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De-agglomeration of thorium oxalate – a method for the synthesis of sinteractive thoria

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Abstract

Thorium oxalate was obtained by precipitation in water and in non-aqueous solvents and de-agglomerated by ultrasonication in both aqueous as well as non-aqueous media. Sinteractive thoria (crystallite size 6–20 nm) obtained from the de-agglomerated thorium oxalate was characterised for residual carbon, crystallite size, specific surface area, particle size distribution and bulk density. Microstructure of the precursor and the product was studied using TEM and HRTEM. The morphology of the sintered pellets was studied using SEM. The reactivity of the calcined powders was determined by measuring the density of the sintered compacts. The solvent used for de-agglomeration was found to have significant influence on the microstructure of the powders. Thoria derived through aqueous precipitation route could be sintered to a density of 9.7 $\mathrm{Mg\,m^{-3}}$ at 1673 K. It was demonstrated that ultrasonic de-agglomeration could be a useful method for obtaining sinteractive thoria.

1. Introduction

Thoria finds application as a blanket material in fast breeder reactors (FBR) [1]. The solid solutions ThO_2–PuO_2 and ThO_2–UO_2 are candidate fuel materials for the advanced heavy water reactors (AHWR) [2]. Owing to its chemical stability, high melting point and low vapour pressure at elevated temperatures, thoria serves as a container material for many molten metals and alloys [3]. Thoria doped with 10–15 mol.% yttria is used as an oxide ion conducting solid electrolyte. All these applications require the use of dense ceramic bodies. Very often these applications call for densities in excess of 96% theoretical density (TD). In order to obtain thoria bodies with such high densities, conventional powder metallurgical processes are used. These processes employ high temperatures (>1900 K), for sintering and are energy and cost intensive [4].

In order to reduce the cost of fabrication of thoria ceramics, many ‘advanced techniques’ which are energy efficient, were developed in the past [4–21]. Some of these techniques aim at enhancing the surface activity of the press feed [4–14] while the others bring about accelerated sintering in thoria by doping it with an aliovalent cation [15–21]. Recent studies [7,8,11,12] have demonstrated that the gel combustion synthesis yields nanocrystalline powders of pure thoria that are highly sinteractive and free flowing. However, the sintered bodies produced from these powders have relatively higher quantities of carbon residue, significant microporosity and are prone to physical defects [14]. On the contrary, sintered compacts obtained from thoria derived by the calcination of ‘de-agglomerated’ oxalate are less prone to defects [14].

Several authors [22–27] demonstrated that the presence of strong agglomerates could seriously impair the sinterability of ceramic powders (oxides). It has also

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been established that the effective removal of the residual moisture present in the precursor helps in reducing the strength of the agglomerates in the final product [24–27].

Thoria obtained from thorium oxalate has cuboid morphology and is pseudomorphic with its precursor [28]. Factors such as the temperature of precipitation, pH, order of addition of the precipitant and the degree of agitation are known to affect the distribution as well as the strength of the agglomerates in the thorium oxalate precipitate [29,30] and the properties of the thoria powder derived from it [28]. Recently, Oktay and Yayli [31] demonstrated that ultrasonication brings down the size of the thorium oxalate particles. A recent study [14] carried out in our laboratory, revealed that sinteractive powders of thoria obtained from thorium oxalate that was ultrasonicated in ethanol or methanol could be sintered to a density of about 9.6 $\mathrm{Mg\,m^{-3}}$ at 1873 K. So far, no systematic study has been reported, in which the simultaneous influence of the dispersion medium as well as ultrasonication on the sinterability of thoria was investigated. Hence, in the present study the sinterability of the thoria powders derived from thorium oxalate that was precipitated, dispersed and ultrasonicated in five solvents of varying polarity was investigated.

2. Experimental

2.1. Chemicals

Nuclear grade thorium nitrate was obtained from M/s. Indian Rare Earths Ltd., Mumbai, India. Nitric acid (AR grade) and methanol (AR grade) were supplied by M/s. E. Merck (India) Ltd., Mumbai, India. Propan-2-ol was supplied by M/s. S.D. Fine-Chem Pvt. Ltd., Boisar, India. Absolute ethanol (99.7–100% v/v) was procured from M/s. Shymlakhs International, London, UK. Propan-2-one (AR grade) was obtained from M/s. Fischer Inorganics and Aromatics Ltd., Chennai, India.

2.2. Experimental procedure

2.2.1. Precipitation in aqueous medium

Thorium oxalate was quantitatively precipitated from thorium nitrate solution by the slow addition of oxalic acid (298 K) and filtered under suction. This precipitate was de-agglomerated twice, in about 250 ml of the dispersion medium by agitating it (15 min) in an ultrasonic agitator (M/s. Imeco Ultrasonics, Mumbai, India) and filtered under suction. The precipitate was dried under an infrared (IR) lamp. Five different dispersion media, viz., water, methanol, ethanol, propan-2-ol, and propan-2-one were used.

