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Combustion synthesis of urania–thoria solid solutions

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Abstract

The feasibility of the combustion synthesis using citric acid as the fuel was studied in order to prepare a homogeneous mixture of uranium dioxide–thorium dioxide feed powder that could be cold compacted without binder or lubricant and sintered to a high density ($\geqslant$95% theoretical density) at relatively low temperatures ($\geqslant$1573 K). Systematic studies were carried out to optimize various process parameters such as fuel-to-oxidant mole ratio, method of heating and sintering temperature. The powders were characterized for their carbon content, specific surface area, particle size distribution and bulk density. The crystallite size of the powders was determined by the X-ray line-broadening technique. The microstructure and surface morphology of the powders were studied using scanning electron microscopy. The reactivity of the calcined powders was determined by measuring the density of the sintered compacts prepared from them. The performance of citric acid as a combustion fuel was compared with that of poly vinyl alcohol. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Homogeneous solid solutions containing uranium and thorium oxides with $U/(U+Th) \leqslant 0.3$ are being developed as fuels for thermal breeder reactors and advanced gas-cooled reactors. India has vast resources of thorium and utilization of thorium can diversify the nuclear energy resources for a long-term nuclear energy programme. As a part of the thorium utilization programme in India, ThO_2–$^{233}UO_2$ ($\leqslant$2% $^{233}UO_2$) fuel is being developed in Bhabha Atomic Research Centre, Trombay for pressurized heavy water reactors [1,2]. Studies are being carried out at the Indira Gandhi Centre for Atomic Research, Kalpakkam (i) to develop alternative low-cost methods for the fabrication of thoria and (U,Th) mixed oxides [3–5] and (ii) to measure the physicochemical properties of these compounds [6].

High density (U,Th) mixed oxide pellets can be prepared by various methods. The commonly employed methods are: (i) direct mixing of the two oxides followed by compaction and sintering, (ii) co-precipitation of thorium and uranium as hydroxides or oxalates and subsequent calcination and sintering, (iii) direct denitration of the nitrates of uranium and thorium, (iv) sol–gel techniques, etc. A detailed description and comparison of these methods, their relative merits and demerits have been discussed elsewhere [4]. In general, these methods use very high temperatures ($\geqslant$2000 K) for sintering which is an energy and cost-intensive process. Hence, studies are being carried out to examine the feasibility of preparing ThO_2 and $(U,Th)O_2$ powder feed that can be compacted and sintered to high densities at relatively low sintering temperatures in order to reduce the overall production cost. Recently, a novel method based on combustion synthesis using poly vinyl alcohol (PVA) as the fuel was successfully developed in our laboratory for the preparation of nanocrystalline ThO_2 [3] and $(U,Th)O_2(U/(U+Th) = 0.15, 0.50, 0.65, 0.8)$ powder feed [4]. A systematic study was also carried out to examine the suitability of various combustion fuels such as PVA, urea and citric acid for the preparation of thoria. Among the fuels examined, citric acid was found the most suitable combustion fuel for the preparation of

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thoria [5]. Such systematic studies have not been carried out for the preparation of (U,Th)O_2 powder feed. Hence, in the present work, studies were carried out to examine the suitability of citric acid as the combustion fuel for the preparation of (U,Th)O_2 powder feed. Various process parameters were optimized to prepare a powder feed that could be cold compacted and sintered to high densities.

2. Experimental

2.1. Chemicals

Nuclear grade uranium dioxide (99.99%) was obtained from the Nuclear Fuel Complex, India and thorium nitrate was from M/s Indian Rare Earths, India. Citric acid was of Analytical Reagent grade from M/s Sarabhai M. Chemicals, Mumbai, India.

2.2. Experimental procedure

The reactants such as uranyl nitrate, thorium nitrate and citric acid, used in this study were analyzed for their impurity content by inductively coupled plasma mass spectrometry and optical emission spectroscopy. Uranyl nitrate was prepared by dissolving U_3O_8 (obtained by heating nuclear grade UO_{2+x} in air at 1073 K for 5 h) in analytical reagent grade nitric acid followed by evaporation to dryness. The aqueous solution containing uranyl nitrate, thorium nitrate, and citric acid was heated using either a hot plate or a microwave oven (frequency 2450 MHz with an output of 600–700 W) till the whole solution was converted into a solid/powder. The resultant solid/powder (designated as 'as-prepared' powder) was then transferred into an alumina cup and calcined at 973 K for 5 h in air using a resistance-heating furnace in order to remove the residual carbon in the 'as-prepared' powders. No efforts were made to measure the temperature of the combustion reactions.

Different powders were obtained by hot plate as well as microwave combustion of mixtures of aqueous nitrate solutions of uranium and thorium with various citric acid-to-nitrate mole ratios (henceforth referred to as CA/NO_3^- ratio) followed by calcination of the resultant products in air. The preparation details are given in Tables 1–3.

The sinterability of the calcined powders was studied by measuring the sintered density of the compacts prepared from them. The compacts were prepared by pressing the calcined powders at 300 MPa into 10 mm diameter and 2–3 mm thick pellets by employing an electrically operated double action hydraulic press. No binder or lubricant was added for the preparation of the compacts. The compacts thus prepared were sintered at

Table 1
Physicochemical properties of powders obtained by combustion of a mixture of aqueous nitrate solutions of uranium and thorium corresponding to $U/(U+Th) = 0.30$, with various CA/NO_3^- ratios in the initial combustion mixture

Mode of heating/description	CA/NO_3^- ratio	Sample designation	SSA[a] ($m^2\ g^{-1}$)	Crystallite size (nm)	Bulk density ($Mg\ m^{-3}$)
Microwave combustion	1.50	MC1	12.5	5	1.01
	1.25	MC2	14.3	6	1.01
	0.75	MC3	23.7	6	0.97
	0.50	MC4	18.8	6	0.60
	0.25	MC5	6.8	23	0.31
Calcination of MC1 powder	–	MC1A	11.9	7	1.00
Calcination of MC2 powder	–	MC2A	13.4	8	1.14
Calcination of MC3 powder	–	MC3A	12.4	9	1.05
Calcination of MC4 powder	–	MC4A	5.9	11	0.66
Calcination of MC5 powder	–	MC5A	3.79	15	0.36
Hot plate combustion	1.50	HC1	12.9	5	1.08
	1.25	HC2	15.6	5	1.14
	0.75	HC3	15.9	5	1.05
	0.50	HC4	12.74	6	0.61
	0.25	HC5	6.7	15	0.21
Calcination of HC1 powder	–	HC1A	10.55	6	1.16
Calcination of HC2 powder	–	HC2A	12.09	7	1.29
Calcination of HC3 powder	–	HC3A	12.21	8	1.00
Calcination of HC4 powder	–	HC4A	6.0	8	0.52
Calcination of HC5 powder	–	HC5A	5.3	13	0.31

[a] Specific surface area.

