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Studies on the synthesis and sintering of nanocrystalline yttria

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Abstract

Nanocrystalline yttria powders were synthesized from yttrium nitrate by the citrate gel-combustion technique. The auto-ignition of five different gels with fuel to oxidant (citric acid/nitrate) ratios 0.25, 0.5, 0.75, 1.0 and 1.1 was studied. All these mixtures yielded precursors which upon calcination in air at 1073 K yielded yttria. The bulk densities, specific surface area, X-ray crystallite size, size distribution of particles as well as the residual carbon present in these powders were determined. The influence of the fuel to oxidant ratio on the powder properties was analyzed. Scanning electron microscopy (SEM) showed that these powders were porous while the high resolution transmission electron microscopy (HRTEM) revealed that they consist of randomly oriented cuboidal nanocrystallites with an average crystallite size of 25 ± 7 nm. These powders were compacted at 120 MPa without any lubricant or binder and their sinterability was studied. Pellets with a sintered density as high as 98–99% T.D. (theoretical density) could be obtained at a relatively low sintering temperature of 1673 K. Studies on the dependence of the properties of nanocrystalline yttria powders on the composition of the initial mixture used in the citrate gel-combustion as well as the sintering characteristics of these powders are being reported for the first time. Our investigations revealed that an initial mixture comprising equimolar quantities of the nitrate and citric acid yielded a powder with characteristics most suitable for fabricating yttria crucibles.

Keywords: A. Sintering; Yttria; Citric acid; Gel-combustion

1. Introduction

Yttria is a ceramic that finds extensive application in sensors, optics and as a transparent material [1–6]. It is used as a catalyst in the selective catalytic reduction of NO_x with methane [7] and as a "catalyst binder" in hydrogen fuel cell [8]. Yttria also finds application as a ceramic insert in the tools for cutting gray cast iron [9]. Yttria is also used in medical imaging applications, as an alternative for CdSe quantum dots for cellular imaging by suitably modifying its hydrophilicity [10]. Its high chemical stability and refractoriness make it suitable to be used as a coating material in the crucibles used for melting alloys and salts [11–13], and in the fabrication of nozzles for jets [14]. Melting and containment of uranium in crucibles made out of yttria and yttria coated crucibles and their interfacial reactions have been studied by various authors [15–19]. The feasibility of using yttria as an electrode material in laser enrichment of ^{235}U has also been studied [20]. Yttria is also used for improving the creep resistance properties of oxide dispersion strengthened (ODS) alloys [21–24]. Yttria stabilized zirconia is being considered as one of the most promising matrix for bearing plutonia for incineration in reactors in the form of inert matrix fuel [25] and in other applications pertaining to improved mechanical properties and solid oxide fuel cells [26–28]. In most of these applications the components are fabricated from yttria powders, which in turn, could be prepared by a variety of methods [29–33] that include precipitation [5,6,14,34,35], solution combustion [36–45], and sol–gel processing [46]. Among these, the solution combustion has gained prominence in recent years and has proved to be an attractive energy efficient alternative.

Small yttria crucibles with custom made dimensions in large numbers are required for use in our laboratory in order to hold molten uranium bearing alloys. High density crucibles with the

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desired dimensions could be easily fabricated by die casting nanocrystalline yttria powders and sintering at relatively low temperatures.

In view of the above, investigations on the citrate gel-combustion synthesis of nanocrystalline yttria powders were undertaken in order to identify the optimum process conditions. However, no systematic study has so far been reported, in which the dependence of the characteristics of the powders on fuel/nitrate ratio (R) as well as the sinterability has been studied. Hence, in this study yttria powders were synthesized by using combustion mixtures with R values varying from 0.25 to 1.1 and their sinterabilities were studied.

2. Experimental

2.1. Chemicals

Yttrium nitrate hexahydrate with a purity better than 99.9% supplied by MFTC Group, China and citric acid ($>99.5\%$) supplied by Merck were used in the synthesis of yttria.