2.2.2. Precipitation in non-aqueous medium

Precipitation experiments similar to those described above were carried out in five different non-aqueous solvents, viz., methanol, ethanol, propan-2-ol or propan-2-one. This precipitate was dispersed in the solvent by ultrasonication, filtered under suction and dried under an IR lamp.

2.2.3. Calcination, consolidation and sintering

Thoria powders obtained by calcining the thorium oxalate powders in air at 973 K for 4 h were compacted (120 MPa) into pellets (10 mm diameter 2–3 mm thick). These pellets were sintered for 4 h in air between 1473 and 1873 K. A heating/cooling rate of 300 $\mathrm{K\,h^{-1}}$ was employed.

2.3. Characterisation of starting materials, powders and compacts

The impurities present in the starting materials were analysed using an inductively coupled plasma mass spectrometer (ICPMS), model Elan 250, supplied by M/s. Sciex, Toronto, Canada.

The surface area of the powders was measured by the BET method (Monosorb MS-16, M/s. Quantachrome Inc., USA). The particle size analyses were carried out by Mastersizer (M/s. Malvern, UK). The X-ray powder diffraction patterns were obtained using XPERT MPD system supplied by M/s. Philips, The Netherlands. The average crystallite size of the powders was measured by X-ray line broadening technique by the Scherrer formula [32] using the profiles of the (220) peak of thoria. The instrumental broadening was determined using standard silicon sample.

In order to examine the microstructure by TEM (200 kV, JEOL, model 2000 EX-II), a small quantity of the powder under investigation was suspended in methanol, de-agglomerated by sonicating in an ultrasonic cleaner and a drop of this suspension was placed on a copper grid coated with holey carbon film.

The densities of the sintered pellets were measured by using the Archimedes' principle with di-butyl phthalate as the pycnometric liquid.

The carbon residue present in thoria powders as well as in the sintered pellets, was determined by oxidising these samples in a stream of oxygen. The carbon dioxide thus evolved was measured using an infrared detector. The morphology of the pellets were obtained using a scanning electron microscope (SEM; model No. XL 30 ESEM, TMP, Holland).

3. Results and discussion

3.1. Purity of the starting materials

The starting materials used in this study had less than 100 ppm of metallic impurities. Cationic impurities such as Mg, Ca, V, Nb, Ta and Ti that can affect the sinterability of thoria were found to be insignificantly low.

3.2. Characteristics of the powders

3.2.1. Dispersion characteristics and morphology of the thorium oxalate precipitate

Dispersions of thorium oxalate in the non-aqueous solvents were viscous. The suspensions made in propan-2-one were voluminous.

All the thorium oxalate powders obtained through the aqueous route excepting the powder de-agglomerated in propan-2-one exhibited cuboidal morphology (Fig. 1(a)). The hydroxyl group present in water and alcohols facilitates the dispersion of oxide [26] and probably oxalates in these solvents. The nature of the interaction between the oxalate particles and propan-2-one (which does not possess a hydroxyl group) is different. Probably the inter-particle cohesion is stronger than the interaction between the oxalate particle and propan-2-one, which makes a given assembly of platelets to 'floc' together, leading to the formation of the spheroids, which are shown in Fig. 1(b). The HRTEM picture of this powder (Fig. 2) reveals that the orientation of the lattice planes in this thorium oxalate particle is parallel to its boundary. This provides a direct proof for the interaction between the oxalate particles and propan-2-one.

Fig. 3(a) and (b) show that the thoria powders obtained from thorium oxalate de-agglomerated in methanol and propan-2-one are pseudomorphic with their precursors. The thoria platelets were about 50 nm thick and consisted of grains that were a few nanometers in