Table 2
Physicochemical properties of powders obtained by combustion of a mixture of aqueous nitrate solutions of uranium and thorium corresponding to $U/(U+Th) = 0.75$, with various CA/NO_3^- ratio in the initial combustion mixture[a]

Mode of heating/description	CA/NO_3^- ratio	Sample designation	SSA ($m^2\ g^{-1}$)	Crystallite size (nm)	Bulk density ($Mg\ m^{-3}$)
Microwave combustion	1.50	MCC1	13.4	7	0.79
	1.25	MCC2	15.0	8	0.96
	0.75	MCC3	6.7	10	0.39
	0.50	MCC4	4.2	15	0.26
	0.25	MCC5	4.5	16	0.19
Calcination of MCC1 powder	–	MCC1A	11.7	9	0.77
Calcination of MCC2 powder	–	MCC2A	11.1	9	0.97
Calcination of MCC3 powder	–	MCC3A	6.6	11	0.47
Calcination of MCC4 powder	–	MCC4A	3.1	17	0.24
Calcination of MCC5 powder	–	MCC5A	1.7	20	0.21
Hot plate combustion	1.50	HCC1	12.5	5	0.98
	1.25	HCC2	14.2	5	0.98
	0.75	HCC3	6.8	6	0.93
	0.50	HCC4	4.4	12	0.20
	0.25	HCC5	3.1	15	0.16
Calcination of HCC1 powder	–	HCC1A	11.5	6	0.97
Calcination of HCC2 powder	–	HCC2A	11.0	6	0.94
Calcination of HCC3 powder	–	HCC3A	6.3	7	0.67
Calcination of HCC4 powder	–	HCC4A	2.5	17	0.39
Calcination of HCC5 powder	–	HCC5A	1.0	22	0.20

[a] Both the 'as-prepared' and the calcined powders contain a biphasic mixture $yU_aTh_{1-a}O_{2+x}+(1-y)U_3O_8$ corresponding to the overall composition $(U_{0.75}Th_{0.25})O_{2+x}$.

various temperatures (1473–1773 K) for 5 h in a flowing argon-2 vol.% hydrogen gas mixture (flow rate: $8.3 \times 10^{-6}\ m^3\ s^{-1}$).

2.3. Characterization of the powders, green compacts and sintered compacts

The completion of the combustion synthesis was determined by quantitative infrared (IR) spectroscopic analysis by using a Bomem MB 100 Fourier transform infrared spectrometer. The surface area of the powders was measured by the BET method using Monosorb MS-16 surface area analyzer supplied by M/s Quantachrome, USA. The particle size analysis was carried out with Mastersizer particle size analyzer supplied by M/s Malvern, Worcestershire, UK. The X-ray powder patterns were obtained by using Philips X-ray diffractometer (XPERT MPD system obtained from M/s Philips, The Netherlands), employing filtered Cu-Kα radiation. The average crystallite size of the powders was measured by X-ray line broadening technique employing the Scherrer formula using the profiles of the (2 2 0) peak [7]. Standard silicon was used for estimation of the instrumental broadening.

'As-prepared' powders and calcined powders were characterized for microstructure and morphological characteristics by using a Philips SEM 501 scanning electron microscope. The densities of the compacts were measured by liquid immersion technique employing dibutyl phthalate as the immersion liquid. The density reported is the average value for 10 pellets.

The amount of carbon present in the powders and sintered compacts was determined by oxidizing the sample in a stream of oxygen in an induction furnace. The carbon dioxide thus evolved was measured by an infrared detector.

The chemical composition of the mixed oxide was determined by both chemical characterization, involving the elemental analyses of uranium and thorium, and lattice parameter measurements. The details of the analytical method for the elemental analyses are given in Ref. [4]. The oxygen-to-metal ratio (O/M ratio) of the mixed oxide (sintered compacts) was determined by equilibrating the sample at 1073 K with a flowing stream of H_2–H_2O gas mixture. The oxygen potential of the gas mixture was maintained at -510 kJ mol^{-1}. After attainment of the equilibrium between the gas phase and the oxide sample (determined by using an oxygen probe based on calcia-stabilized zirconia solid electrolyte), the weight change of the sample was measured. From the weight change of the sample, the O/M was derived. A schematic diagram of the experimental set-up and the details of measurement are described elsewhere [6].

Table 3
Physicochemical properties of powders obtained by combustion of a mixture of aqueous nitrate solutions of uranium and thorium corresponding to various $U/(U+Th)$ ratios (CA/NO_3^- ratio in the initial combustion mixture is 1.0)

