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Synthesis of Nanocrystalline Cerium Oxide by both Solid and Liquid Processing Routes

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Abstract— **In the present study nanocrystalline CeO_2 powder has been synthesized by both high energy ball milling and liquid processing route. The ball milling is carried out using a WC balls and vials with WC balls and vials with a ball to powder weight ratio 10:1. The liquid processing route involved combustion reaction to form ceria at a high temperature from aqueous solution of cerium ammonium nitrate (CAN) as an oxidizer and citric acid (CA) plus glycine (G) as fuel processed at a high temperature. The powder has been characterized using techniques of x-ray diffraction, scanning electron microscopy and transmission electron microscopy. The microstructural analysis show that the particle size distribution of the ball milled ceria powder is wider than the particle size distribution of ceria produced by the solution combustion method. The scanning electron micrographs show that the ball milled ceria powders are compact and dense structure while solution combustion synthesised ceria powders are flaky and porous type.**

Keywords- high energy ball milling; solution combustion synthesis; cerium oxide (key words)

I. INTRODUCTION

Cerium oxide based materials have been extensively studied for various electronic and photonic applications [1, 4]. There are various fabrication routes of producing the nanosized materials, for example, mechanical alloying, solution combustion synthesis, spray pyrolysis, sputter deposition, pulse electrodeposition, sol-gel process, hydrothermal routes, etc. [5-9]. Among these, high energy ball milling is commonly used technique due to its simple nature and environmental friendliness, while the other techniques require either high temperature or hazardous chemicals [6-9]. While solution combustion synthesis involves primarily the generation of a high reaction temperature, which can vaporize low boiling point components resulting in higher purity products than those produced by other methods[10].

In the present work nanocrystalline cerium oxide powder has been synthesized by high energy ball milling and solution combustion synthesis. In the ball milling technique the nano-sized ceria particles have been produced after 30h milling of as-received ceria powders. Solution combustion synthesis has been carried out by using (a) CAN and G + CA, where CAN is cerium ammonium nitrate, G is glycine and CA is citric acid.

The ceria powders thus produced have been characterized for their particle size, size distribution and microstructural evolution by the X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

II. EXPERIMENTAL PROCEDURE

A. Solid Route - high energy ball milling)

High energy ball milling (HEBM) of ceric oxide powder (Loba chemie, 99.5%) is carried out in a Fritsch Pulverisette P4 planetary mill using tungsten carbide balls and vials where toluene is the process control agent. The powder is milled at rotational speed of 300 rpm and the ball to powder mass ratio of 10:1. The ball milling is continued upto 30 hrs and approximately 1 g powder is collected at different intervals of time to calculate the reduction in particle size. After attaining a reasonably small particle size, the mill is stopped and the powder is washed with distilled water and then with ethyl alcohol followed by drying in air.

B. Liquid Processing - Solution combustion synthesis

Nanocrystalline cerium oxide particles are synthesized by the combustion of aqueous solutions containing ceric ammonium nitrate and citric acid plus glycine.

The aqueous solution is prepared by dissolving the stoichiometric amount of ceric ammonium nitrate (CAN), ($(NH_4)_2Ce(NO_3)_6$) (Loba chemie, 99.5%) and glycine (G) and citric acid (CA) (Merck, 99.7%) in distilled water. The solution is then agitated in a beaker using magnetic stirrer for 3h. The resulting solution is kept in an electric furnace set at 200ºC, during which it evaporates foams and then undergoes flameless combustion resulting nanocrystalline oxide. This fine powder is very light and porous. These as synthesised ceria powder are still impure as it contains the undissolved gases which are removed by calcinations at 400 ºC for 3 hrs in a muffle furnace.

Assuming complete combustion, the theoretical equation for the formation of ceria can be written as follows:

$$CAN\,(aq) + (4/3)\,G\,(aq) + (2/3)\,CA\,(aq) \rightarrow CeO_2\,(s) + (20/3)\,CO_2\,(g) + 10\,H_2O\,(g) + (14/3)\,N_2\,(g)$$

C. *X-ray diffraction*

Mechanically milled samples have been characterized in a Phillips X-pert system diffractometer equipped with a Co radiation. The particle size and lattice strain are calculated by the most commonly followed technique (Scherrer formula) to determine the particle size:

$$d = 0.9 \times \lambda / B \cos(\theta) \quad (1)$$

where d is the particle size, θ the Bragg angle and λ is the wavelength of the X-ray radiation. The width B in (1) is obtained from the relation $B_2 = B_{2S} - B_{2m}$,

where B_S is the width at half maximum intensity of the most prominent peak of the sample. The B_m, the machine broadening, is the width at half maximum intensity of the corresponding peak from a well-annealed, coarse-grained sample.