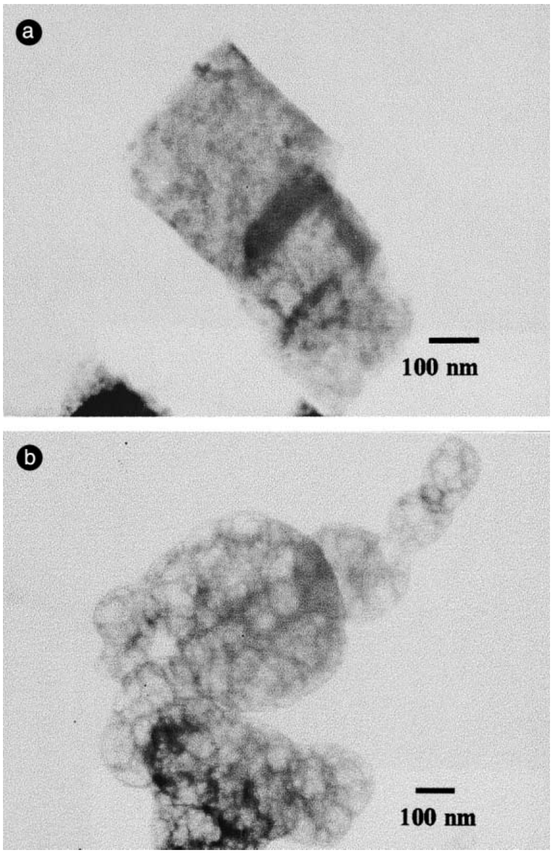

Fig. 1. TEM micrograph of (a) thorium oxalate de-agglomerated in methanol showing particles with platelet morphology, (b) thorium oxalate de-agglomerated in propan-2-one showing spheroidal morphology.

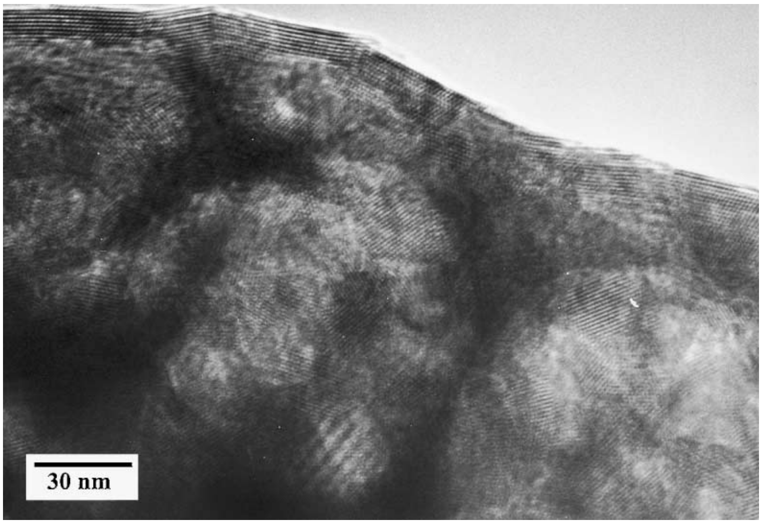

Fig. 2. HREM micrograph of thorium oxalate particles obtained by de-agglomeration in propan-2-one.

size. The powder shown in Fig. 3(b) reveals the presence of particles with irregular shape.

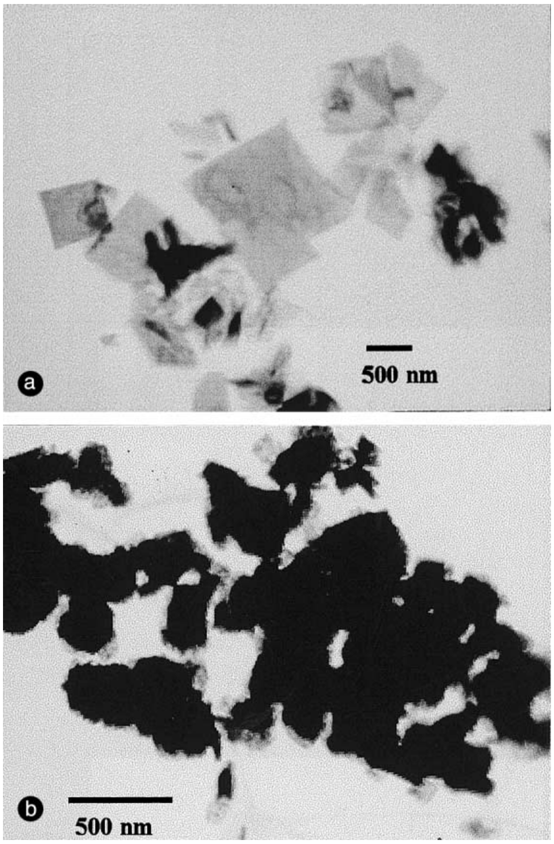

Fig. 3. TEM micrograph of thoria powder obtained by calcining thorium oxalate (a) de-agglomerated in methanol, (b) de-agglomerated in propan-2-one. These powders are pseudomorphic with their precursors (thorium oxalate).

3.2.2. Bulk density of the thoria powders

The bulk densities of the thoria powders obtained through the aqueous and non-aqueous precipitation routes are different (Table 1) and do not show any systematic dependence on the nature of the dispersion (or precipitation) medium. The non-aqueous route yields thoria with higher bulk densities and hard agglomerates while soft free flowing powders are obtained through aqueous precipitation.

The bulk density and morphology of 'oxalate-derived' thoria depend upon the precipitation conditions [29,30]. It is known [26] that the incomplete removal of anionic impurities in the precursor results in the formation of hard agglomerates in the product. The higher concentration of residual nitrate ions in the oxalate powders derived through the non-aqueous route led to the formation of hard agglomerates and enhanced the bulk density of the product.