Mode of heating	U/(U + Th) ratio	Sample designation	Phases present	SSA (m^2 g^{-1})	Crystallite size (nm)	Bulk density (Mg m^{-3})
Microwave combustion	0.15	M1	$(U_{0.15}Th_{0.85})O_{2+x}$	23	7	0.93
	0.30	M2	$(U_{0.3}Th_{0.7})O_{2+x}$	28	8	0.95
	0.50	M3	$(U_{0.5}Th_{0.5})O_{2+x}$	29	7	1.02
	0.75	M4	$(U_{0.75}Th_{0.25})O_{2+x}$ $[MO_{2+x}+U_3O_8]$	15	10	0.96
	0.90	M5	$(U_{0.9}Th_{0.1})O_{2+x}$ $[MO_{2+x}+U_3O_8]$	7	12	1.00
Calcination of M1 powder	0.15	M1A	$(U_{0.15}Th_{0.85})O_{2+x}$	14	8	1.09
Calcination of M2 powder	0.30	M2A	$(U_{0.3}Th_{0.7})O_{2+x}$	16	9	1.05
Calcination of M3 powder	0.50	M3A	$(U_{0.5}Th_{0.5})O_{2+x}$	17	8	0.94
Calcination of M4 powder	0.75	M4A	$(U_{0.75}Th_{0.25})O_{2+x}$	12	9	0.95
Calcination of M5 powder	0.90	M5A	$(U_{0.9}Th_{0.1})O_{2+x}$	5	11	0.96
Hot plate combustion	0.15	H1	$(U_{0.15}Th_{0.85})O_{2+x}$	20	4	0.90
	0.30	H2	$(U_{0.3}Th_{0.7})O_{2+x}$	18	5	1.01
	0.50	H3	$(U_{0.5}Th_{0.5})O_{2+x}$	18	5	0.97
	0.75	H4	$(U_{0.75}Th_{0.25})O_{2+x}$ $[MO_{2+x}+U_3O_8]$	12	7	0.96
	0.90	H5	$(U_{0.9}Th_{0.1})O_{2+x}$ $[MO_{2+x}+U_3O_8]$	6	7	0.98
Calcination of H1 powder	0.15	H1A	$(U_{0.15}Th_{0.85})O_{2+x}$	14	7	1.06
Calcination of H2 powder	0.30	H2A	$(U_{0.3}Th_{0.7})O_{2+x}$	14	7	1.10
Calcination of H3 powder	0.50	H3A	$(U_{0.5}Th_{0.5})O_{2+x}$	17	7	0.91
Calcination of H4 powder	0.75	H4A	$(U_{0.75}Th_{0.25})O_{2+x}$ $[MO_{2+x}+U_3O_8]$	12	8	0.98
Calcination of H5 powder	0.90	H5A	$(U_{0.90}Th_{0.10})O_{2+x}$ $[MO_{2+x}+U_3O_8]$	4	6	1.02

3. Results and discussion

3.1. Purity of the initial combustion mixture

The total metallic impurity present in a typical combustion mixture, used in this study, was less than 100 ppm (by weight). The content of impurities in the sintered product did not differ significantly from the values for the reactant powders. The metallic impurities such as Nb, Mg, Ti, V etc. which can act as sintering aids were found to be insignificantly low. Hence, the sinterability of the powders used in this study was determined only by the powder characteristics such as surface area, particle size distribution, crystallite size, etc.

3.2. Combustion process

The combustion process involves dehydration followed by denitration of the nitrates and destruction of CA as in the case of PVA-aided combustion syntheses of thoria and urania–thoria solid solutions [3,4]. The final product was porous, fluffy, crystalline and highly free flowing powder. The 'as-prepared' powders contained about 2000–4000 ppm of carbon. This is much less than the amount of carbon retained in the powders prepared using PVA as the fuel [3,4]. The amount of carbon present in the 'as-prepared' powders did not vary significantly whether the denitration was carried out using a microwave oven or a hot plate.

The IR spectra of the reactants and typical 'as-prepared' powders and calcined powders are shown in Fig. 1. The IR spectra of the 'as-prepared' powders reveal that the CA is destroyed completely and the uranyl nitrate and thorium nitrate are completely denitrated during combustion. A very small peak at 1384 cm^{-1} corresponding to the N–O stretching frequency of the free nitrate is seen in some of the 'as-prepared' samples. This may be due to the nitric acid adsorbed on the $(U,Th)O_2$ powder surface as observed in the case of PVA-aided denitration of thorium nitrate [3]. Quantitative Fourier transform infrared analysis reveals that the amount of nitrate in these samples is less than 0.01% of the initial nitrate taken for the combustion process. However, in the case of PVA-aided combustion

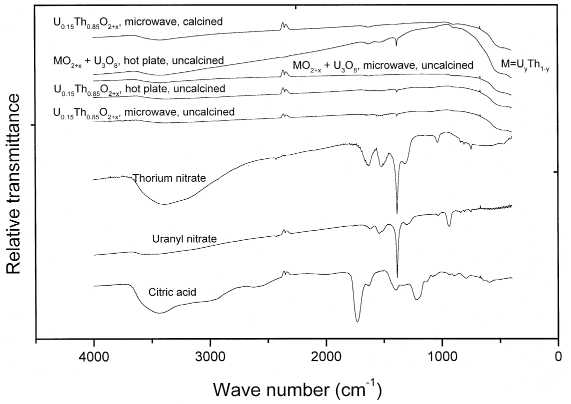

Fig. 1. The IR spectra of typical 'as-prepared' powders, calcined powder and the reactants.

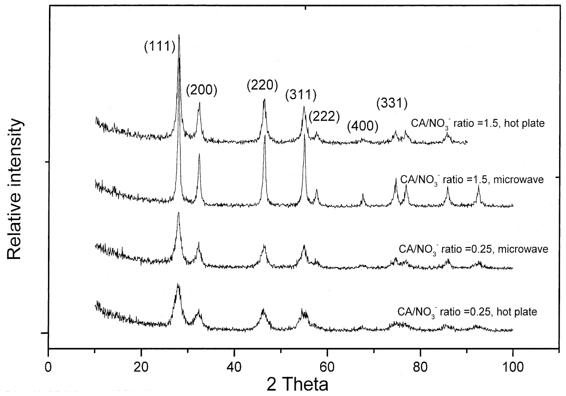

Fig. 2. X-ray diffraction patterns of the 'as-prepared' powders with $U/(U+Th) = 0.3$.

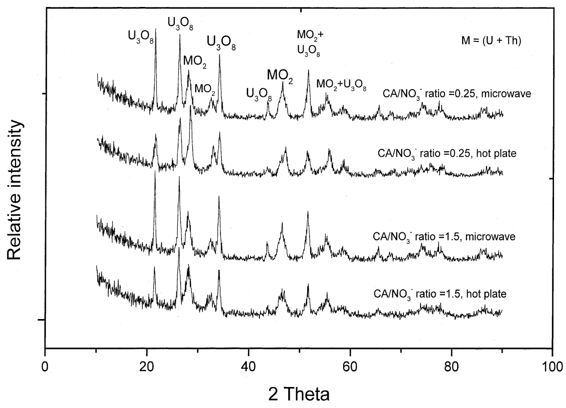

Fig. 3. X-ray diffraction patterns of the 'as-prepared' powders with $U/(U+Th) = 0.75$.