2.2. Experimental procedure

In a typical experiment, appropriate amounts of yttrium nitrate and citric acid were weighed and dissolved in 100 mL of distilled water. This mixture was warmed on a hot plate at 373 K till a viscous sticky gel was formed. The temperature was then raised to 473 K to obtain the precursor and the duration of the overall reaction was about 3 h. Mixtures with five different compositions, defined by the value of the ratio "R" of 0.25, 0.5, 0.75, 1 and 1.1 (where R = number of moles of citric acid / number of moles of nitrate), were used. The product obtained after the gel combustion was called as the "as-prepared" powder. This powder was calcined in air at 1073 K for 4 h.

The following nomenclature is used to identify the samples prepared in this study. The alphabet "Y" denotes yttria followed by numerals to denote the value of R. The suffices "A" or "C" were incorporated to indicate if the sample is an "as-prepared" or "calcined" powder, respectively. Mangalaraja et al. [42] prepared yttria powder through citrate gel combustion from a mixture in which $R=0.278$. Roy et al. [43] employed mixtures having a value of R varying from 0.098 to 0.7 to synthesize nanocrystalline yttria. In this study combustion experiments were carried out over a series of mixtures with the value of R varying from 0.25 to 1.1.

These calcined powders were then compacted at 120 MPa in a die lined with tungsten carbide into pellets having a diameter of about 10 mm and a thickness of about 2–3 mm by using punches made out of tungsten carbide. An automated double action hydraulic press supplied by Bemco Ltd. India, was used for the compaction. The green densities of these compacts were measured from their weight and geometrical volume and the average value of five such measurements was reported. They were subsequently sintered in air at 1473 K, 1673 K and 1873 K for 4 h with a heating and cooling rate of 5 K/min. A furnace equipped with molybdenum di-silicide heating elements was used for sintering.

2.3. Characterization of the reactants, powders and compacts

The impurities present in the yttrium nitrate used in the present investigation were analyzed by using an inductively coupled plasma mass spectrometer (ICPMS), model Elan 250, supplied by Sciex, Toronto, Canada. Infra-red (IR) spectra were recorded by using an IR spectrometer (MB-100 FT-IR by BOMEM, Canada) with a typical resolution of 4 cm^{-1}. The samples were mixed along with spectrographic grade KBr and pelletized. The specific surface area (BET) of the powders was measured by using the Nelson Eggertson continuous flow method (Monosorb-16, Quantachrome Inc., USA). The particle size analysis was carried out by using Mastersizer particle size analyzer by Malvern, Worcestershire, UK. The X-ray powder diffraction patterns were obtained by using an X-ray diffractometer (XPERT MPD system) by Philips, Holland. Scherrer formula was used for determining the mean crystallite size of these powders. Gaussian profiles of the most intense peak (222) were used for this purpose. The instrumental broadening (obtained from silicon single crystal diffraction) was taken into account for the crystallite size determination. The densities of the compacts were measured by the liquid immersion method with dibutyl phthalate as the pycnometric liquid. The residual carbon present in these powders was determined by heating these samples in a stream of oxygen. The carbon dioxide thus evolved was quantitatively measured with an infrared detector.

Morphology and microstructure of the powders were investigated by using a scanning electron microscope (SEM) and a high resolution transmission electron microscope (HRTEM), LIBRA 200 FE, Carl Zeiss operated at 200 kV equipped with Schottky field emission gun (FEG) source and energy dispersive X-ray spectroscopy (EDXS). In order to record the TEM images, specimens were prepared by suspending a small quantity of the powder in propan-2-ol and ultrasonicating it for 15 min. A drop of this suspension was placed on the copper grid coated with holey carbon and dried.

3. Results and discussion

3.1. Purity of the starting materials

ICPMS analyses revealed that the total transition metal impurities present in the yttrium nitrate were less than 100 ppm. The concentrations of these impurities are so low that they would not influence the sinterability of the yttria powder.

3.2. Combustion synthesis

During the citrate gel combustion synthesis, the aqueous solution got dehydrated and became a sticky gel upon heating. Subsequent heating resulted in the denitration and destruction of the citrate–nitrate complex with the attendant evolution of a large quantity of gas. The completion of the combustion