3.2.3. Specific surface area and X-ray crystallite size

Calcination of thorium oxalate at 873 K yields a thoria powder that has maximum specific surface area [15,28,33,34]. At temperatures higher than 873 K a thoria powder with less carbon residue [15,30] and lower surface area is obtained. In order to obtain thoria powders with optimum specific surface area, containing reasonably low levels of carbon residue (Fig. 4), the thoria powders were calcined at 973 K.

The X-ray crystallite size of the thoria powders obtained through the non-aqueous route (average of 2–4 measurements) was in the range 2–6 nm while the aqueous precipitation yielded thoria powders with an average crystallite size of about 17 nm (Fig. 5). The crystallite size of the thorium oxalate (primary) particles is governed by the precipitation conditions. The crystallite size of the thoria (secondary) particles depends upon on the size of the precursor as well as on the temperature and duration of calcination. The depen-

Table 1
Properties of the thoria powders obtained from 'de-agglomerated' thorium oxalate

Dispersion medium	Bulk density ($Mg\,m^{-3}$)	Specific surface area (m^2/g)	Residual carbon (ppm)	X-ray crystallite size (nm)
Aqueous precipitation				
Water	–	12.51	1531	15.6
Ethanol	1.13	13.85	1274	15.2
Methanol	1.10	15.79	1295	14.8
Propan-2-ol	–	12.24	1094	19.3
Propan-2-one	1.10	10.17	1131	19.1
Non-aqueous precipitation				
Ethanol	1.32	14.34	1410	5.5
Methanol	1.44	17.45	1623	2.3
Propan-2-one	1.83	17.65	1601	3.4
Propan-2-ol	1.17	30.63	2072	2.2

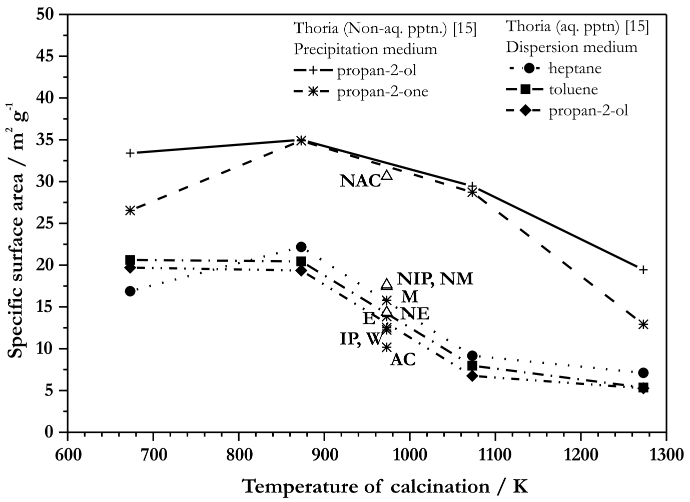

Fig. 4. Dependence of the surface area of thoria on the temperature of calcination of thorium oxalate. The labelled data were obtained in this study. The labels W, E, M, IP and AC denote the solvents, water, ethanol, methanol, propan-2-ol and propan-2-one respectively. N denotes non-aqueous precipitation.

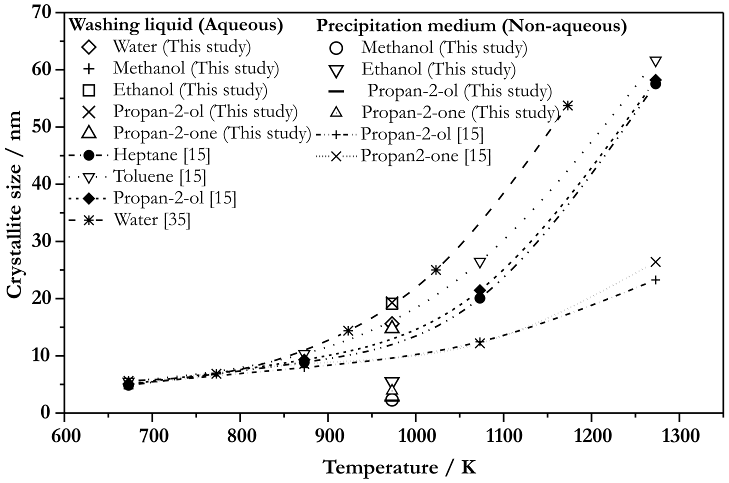

Fig. 5. Dependence of the X-ray crystallite size of thoria on the calciniation temperature.

dence of the X-ray crystallite size on the calcination temperature observed by Radhakrishnan et al. [15] for thoria derived through the de-agglomeration technique was similar to that reported by Allred et al. [35]. However thoria crystallites obtained through the de-agglomeration route were [15] smaller.