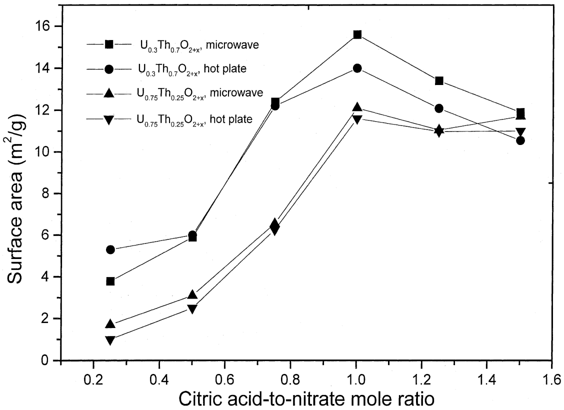

Fig. 4. Dependence of specific surface area of the calcined powders on the CA/NO_3^- ratio.

syntheses of urania–thoria solid solutions, Chandramouli et al. [4] have reported that PVA was destroyed only partially during the combustion process. They have reported the presence of a large amount of residual carbon (3–6 wt%) with filamentary morphology in the 'as-prepared' powders, due to incomplete destruction of PVA.

Chandramouli et al. [4] have also demonstrated that, both H^+ and NO_3^- (in addition to oxygen) played a role in the oxidation of PVA and insufficient amount of oxygen, H^+ and NO_3^- were responsible for the incomplete destruction of PVA. In order to examine whether H^+ and NO_3^- play a role in the oxidation of CA, the following three mixtures were heated by using a hot plate as well as a microwave oven: (i) an aqueous solution of CA, (ii) CA + HNO_3 and (iii) CA + $NaNO_3$. In both case (i) and case (ii), water/HNO_3 was evaporated completely on heating either by a hot plate or by a microwave oven. However, molten CA could be charred to a black residue on further heating only on a hot plate since molten CA is microwave inactive under these experimental conditions. In case (iii), the reaction was violent and CA could be completely oxidized on a hot plate. A mixture of molten CA and $NaNO_3$ was microwave inactive. These results suggest that, in addition to thermal energy, the oxidant NO_3^- plays a role in the oxidation of CA. In the present study, combustion of CA could be carried out using a microwave oven because of the presence of microwave active species such as uranyl nitrate and U_3O_8 (formed during combustion process). The standard enthalpy of reaction, $\Delta_f H^0_{298}$, for the oxidation of one mole of CA in air to give CO_2 and H_2O is –(1961 ± 4.6) kJ mol^{-1} [8]. The high exothermicity of this reaction along with the thermal energy supplied externally leads to the ignition and combustion of the reaction mixture. The oxidation of CA is further aided by the strong oxidant NO_3^-.

In general, the denitration of aqueous nitrates of uranium and thorium corresponding to

$U/(U+Th) \leqslant 0.5$, in the presence of CA leads to the formation of a single-phase $U_yTh_{1-y}O_{2+x}$ solid solution. The values of x were found to be 0.08 ± 0.005, 0.15 ± 0.005 and 0.22 ± 0.01 for the compounds with $y = 0.15, 0.30$ and 0.50, respectively. A mixture of a MO_{2+x} [where $M = U + Th$] solid solution and U_3O_8 (overall composition is represented as $U_yTh_{1-y}O_{2+x}$) is obtained when $U/(U+Th) > 0.5$. The values of x were found to be 0.35 ± 0.01 and 0.37 ± 0.01 for the compounds with $y = 0.75$ and 0.90, respectively. This is true whether the denitration is carried out on a hot plate or in a microwave oven. It has been established in the literature that thoria is insoluble in U_3O_8 [9].

The effect of CA content in the initial combustion mixture on the physical characteristics of the powders formed during combustion was studied in detail by varying the CA/NO_3^- ratio from 0.25 to 1.5 in steps of 0.25. Fig. 2 shows the X-ray diffraction patterns of the 'as-prepared' powders with $U/(U+Th) = 0.3$. The combustion product was always a single-phase $(U_yTh_{1-y})O_{2+x}$ solid solution with $y = 0.3$, irrespective of the values of CA/NO_3^- ratio and the method of heating. The figure also shows that even when the CA content is very low (CA/NO_3^- ratio $\leqslant 0.5$), well-developed crystalline single-phase solid solutions are formed.

The U–Th–O phase diagram [10] indicates that a single-phase solid solution $(U_yTh_{1-y})O_{2+x}$ is stable in air only when $y \leqslant 0.5$. When the value of y is higher than 0.5, U_3O_8 is precipitated. The effect of the precipitation of U_3O_8 (during combustion process), on the characteristics of the resultant powders was also examined. Fig. 3 shows the X-ray diffraction patterns of the 'as-prepared' powders with $U/(U+Th) = 0.75$. The combustion product was a biphasic mixture containing MO_{2+x} and U_3O_8, irrespective of the CA/NO_3^- ratio and the method of heating. However, the denitration in the presence of PVA always leads to the formation of a single-phase $U_yTh_{1-y}O_{2+x}$ solid solution, irrespective of the uranium content [4]. Oxidation of PVA during the combustion synthesis is reported to be incomplete [4] and the residual carbon in the sample results in a reducing atmosphere. Therefore, the solid solution formed does not undergo further oxidation to form a thermodynamic equilibrium phase mixture of MO_{2+x} and U_3O_8. In the present study, in addition to complete destruction of CA, the mixed oxides with $U/(U+Th) > 0.5$ are further oxidized to give the equilibrium phase mixture of MO_{2+x} and U_3O_8. Calcination of the 'as-prepared' powders in air at 973 K for 5 h, reduces the carbon content of the powders to 400–900 ppm.