However, this method is not free from contributions of both the lattice strain and the crystal size on peak broadening, but it can be refined.

The peak broadening due to the lattice strain is proportional to tan(θ) and that due to the particle size is inversely proportional to cos(θ)

$$B\text{cs} = 0.9 \times \lambda / d \cos(\theta) \quad (2)$$

$$B\text{ls} = \mu \tan(\theta) \quad (3)$$

where μ is the r.m.s. strain. Hence, the total broadening is

$$B = 0.9 \times \lambda / d \cos(\theta) + \mu \tan(\theta) \quad (4)$$

On rearranging the terms, we get

$$B \cos(\theta) = 0.9 \times \lambda / d + \mu \sin(\theta) \quad (5)$$

III. Results And Discussion

A. *X-ray diffraction analysis*

Figure 1(a-c) shows the X- ray diffraction patterns of the nanocrystalline cerium oxide powder (a) ball milled for 0 to 30 h, and fig (b) change in particle size with milling time for 30 hr and (c) solution combustion synthesised ceria powder. The average particle size and lattice strain of ceria powder are calculated from the x-ray diffraction patters and are shown in Figure 2.

It is noted that for ball milled ceria the particle size varies from (30-60) nm and lattice strain ($25 \times 10^{-2} - 48 \times 10^{-2}$) are larger than the particle size (20-30) nm and lattice strain (19×10^{-2} - 39.5×10^{-2}) of ceria produced by the solution combustion method.