The non-aqueous precipitation route is expected to yield a precipitate with a lower crystallite size than that obtained from aqueous precipitation [30]. The results shown in Fig. 5 are in agreement with this conclusion. However, no discernible correlation seems to exist between the polarity of the solvents and the crystallite sizes of the corresponding product.

3.2.4. Carbon residue in thoria

It is well known [30,34] that thoria derived from thorium oxalate contains some carbon residue. Higher quantity of carbon residue was found in the thoria powders that were obtained through the non-aqueous route (Table 1) probably due to higher levels of adsorbed solvents in their precursors.

3.2.5. Particle size distribution and strength of agglomerates

The particle size distribution in the thoria powders (Fig. 6 and in Table 2) reveal that the size distribution of particles in thoria powders derived through the aqueous

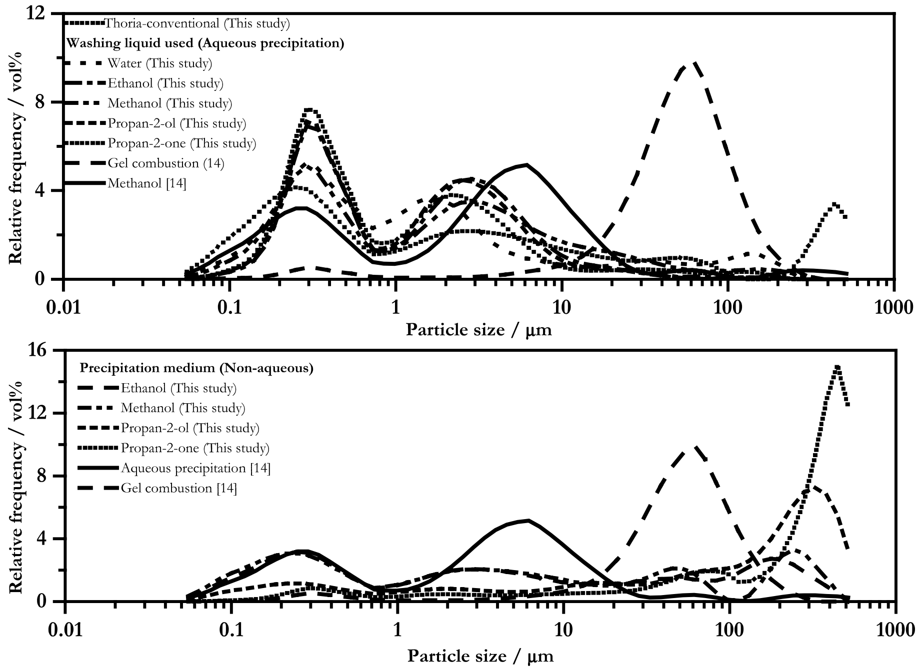

Fig. 6. Particle size distribution in thoria powders obtained by de-agglomerating thorium oxalate using ultrasonication.

route are similar and that the dispersion media does not influence the same. Even though propan-2-one was found to alter the particle morphology, it did not alter the distribution of sizes. It was also observed that ultrasonication brings about a reduction in the mean size of the particles (Fig. 6). The powders derived through the aqueous route were free flowing.

Among the thoria powders studied those obtained through the non-aqueous route had a higher fraction of 100 μm particles. Precipitation in propan-2-ol and propan-2-one yielded free flowing granular powders, with hard granules that had the maximum fraction of 100 μm particles. Thoria derived through precipitation in methanol and ethanol had similar size distributions and comprised of smaller granules.

Experimental determination of the agglomerate strength (using a method described in Ref. [23]) of the thoria powders obtained in this study revealed that neither the dispersion medium nor the medium of precipitation influence the strength of the agglomerates. All

Table 2
Particle size distribution in calcined powders

Dispersion medium	Particle size distribution (vol.%)		
	10 vol.% of sample has size less than (μm)	50 vol.% of sample has size less than (μm)	90 vol.% of sample has size less than (μm)
Aqueous precipitation			
Water	0.18	0.93	37.55
Methanol	0.20	1.60	18.70
Ethanol	0.23	1.19	6.59
Proapn-2-ol	0.23	0.98	5.76
Propan-2-one	0.22	0.61	6.10
Non-aqueous precipitation			
Methanol	0.15	3.30	230.43
Ethanol	0.16	3.57	189.26
Propan-2-ol	0.35	125.90	397.75
Propan-2-one	3.08	299.28	489.87

the green compacts had similar densities revealing that the strength of the agglomerates (granules) was not high enough to cause a reduction in the green density.