3.3. Powder characteristics

3.3.1. Surface area and particle size distribution

The BET surface areas of the 'as-prepared' and calcined powders are given in Tables 1–3. The particle size distribution of the calcined powders is given in

Table 4
Particle size distribution of calcined powders

Sample	Particle size distribution (vol.%)		
	10 vol.% of the sample has particle size less than (μm)	50 vol.% of the sample has particle size less than (μm)	90 vol.% of the sample has particle size less than (μm)
MC1A	11	47	121
MC2A	13	43	100
MC3A	1	18	56
MC4A	13	100	283
MC5A	6	126	349
HC1A	6	36	99
HC2A	6	32	89
HC3A	9	40	128
HC4A	7	37	116
HC5A	1	31	210
MCC1A	7	37	139
MCC2A	3	48	168
MCC3A	3	57	201
MCC4A	2	47	327
MCC5A	15	143	396
HCC1A	1	43	258
HCC2A	4	65	253
HCC3A	22	103	260
HCC4A	4	39	237
HCC5A	25	108	290

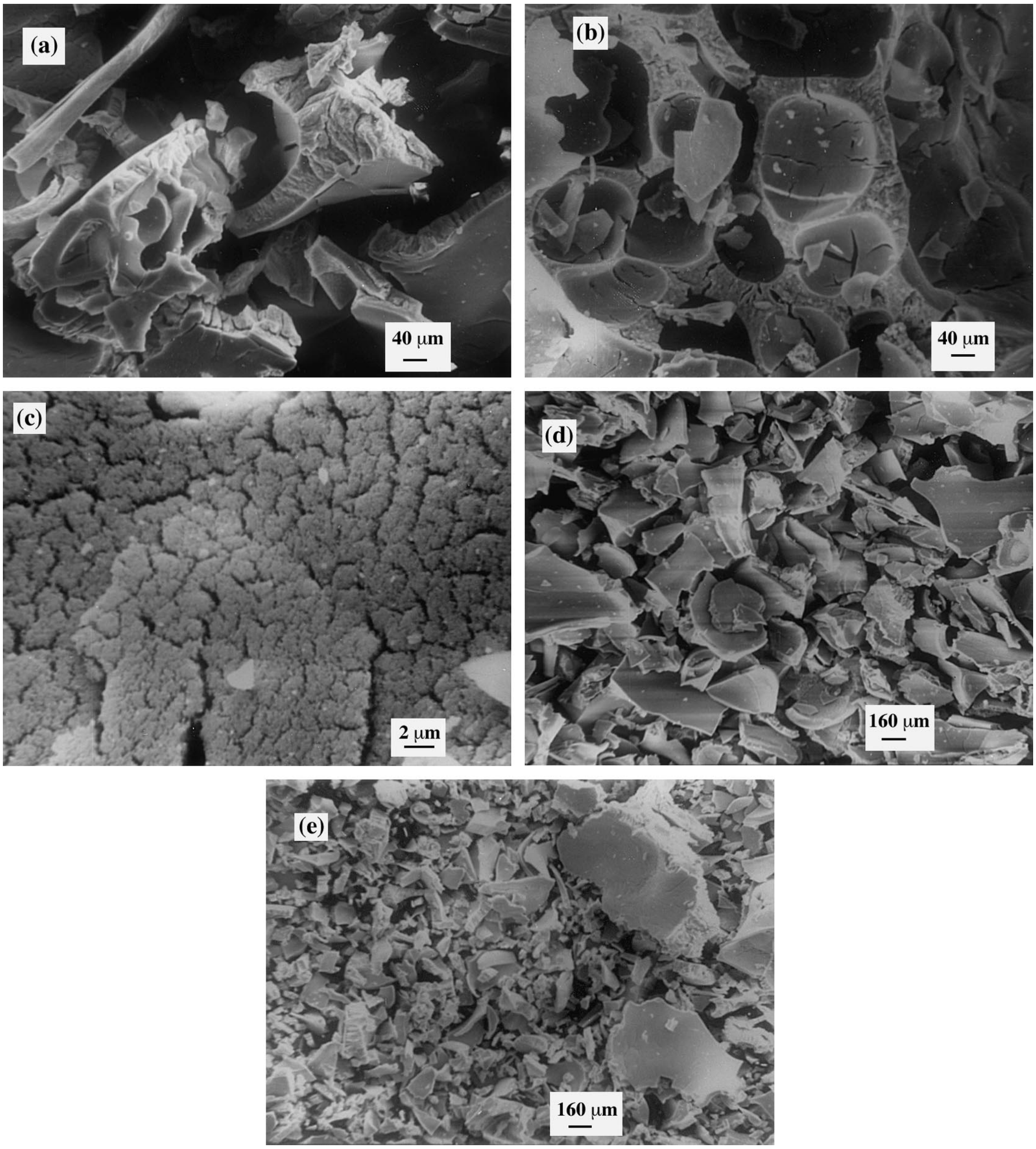

Fig. 5. SEM micrographs of typical 'as-prepared' and calcined powders. (a) Microwave-derived, calcined powder, $U_{0.3}Th_{0.7}O_{2+x}$, showing fractured surfaces and pores. (b) Microwave derived 'as-prepared' powder, $U_{0.75}Th_{0.25}O_{2+x}$, showing porosity in the particle. (c) Surface of a particle in powder $U_{0.3}Th_{0.7}O_{2+x}$. (d) SEM showing the particle size distribution in microwave-derived powder $U_{0.3}Th_{0.7}O_{2+x}$. (e) SEM showing the particle size distribution in hot plate-derived powder $U_{0.3}Th_{0.7}O_{2+x}$.

Table 4. Fig. 4 shows the dependence of surface area of the calcined powders on the CA/NO_3^- ratio. The surface area of the powders increases with increasing CA/NO_3^- ratio whereas the average particle size decreases with increasing CA/NO_3^- ratio. The same trend is observed for both microwave-derived powders as well as hot plate-derived powders. During the combustion/denitration process, a large amount of gaseous material is evolved and hence the combustion product is highly porous with fractured surfaces as shown in the SEM micrographs (Fig. 5(a)–(c)). As the CA/NO_3^- ratio increases, the amount of gaseous material evolved also increases. Consequently, the resultant powders have a higher surface area and lower mean agglomerate size. However, the increase in surface area of the powders is not significant when the CA/NO_3^- ratio is more than 1.0. This may be due to partial sintering of powder particles when excess heat is liberated during the combustion of

excess CA. The mean particle size also does not vary significantly when the CA/NO_3^- ratio is more than 1.0. The above results suggest that powders with maximum surface area and minimum agglomerate size can be obtained when the CA/NO_3^- ratio in the combustion mixture is 1.0. The surface area of the calcined powders obtained in this study (CA/NO_3^- ratio $\geqslant 1.0$) is significantly higher than the surface area of the calcined powders obtained from PVA-aided denitration process [4]. This is mainly due to the evolution of larger amounts of gaseous material during the complete oxidation of CA compared to the lesser amount of gaseous material evolved during the partial oxidation of PVA. Moreover, in the present study, the 'as-prepared' powders were calcined at 973 K, whereas the PVA-derived powders were calcined at 1073 K.

