluded that thermal decomposition of ammonium uranyl carbonate and co-precipitated gadolinium carbonate trihydrate cannot be used as a method for the preparation of $(U,Gd)_3O_8$ solid solution at or below 800°C. As no evidence for the formation of a solid solution was obtained from X-ray diffraction measurements even on heating the mixture of oxides formed from the carbonate precursor up to 800°C, the earlier report on the formation of a solid solution on heating ammonium diuranate and co-precipitated gadolinium hydroxide may not be acceptable.

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