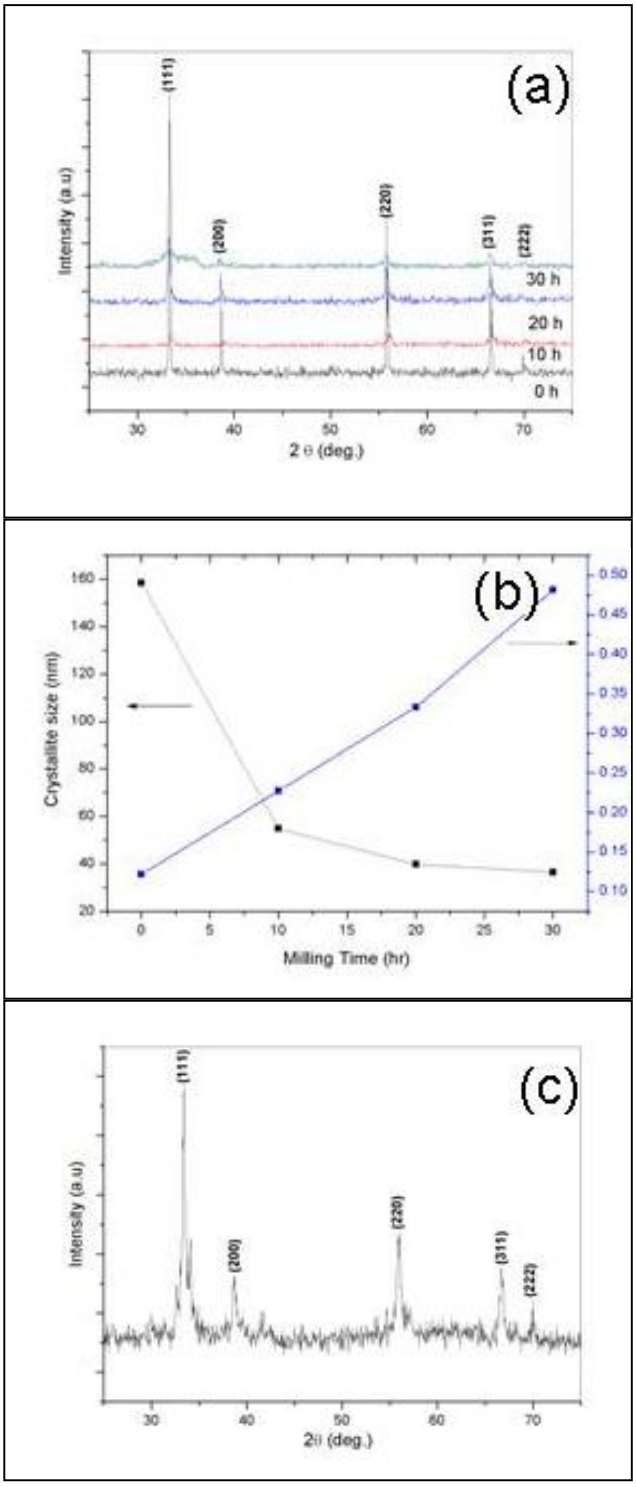


Figure 1. (a) X-ray diffraction patterns of (0, 10h, 20h and 30) h ball milled ceria, (b) effect of milling time on particle size and lattice strain of ball milled ceria, and (c) x-ray diffraction pattern for solution combustion synthesised ceria

B. Particle size distribution analysis

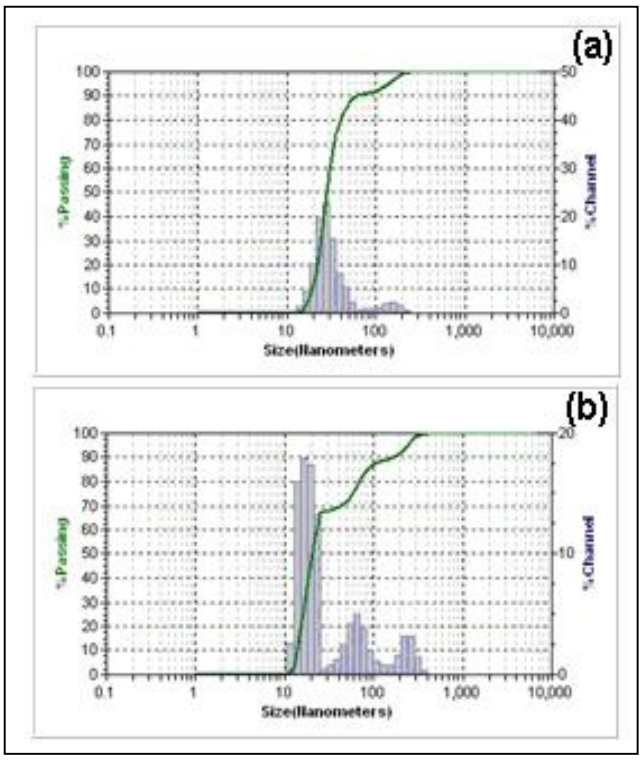
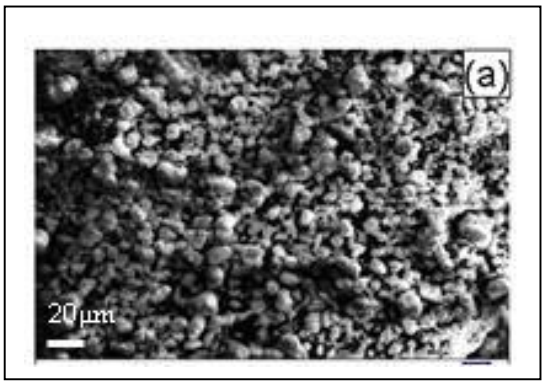


Figure 2. Particle size distributions of ceria (a) 30 hrs ball milled, and (b) combustion synthesised

From figure 2 it is observed that the size distribution of the ceria powder particles produced by ball milling technique follows a normal gaussian distribution with particle size varying from 10 to 80 nm with some agglomerated particles upto 150 nm. While the combustion synthesised ceria particle size containing CAN and citric acid possess trimodal particle size distribution, varying from 10 to 50 nm, 50-200 nm and some particles are in micron sized indicating severe agglomeration, which is much wider and lighter than ball milled ceria.

