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Freeze drying vs microwave drying—methods for synthesis of sinteractive thoria powders

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ABSTRACT

Thoria powders were synthesized by oxalate precipitation from an aqueous solution of the nitrate. The filtered precipitates were freeze dried or microwave dried before being calcined at 1073 K. The thoria powders obtained were characterized for crystallite size, specific surface area, bulk density, particle size distribution and residual carbon. Microstructure of the product was studied using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Sinterability of the synthesized powders was studied by measuring the density of the sintered compacts. Powders that can be consolidated and sintered to densities ~96% theoretical density (TD) at 1773 K were obtained.

1. Introduction

Thorium dioxide is a ceramic oxide that finds application as a blanket material in Fast Breeder Reactors. It is also used for initial flux flattening in pressurized heavy water reactors. The solid solutions ThO_2—$^{239}PuO_2$ and ThO_2—$^{233}UO_2$ are proposed fuels for the Indian Advanced Heavy Water Reactors (AHWR) [1]. Thoria based solid electrolytes are used in oxygen sensors in coolant systems of nuclear reactors [2]. These applications require compacts with densities >96% TD [3]. Conventional powder metallurgical processes for the fabrication of thoria and its solid solutions employ very high temperatures for sintering (>1900K) to obtain such high density compacts. Sintering at such high temperatures, apart from being energy and cost intensive, causes grain growth, which results in poor mechanical strength of the sintered product [4]. Recently, Baena et al. [5] proposed an activated sintering procedure by doping thoria with alumina to aid sintering under reducing and oxidizing conditions. However, this process does not eliminate the sintering aid during fabrication which can affect its performance in the nuclear reactor. Moreover, it would require additional effort to separate the sintering aid during reprocessing of the spent fuel. Synthesis of nanocrystalline materials is known to produce powders that can be sintered to a high density at relatively lower temperatures [6]. To produce nanocrystalline thoria powders precipitation as oxalate, hydroxide, peroxide, carbonate or oxycarbonate from an aqueous solution of the nitrate followed by calcination is widely used [3,7,8]. However, complete removal of moisture from the precipitates, which is one of the main factors affecting the sintering process, poses a difficulty. Adsorption studies carried out by Holmes et al. [9] indicate that thorium dioxide powders prepared from thorium oxalate calcined at 1273 K still possess water adsorbed irreversibly. The presence of water leads to the formation of strong agglomerates that resist compaction thus influencing the sinterability of oxide powders. It has been established that the effective removal of moisture present in the precursor helps in reducing the strength of the agglomerates in the final product thereby improving the sintered density. It has also been reported that washing with propanol improves the compressibility of the agglomerates [10]. Studies by Chandramouli et al. [11,12] indicate that process parameters like temperature of precipitation and calcination, and solvent used for washing the precipitates can be tailored to obtain powders with more uniform grains and thereby better sinterability. Ananthasivan et al. [3] suggested deagglomeration by sonication to obtain highly sinteractive thoria.

In the quest for synthesis of highly sinteractive powders, the use of microwaves has been explored [13,14]. Microwave heating increases the heating efficiency by concentrating the heating process

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within the material and also transfers heat homogeneously on a molecular scale throughout the bulk. Qi et al. [15] have investigated the effect of microwave drying on the preparation and properties of alumina-doped yttria-stabilized-zirconia and reported shorter drying time and reduced aggregation in the powders obtained. Rahman et al. [16] have studied the effects of microwave drying on the properties of alumina zeolite foam and reported higher flexural strength of the resultant foam in addition to shortened drying time. Aggarwal [17] suggested microwave sintering of ceramics, composites, metals and transparent materials for rapid densification and enhanced sintering. Studies on microwave sintering of zirconia–8 mol% yttria [18] and uranium dioxide [19] indicate enhanced densification. Microwave heating of Pu-U nitrate mixed solutions have been reported to yield Pu-U oxide powders with good homogeneity and no impurity pickup [20].