The amount of uranium in the initial reaction mixture also influences the surface area and particle size distribution of the 'as-prepared' powders. For a given CA/NO_3^- ratio, the surface area of the 'as-prepared' powder decreases as the uranium content increases. This is due to effective coupling of aqueous uranyl nitrate and uranium oxides with the microwaves [4]. Consequently, the 'as-prepared' powder particles with higher uranium content sinter to yield a lower surface area. The above results are in agreement with the results reported by Chandramouli et al. [4] for the preparation of $(U,Th)O_2$ powders by the PVA-aided denitration process.

The particle size distribution of powders obtained from microwave combustion as well as hot plate combustion are shown by SEM micrographs, Fig. 5(d) and (e), respectively. The mean particle size of the powders derived through microwave combustion is relatively larger and more uniform compared to the hot plate-derived powders. However, for a given CA/NO_3^- ratio and U/(U + Th) ratio, the microwave-derived powders have relatively higher surface areas, compared to the hot plate-derived powders. This may be due to more uniform heating (hence more uniform gas evolution) used for the combustion that can be achieved in a microwave oven, although the temperatures reached in the microwave heating may be more than that obtained with the hot plate. Hence, microwave-derived powders seem to be more surface active.

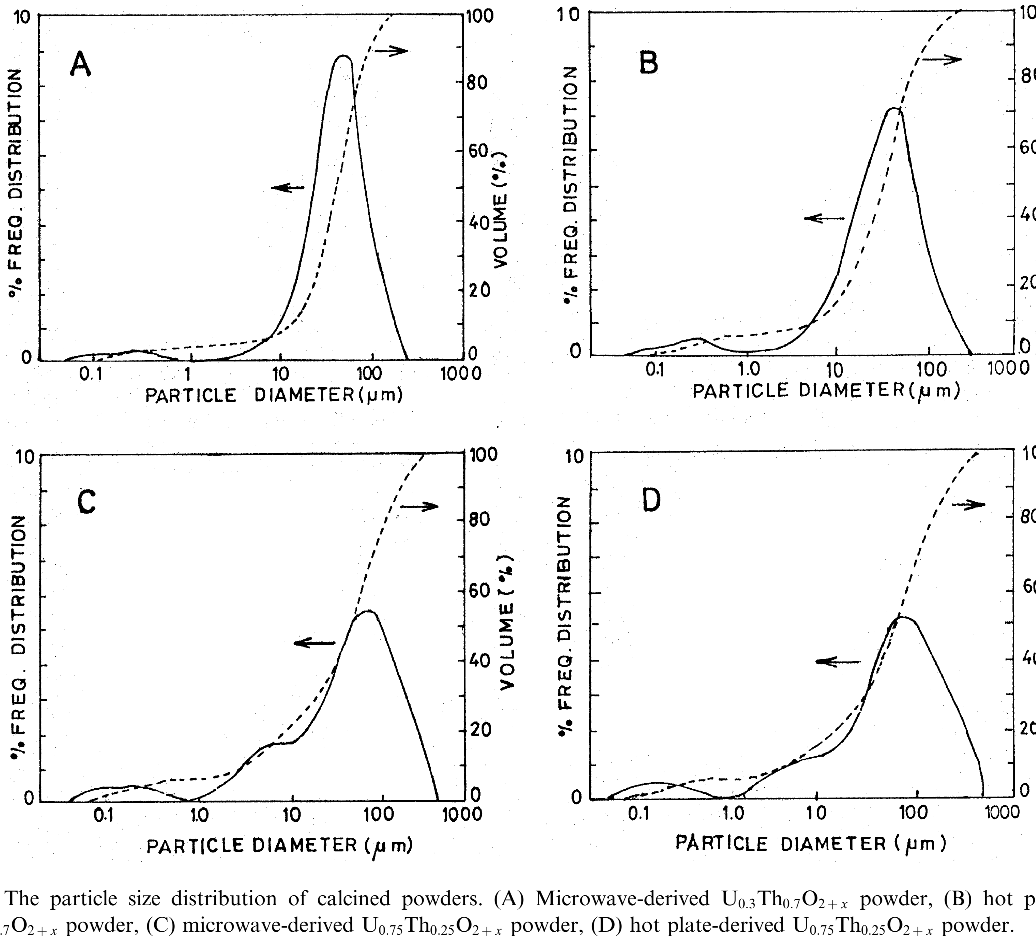

Fig. 6. The particle size distribution of calcined powders. (A) Microwave-derived $U_{0.3}Th_{0.7}O_{2+x}$ powder, (B) hot plate-derived $U_{0.3}Th_{0.7}O_{2+x}$ powder, (C) microwave-derived $U_{0.75}Th_{0.25}O_{2+x}$ powder, (D) hot plate-derived $U_{0.75}Th_{0.25}O_{2+x}$ powder.

The mean particle size of the calcined powders increases with increasing uranium content in the combustion mixture. Powders with lower uranium content have a sharp uni-modal distribution, whereas bi-modal or poly-modal distributions are observed in the case of powders with higher uranium content as shown in Fig. 6.

3.3.2. Bulk and green density

The bulk-density of the 'as-prepared' and calcined powders was found to be ≈1 Mg m^{-3} when the CA/NO_3^- ratio is $\leqslant 1.0$ (see Tables 1–3). This is true for both microwave and hot plate-derived powders. However, when the CA/NO_3^- ratio is < 1.0, the bulk-density of the resultant powders decreases to about 0.3–0.2 g/cm^3 because of agglomeration of particles.

Burke et al. [11] have studied the relationship between the densities of green compacts and sintered compacts of $(U_yTh_{1-y})O_{2+x}$ in detail. The results of the study indicated that green compacts with 50–60% theoretical density (TD) on sintering at a given temperature yielded compacts with maximum density. Hence in the present study, green compacts with 50–60% TD were used for sintering studies.