4. Characteristics of the sintered pellets

4.1. Density and microstructure of sintered pellets

From Table 3 and Fig. 7 it is seen that the thoria obtained through precipitation in aqueous and non-aqueous media (excepting propan-2-one) could be sintered to a density of 9.5–9.7 $\mathrm{Mg\,m^{-3}}$ and 9.3–9.7 $\mathrm{Mg\,m^{-3}}$ (1473–1873 K) respectively. Even though thoria obtained by precipitation in propan-2-ol could be sintered to a density of 9.66 $\mathrm{Mg\,m^{-3}}$ at 1473 K, an increase in the sintering temperature was found to cause a reduction in the density of these samples.

Balakrishna et al. [16] reported that a maximum density of 9.14–9.31 $\mathrm{Mg\,m^{-3}}$ could be obtained by sintering thoria derived ex-oxalate in air at 1973 K. Pope and Radford [4] observed that thoria powders obtained by calcining thorium oxalate at 873 K could be sintered to a density of 9.0 $\mathrm{Mg\,m^{-3}}$ at 1873 K. Since the thoria powders obtained through the de-agglomeration route could be sintered to a density as high as 9.6 $\mathrm{Mg\,m^{-3}}$ even at 1473 K, it is evident that this product exhibits enhanced sinterability. The factors responsible for the enhanced sinterability exhibited by these powders are discussed below.

Pope and Radford [4] compared the sinterabilities of thoria derived from direct denitration and by decomposing thorium oxalate, and established that the influence of powder morphology is of overwhelming importance in determining the sinterability of thoria. These authors observed that thoria derived ex-oxalate, is soft and sinters well unlike that obtained through direct denitration of thorium nitrate which contained hard agglomerates. Recent studies [8,11,12] indicate that denitration of thorium nitrate through gel-combustion yields thoria powders with weak agglomerates containing a high fraction of pores which could be sintered to very high densities at relatively low temperatures. The results obtained in the present study shows that ultrasonication helps to bring down the sizes, de-agglomerates and enhances the surface area of the product.

The thoria obtained by decomposing thorium oxalate powders precipitated in propan-2-ol was found to yield lower densities when it was sintered at 1873 K. Among the powders that were investigated in the present study, this thoria powder had the highest surface area. The microstructure of the sintered pellet (1873 K) obtained from this powder, shown in Fig. 8, reveals that these pellets consisted of fine grains (<5 μm). Morgan et al.

Table 3
Densities of sintered pellets of thoria obtained from thorium oxalate precipitated in aqueous and non-aqueous medium

Aqueous precipitation				Non-aqueous precipitation			
Dispersion medium	Temperature/K	Sintered density		Precipitation medium	Temperature/K	Sintered density	
		$\mathrm{Mg\,m^{-3}}$	% TD			$\mathrm{Mg\,m^{-3}}$	% TD
Water	1473	9.61	96.1	Methanol	1473	9.66	96.6
	1673	9.69	96.9		1673	9.34	93.4
	1873	9.60	96.0		1873	9.60	96.0
	1873	9.61	96.1		1873	9.62	96.2
Methanol	1473	9.58	95.8	Ethanol	1473	9.66	96.6
	1673	9.66	96.6		1673	9.34	93.4
	1873	9.61	96.1		1873	9.60	96.0
	1873	9.69	96.9		1873	9.56	95.6
Ethanol	1473	9.64	96.4	Propan-2-ol	1473	9.51	95.1
	1673	9.68	96.8		1673	9.37	93.7
	1873	9.54	95.4		1873	9.21	92.1
	1873	9.41	94.1		1873	9.19	91.9
Propan-2-ol	1473	9.62	96.2	Propan-2-one	1473	9.66	96.6
	1673	9.70	97.0		1673	9.49	94.9
	1873	9.64	96.4		1873	9.48	94.8
	1873	9.62	96.2		1873	9.52	95.2
Propan-2-one	1473	9.62	96.2				
	1673	9.73	97.3				
	1873	9.60	96.0				
	1873	9.57	95.7				

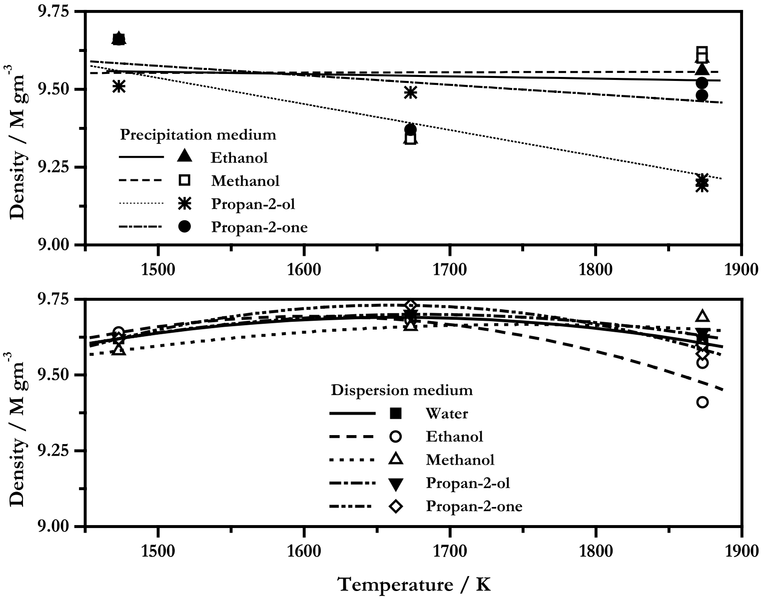

Fig. 7. Dependence of the sintered density of thoria on the temperature of sintering.