Freeze-drying or lyophilization is another technique that has been studied to obtain sinteractive powders [21–23]. It is an effective way of drying materials without harming the basic structure. It makes use of the physical phenomenon of sublimation of the solvent. In this process moisture is removed by sequentially freezing the water/solvent and subliming it at low pressures. Rasmussen et al. [21] have reported that freeze drying of precursor in case of hydroxide derived yttria yields powders with better sinterability. Studies by Mouzon et al. [22] on the effect of drying and dewatering on yttria precursors suggest less agglomeration in freeze dried powders. Dogan and Hausner [23] have investigated the role of freeze drying in ceramic powder processing and concluded that freeze dried precipitates can be sintered to a high relative density at substantially lower temperatures. Burke [24] had used freeze drying of an aqueous solution of thorium nitrate to produce sinterable, free-flowing thoria powder.

The present work is an attempt to study and compare the effect of freeze drying and microwave drying of the precursor on the sinterability of thoria powders. Deagglomeration of the precipitates using sonication was carried out prior to drying to reduce the time taken for drying.

2. Experimental

2.1. Reagents and chemicals

Thorium nitrate hexahydrate of purity >99% was procured from M/s. Indian rare earths Ltd, India, and analytical grade oxalic acid was obtained from M/s. Hi Pure fine chem Industries, India.

2.2. Precipitation of thorium oxalate

Thoria powders were prepared by oxalate precipitation of an aqueous solution of the nitrate. Thorium oxalate was obtained by both direct strike (addition of aqueous oxalic acid solution to an aqueous thorium nitrate solution) and reverse strike (addition of aqueous thorium nitrate solution to excess aqueous oxalic acid solution).

The precipitates obtained were filtered under suction after allowing an ageing time of 1 h.

2.3. Deagglomeration and drying

The filtered precipitates were deagglomerated by dispersing in ethanol and sonicating for 30 min and again filtered. The powders thus obtained were dried under an IR lamp for 5 h before being subjected to freeze drying or microwave drying. The sample designations are listed in Table 1.

Table 1
Sample designations and descriptions.

S.No	Designation	Description
1	DFD	Thoria prepared from freeze dried precursor (direct strike)
2	RFD	Thoria prepared from freeze dried precursor (reverse strike)
3	DMW	Thoria prepared from microwave dried precursor (direct strike)
4	RMW	Thoria prepared from microwave dried precursor (reverse strike)

2.3.1. Freeze drying

Freeze drying was carried out in a TFD series freeze dryer supplied by M/s IlShinBioBase, South Korea, at a temperature of 200 K and 5 mTorr pressure using a rotary vacuum pump. The optimized drying time was observed to be 2 h.

2.3.2. Microwave drying

Microwave drying was carried out in a microwave oven supplied by M/s. LG, India. The oven was operated at a power of 900 W and a frequency of 2.45 GHz in the default mode. The microwave heating was interrupted for 1 min after every five minutes of heating. The optimized drying time was 1 h.

2.4. Calcination, compaction and sintering

The precursor powders after undergoing drying treatments were calcined at 1073 K for 4 h in air. The powders were compacted into pellets (10 mm diameter and 2–3 mm thick) at pressures of 150 MPa by a single action hydraulic press supplied by M/s. Kimaya Engineering, Pune, India and sintered at 1773 K for 4 h in air. The density of the sintered compacts was measured by immersion technique based on the Archimedes principle with di-butyl phthalate as the pycnometric liquid. Sinterability of the powders was estimated by comparing the densities of the sintered pellets.

2.5. Characterizations

2.5.1. Characterizations of the precursor powders

2.5.1.1. Residual moisture of the powders. The moisture content of the IR dried, freeze dried and microwave dried powders was determined using an MA100 infrared moisture analyzer supplied by M/s. Sartorius, Germany. The dried powder was taken in an aluminum sample holder and heated in the moisture balance at 423 K to obtain the moisture content in the precipitate. The precursor powders undergoing drying treatments were analyzed for moisture content at periodic intervals till no further reduction in moisture content was noticeable.

2.5.1.2. Thermal decomposition of powders. Simultaneous thermogravimetric and differential thermal analyses were carried out by using a single pan TGSDTA851e supplied by M/s. Mettler Toledo, Switzerland. The thermal decomposition of the precursor was studied by heating ~8 mg of the powder sample in an alumina crucible at a heating rate of 10 K/min.

2.5.2. Characterizations of the calcined thoria powders

2.5.2.1. Bulk density, particle size and specific surface area of the powders. Bulk density of the powders was determined by measuring the weight of the powder in a cuvette of known volume. The particle size distribution was determined by using Mastersizer 2000 supplied by M/s. Malvern, UK. The specific surface area of the powders was measured by the BET method using Monosorb MS-16