3.3.3. Crystallite size

The X-ray crystallite size of the 'as-prepared' and calcined powders increases with decreasing CA/NO_3^- ratio as can be seen from Tables 1–3. Since the nitrates or the citrate complexes of uranium and thorium [12] are uniformly distributed in the CA matrix, the agglomeration of oxide particles is prevented during the combustion process. When the amount of CA in the reaction mixture is decreased the probability of particle growth increases. Hence, the crystallite size of the particles increases when the CA/NO_3^- ratio is decreased. The

Table 5
Density of compacts as a function of sintering temperature

Sintering temperature (K)	Pellets from M2A		Pellets from M4A		Pellets from H2A		Pellets from H4A	
	Sintered density (Mg m^{-3})	% TD	Sintered density (Mg m^{-3})	% TD	Sintered density (Mg m^{-3})	% TD	Sintered density (Mg m^{-3})	% TD
1473	9.81	95.32	9.97	92.92	9.64	93.71	9.96	92.88
1573	9.90	96.21	10.10	94.17	9.76	94.88	10.02	93.47
1673	9.91	96.36	10.21	95.22	9.78	95.11	10.17	94.87
1773	9.96	96.81	10.27	95.81	9.86	95.87	10.22	95.32

Table 6
Physicochemical properties of compacts

Pellets made from	Green density (Mg m^{-3})	Sintered density (Mg m^{-3})	% theoretical density	Lattice parameter (nm)
MC1A	6.01	9.96	96.81	0.55601 ± 0.00009
MC2A	6.40	9.93	96.52	
MC3A	5.31	9.62	93.50	
MC4A	5.23	9.52	92.56	
MC5A	5.67	9.10	88.41	
MCC1A	6.89	10.11	94.31	0.55034 ± 0.00007
MCC2A	6.10	10.10	94.20	
MCC3A	5.87	9.92	92.54	
MCC4A	6.23	9.78	91.23	
MCC5A	5.98	9.57	89.27	
HC1A	5.58	9.72	94.44	0.55591 ± 0.00003
HC2A	5.87	9.77	94.92	
HC3A	5.40	9.58	93.08	
HC4A	5.23	9.45	91.88	
HC5A	5.55	9.42	91.56	
HCC1A	5.01	10.01	93.42	0.55032 ± 0.00004
HCC2A	5.83	9.96	92.89	
HCC3A	5.40	9.77	91.12	
HCC4A	6.05	9.50	88.62	
HCC5A	5.83	9.21	85.91	

crystallite sizes of the microwave-derived powders are relatively larger than that of the hot plate-derived powders-perhaps the temperatures reached in the microwave heating may be more than that obtained with the hot plate because of the presence of uranium [13]. There is a marginal increase in the crystallite size of the calcined powders as compared to that of 'as-prepared' powders.

3.4. Sintering of $(U_yTh_{1-y})O_{2+x}$ compacts

The details of the sintering experiments carried out in this study are given in Tables 5 and 6. The carbon content of the sintered compacts was found to be 30–90 ppm which is much less than the value (100 ppm) specified for the PHWR thoria pellets [14]. Fig. 7 shows the X-ray diffraction patterns of sintered products. Single-phase $(U_yTh_{1-y})O_2$ solid solutions are obtained, irrespective of the phases present in the calcined powders, after sintering the compacts in argon–2 vol.% hydrogen ($pO_2 \approx 10^{-20}$). The sintered samples on equilibrating with H_2–H_2O gas phase at −510 kJ mol^{-1} did not show any significant weight gain (< 0.1 mg for 10 g mixed oxide sample, which corresponds to ≈0.001 in the O/M value). This shows that the oxygen-to-metal ratio (O/M ratio) of the sintered compacts of mixed oxides is 2.0.

3.4.1. Effect of temperature

In order to examine the influence of temperature on the sinterability of calcined powders, the green compacts prepared from powders M2A, H2A (single-phase MO_{2+x}) and M4A, H4A (biphasic mixture, MO_{2+x} and U_3O_8) were sintered at temperatures varying from 1473 to 1773 K. The densities of the sintered compacts are shown in Fig. 8 and Table 5. In general, increase in sintering temperature increases the density of the compacts, irrespective of the composition of the solid solutions. It is seen from Fig. 8 that microwave-derived

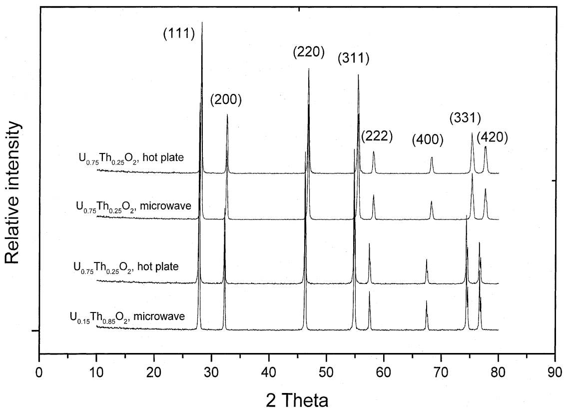

Fig. 7. X-ray diffraction patterns of the sintered compacts.

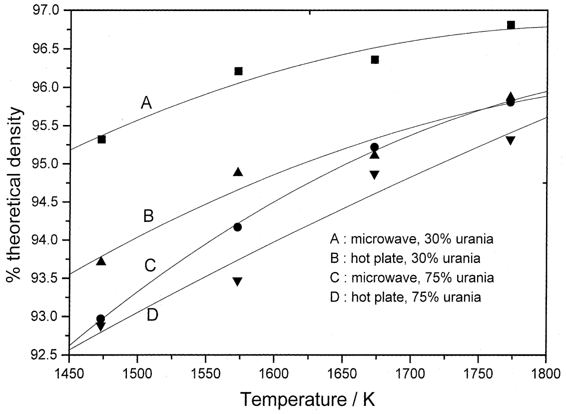

Fig. 8. Variation of density of the sintered compacts with sintering temperature.

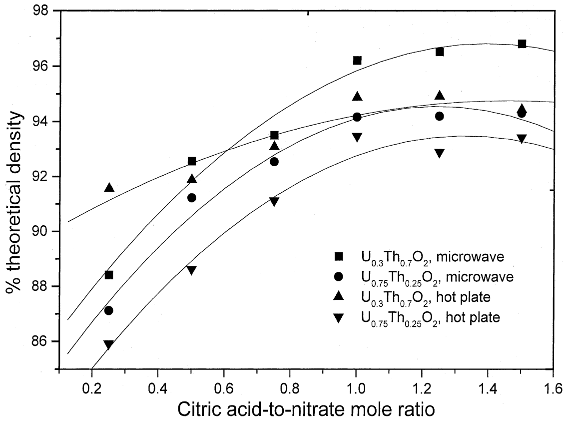

Fig. 9. Variation of density of the sintered compacts with CA/NO_3^- ratios.