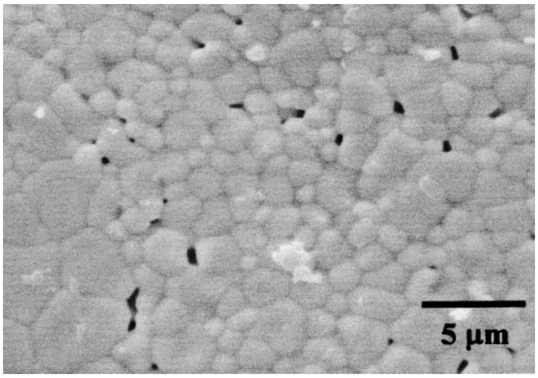

Fig. 8. SEM micrograph of thoria derived from thorium oxalate precipitated in propan-2-ol, sintered at 1873 K showing fine grain structure.

[36] observed that substantial reduction in sintered density resulted when sol–gel derived thoria with a density 9.9 Mg m^{-3} was re-sintered at 2073 K for 12 h. These authors termed this phenomenon as ‘de-sintering’. It appears that this phenomenon is observed when powders with very high surface area are resintered at high temperatures. A reduction in the sintered density with temperature, beyond an optimum value of the latter, appears to be a common feature in the sinterability plots of gel-combustion derived thoria [8,11]. A similar de-sintering mechanism is probably operative in the thoria powders derived through precipitation in propan-2-ol.

4.2. Carbon residue in sintered pellets

The sintered pellets had carbon residues varying from about 100 to 300 ppm. Generally, a higher sintering temperature was found to assist reduction in the quantity of carbon residue (300 ppm at 1473 K and 100 ppm at 1873 K). Among the pellets sintered at a given temperature, those obtained through the aqueous route had lower carbon residue than those derived by non-aqueous precipitation. A higher amount of the residual carbon in the starting powder is probably responsible for the higher amounts of residual carbon found in the latter.

5. Conclusions

Sinteractive thoria was obtained from a thorium oxalate precursor that was de-agglomerated by ultrasonication. The dispersion medium did not influence the properties of thoria significantly. Thoria derived by this procedure could be sintered to a density of 9.7 Mg m^{-3} at a temperature as low as 1673 K. The de-agglomeration technique is simple and does not pose the problems associated with self-sustained, uncontrolled burning encountered in the methods based on the combustion synthesis. Thoria powder derived through the non-aqueous precipitation (methanol, ethanol, propan-2-ol and propan-2-one) was found to be nanocrystalline (2–5 nm) and did not exhibit desirable powder properties. The thoria powder derived through the precipitation in propan-2-ol, exhibited de-sintering when sintered beyond 1473 K.

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References

[1] S. Sivasubramanian, S.M. Lee, S.A. Bhardwaj, in: Proceedings of Annual Conference of the Indian Nuclear Society INSAC 2000, BARC, Mumbai, India, vol. 2, 2000, p. 1.

[2] R.K. Sinha, H.S. Kushwaha, R.G. Agarwal, D. Saha, M.L. Dhawan, H.P. Vyas, B.B. Rupani, in: Proceedings of Annual Conference of the Inidan Nuclear Society INSAC 2000, BARC, Mumbai, India, vol. 2, 2000, p. 81.

[3] W.D. Kingery, H.K. Bowen, D.R. Uhlman, Introduction to Ceramics, II Ed., Wiley, New York, USA, 1970.

[4] J.M. Pope, K.C. Radford, J. Nucl. Mater. 52 (1974) 241.

[5] S.K. Kantan, R.V. Raghaven, G.S. Tendolkar, in: Proceedings of 2nd UN International Conference on Peaceful uses of Atomic Energy, vol. 6, UN, Geneva, 1958, p. 132.

[6] M. Fischer, I. Jacob, Z. Hadari, J. Nucl. Mater. 138 (1986) 242.

[7] V. Chandramouli, S. Anthonysamy, P.R. Vasudeva Rao, R. Divakar, D. Sundararaman, J. Nucl. Mater. 231 (1996) 213.

[8] V. Chandramouli, S. Anthonysamy, P.R. Vasudeva Rao, J. Nucl. Mater. 265 (1999) 255.