C. Scanning electron microscopy



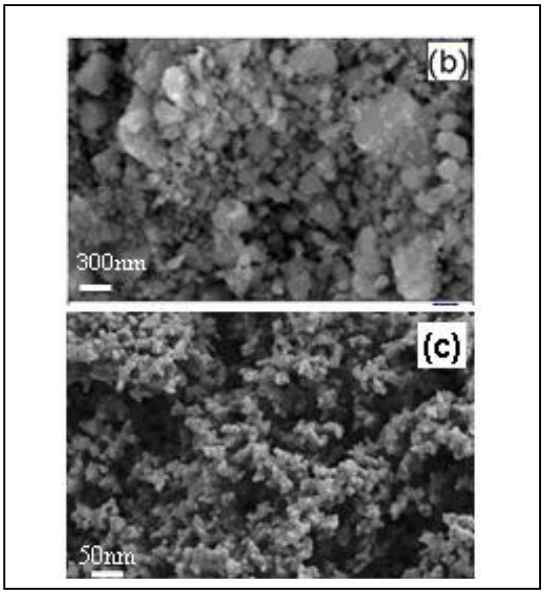


Figure 3. shows the SEM micrograph of ceria powder prepared by ball milling (a) 0 h, (b) 30 h and, (c) solution combustion synthesised ceria.

D. High resolution transmission electron microscopy

From figures 2 and 3, it is clear that the ceria powder produced by combustion synthesis is full of porosity and possess narrow particle size distribution, but ball milled ceria powder is free from porosity and particle size distribution is non uniform.

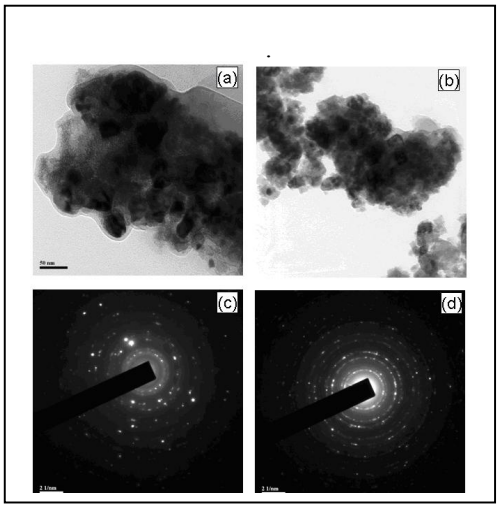


Figure 4. shows the high resolution TEM micrographs of (a), (b) ball milled and (c), (d) combustion synthesised ceria powder.

IV. CONCLUSIONS

1. The nanocrystalline ceria powder is successfully produced by both high energy ball milling and solution combustion synthesis methods.
2. The particle size distribution of ceria produced by ball milling is wider as compared to that

produced by solution combustion synthesis method.

3. There is significant porosity in solution combustion synthesised ceria as compared to that of ball milled ceria.

REFERENCES

[1] Hui-Lung Chen, Meng-Hsiung Weng, Shin-Pon Ju, Jee-Gong Chang, Hsin-Tsung Chen, Ching-Sheng Chang, Journal of Molecular Structure 963 (2010) 2–8

[2] P. Knauth, H.L. Tuller, Solid State Ionics 136–137 (2000) 1215–1224

[3] Yuelan Xuan, Jing Hu, Kailai Xu, Xiandeng Hou, Yi Lv, Sensors and Actuators B 136 (2009) 218–223

[4] Geoffrey I.N. Waterhouse, Mark R. Waterland, Polyhedron 26 (2007) 356–368

[5] Alan V. Chadwick, Shelley L.P. Savin, Journal of Alloys and Compounds 488 (2009) 1–4

[6] Hee Sang Kang, Yun Chan Kang, Hye Young Koo, Seo Hee Ju, Do Youp Kim,

Seung Kwon Hong, Jong Rak Sohn, Kyeong Youl Jung, Seung Bin Park, Materials Science and Engineering B 127 (2006) 99–104

[7] Adele Qi Wang, Prakaipetch Punchaipetch, Robert M. Wallace, and Teresa Diane Golden, J. Vaccum Science Technology B, 21, No. 3, (2003)

[8] S Kanakaraju, S Mohan, A K Sood, Thin solid films, 305 (1997), 191-195

[9] Yasuhiro Konishi, Satoru Asai, Tetuya, Murai, Hirofumi Takemori, Metallurgical and Materials Transactions B, 28B, (1997) 959

[10] John J. Moore and H. J. Feng, Progress in Materials Science, 39, (1995) 243-273.