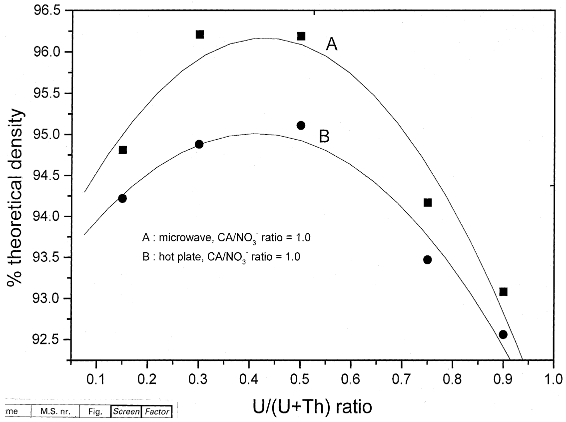

Fig. 10. Variation of density of the sintered compacts with U/(U + Th) ratios.

powder with $U/(U+Th) = 0.75$ (high urania powder) yielded compacts that could be sintered to $> 94\%$ TD at a temperature as low as 1573 K. Similarly, microwave-derived powder with $U/(U+Th) = 0.30$ (low urania powder) yielded compacts that could be sintered to $> 96\%$ TD at temperatures $\geqslant 1573$ K. The increase in density of the compacts with sintering temperatures is not significant beyond 1573 K. This is in agreement with the results reported by Chandramouli et al. [3,4]. They have reported 1573 K to be the optimum temperature for sintering thoria and urania–thoria powders derived through a combustion process using PVA as the fuel. The density of $(U,Th)O_2$ pellets, achieved in the present study is 94–96% TD compared to 89–91% TD reported by Chandramouli et al. [3,4]. The calcined powders prepared through CA-aided denitration are highly porous and crystalline with higher surface area than those of powders derived through PVA-aided denitration, and hence sintered to higher densities. It is also seen from Fig. 8 that, at a given sintering temperature, the green compacts prepared from microwave-derived powders sinter to higher densities compared to the green compacts prepared from hot plate-derived powders. This is because the microwave-derived powders have higher surface areas and relatively larger soft particles with high porosity compared to those of hot plate-derived powders. Hot plate-derived powder has smaller crystallite size which helps in acceleration of the sintering at a lower temperature with the result that no further sintering occurs at high temperatures. Hence, compacts made from hot plate-derived powders sinter to relatively lower densities compared to the compacts made from microwave-derived powders.

3.4.2. *Effect of fuel content*

In order to study the effect of fuel content in the initial reaction mixture on the sinterability of the resultant powders, the compacts prepared from powders, listed in Table 6, were sintered at 1573 K. The resulting densities of the sintered compacts are given in Table 6. From Fig. 9 it is clear that as the CA/NO_3^- ratio increases from 0.25 to 1.0, the sintered density of the corresponding compacts also increases. This is because of the increasing surface area and surface activity due to high porosity and fractured surfaces of the calcined powders. However, there is no significant change in the densities of the sintered compacts when the value of CA/NO_3^- ratio is increased from 1.0 to 1.5 for the preparation of powders. The optimum CA/NO_3^- ratio is found to be 1.0 for the preparation of powders that have suitable characteristics for making high density pellets.

3.4.3. *Effect of urania content*

Compacts (green density: ≈ 6 g cm^{-3}) prepared from powders, with various urania content, obtained through both microwave as well as hot plate combustion were sintered at 1573 K and the results are shown in Fig. 10. The CA/NO_3^- ratio in the combustion mixture was fixed at 1.0. From Fig. 10, it is seen that the density of the compacts increases as the amount of urania in the solid solution increases from 0 to 50 mol%. Beyond 50 mol% the densities decrease significantly with the increase in the urania content of the solid solution. This is due to lower surface area and higher agglomerate size of the powders. Moreover, calcined powders with more than 50 mol% urania, contain the second phase, U_3O_8, which decomposes to UO_2 and oxygen during the sintering process. This may increase the probability of closed pore formation throughout the compacts during sintering.

Microwave combustion of a mixture of aqueous nitrate solution of uranium and thorium (containing CA as fuel) is possible only when $U/(U+Th)$ ratio in the initial combustion mixture is $\geqslant 0.15$ since compositions with lower uranium content do not couple effectively with microwaves. Hence, it would appear that the low uranium-containing mixed oxide compositions relevant to PHWRs cannot be processed through microwave combustion route. However, from Fig. 10, it is seen that the hot plate-derived powders (with $U/(U+Th) \leqslant 0.02$) could be sintered to about 93% TD at 1573 K.

4. Conclusions

The studies lead to the following conclusions:

1. High density ($\geqslant 95\%$ TD) compacts of $U_yTh_{1-y}O_2$ solid solutions with $y \leqslant 0.5$ can be prepared by the following process: (i) Combustion/denitration of a mixture of aqueous uranyl nitrate, thorium nitrate and CA with a CA/NO_3^- ratio of 1.0 in a microwave oven, (ii) calcining the resultant powder in air at 973 K for 5 h, (iii) compacting the calcined powders at 300 MPa to obtain compacts with 55–60% TD and (iv) sintering the compacts at 1573 K in a flowing argon-2 vol% hydrogen gas mixture for 5 h.
2. High density ($\leqslant 95\%$ TD) compacts of $U_yTh_{1-y}O_2$ solid solutions with $y > 0.5$ can be prepared by the same procedure described above excepting the change in sintering temperature from 1573 to 1773 K.
3. The microwave-processed powders yield compacts that can be sintered to relatively high densities compared to the hot plate-derived powders.
4. CA is a better combustion fuel than PVA for the preparation of $(U_yTh_{1-y})O_2$ solid solutions through the combustion route.
5. The products obtained through the combustion route were found nanocrystalline, highly free flowing and porous powders that were found to be suitable as the feed material for making high density compacts.

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