[9] S. Anthonysamy, K. Ananthasivan, V. Chandramouli, I. Kaliappan, P.R. Vasudeva Rao, J. Nucl. Mater. 278 (2000) 346.

[10] V. Chandramouli, K. Ananthasivan, S. Anthonysamy, P.R. Vasudeva Rao, in: Proceedings of Annual Conference of the Indian Nuclear Society INSAC 2000, BARC, Mumbai, India, vol. 2, 2000, p. 175.

[11] V. Chandramouli, PhD thesis, University of Madras, India, 1999.

[12] R.D. Purohit, S. Saha, A.K. Tyagi, J. Nucl. Mater. 288 (2001) 7.

[13] K. Ananthasivan, S. Anthonysamy, A. Singh, P.R. Vasudeva Rao, in: Proceedings of Conference on Inorganic Materials for the New Millennium, Indian Institute of Technology, Madras, India, 18–19 January 2001.

[14] K. Ananthasivan, S. Anthonysamy, V. Chandramouli, I. Kaliappan, P.R. Vasudeva Rao, Trans. Powder Met. Assn. India 26 (1999) 104.

[15] S. Radhakrishnan, K. Ananthasivan, P.R. Vasudeva Rao, unpublished work.

[16] P. Balakrishna, B.P. Varma, T.S. Krishnan, T.R.R. Mohan, P. Ramakrishnan, J. Nucl. Mater. 160 (1988) 88.

[17] P. Balakrishna, G.V.S.R.K Somauajulu, T.S. Krishnan, T.R. Rammohan, P. Ramkrishnan, in: P. Vincenzini (Ed.), Ceramics Today – Tomorrow's Ceramics, Elsevier Science Publishers BV, The Netherlands, 1981, p. 2995.

[18] P. Balakrishna, B.P. Varma, T.S. Krishnan, T.R. Mohan, P. Ramakrishnan, J. Mater. Sci. Lett. 1 (1988) 657.

[19] M.R. Nair, U. Basak, R. Ramachandran, S. Majumdar, Trans. Powder Met. Assn. India 26 (1999) 53.

[20] C.A. Aranberg, H.H. Rice, H.Z. Schofield, J.H. Handwek, Ceram. Bull. 36 (1957) 302.

[21] K. Ananthasivan, S. Anthonysamy, C. Sudha, A.L.E. Terrance, P.R. Vasudeva Rao, J. Nucl. Mater. 300 (2002) 217.

[22] M.A.C.G. Van de Graaf, J.H.H. ter Maat, A.J. Burggraaf, in: P. Vincenzini (Ed.), Ceramic Powders, Elsevier Science Publishers BV, The Netherlands, 1983, p. 783.

[23] A. Roosen, H. Hausner, in: P. Vincenzini (Ed.), Ceramic Powders, Elsevier Science Publishers BV, The Netherlands, 1983, p. 773.

[24] C.D. Sagel-Ransijn, A.J.A. Winnubst, A.J. Burggraaf, H. Verweij, J. Eur. Ceram. Soc. 16 (1996) 759.

[25] M.S. Kaliszewski, A.H. Heuer, J. Am. Ceram. Soc. 73 (1990) 1504.

[26] S. Zha, Q. Fu, Y. Lang, C. Xia, G. Meng, Mater. Lett. 47 (2001) 351.

[27] A. Roosen, H. Hausner, Adv. Ceram. Mater. 3 (2) (1988) 131.

[28] T. Reetz, I. Haase, in: P. Vincenzini (Ed.), High Tech Ceramic, Elsevier Science Publishers BV, The Netherlands, 1987, p. 481.

[29] G.D. White, L.A. Bray, P.E. Hart, J. Nucl. Mater. 96 (1981) 305.

[30] J. Belle, R.M. Berman, Thorium dioxide: Properties and Nuclear Applications, DOE/NE-0060, Dist. Category UC-25, 78, Naval Reactors Office, US Department of Energy, 1984.

[31] E. Oktay, A. Yayli, J. Nucl. Mater. 288 (2001) 76.

[32] H.P. King, L.E. Alexander, X-ray diffraction procedures for ploycrystalline and amorphous materials, Wiley, USA, 1954.

[33] S. Dash, R. Krishnan, M. Kamruddin, A.K. Tyagi, B. Raj, J. Nucl. Mater. 295 (2001) 281.

[34] K. Joseph, R. Sridharan, T. Gnanasekaran, J. Nucl. Mater. 281 (2000) 129.

[35] V.D. Allred, S.R. Buxton, J.P. McBride, J. Phys. Chem. 61 (1957) 117.

[36] C.S. Morgan, K.H. McCorckle, G.L. Powell, J. Am. Ceram. Soc. 59 (34) (1975) 104.