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Powder characteristics and sinterability of ceria powders prepared through different routes

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Abstract

Ultra-fine ceria powders were prepared by three different routes such as citrate–nitrate combustion, hydroxide and oxalate decomposition. The various processes gave ceria powders with different properties. In order to see the effect of powder properties on sinterability, sintering was performed under the identical conditions, i.e., 1250 °C for 1 h. SEM investigations revealed a pronounced correlation between powder properties and sintered microstructure. The combustion derived ceria powder yielded the highest sintered density with ultra-fine grains.

Keywords: A. Sintering; B. Microstructure; D. Ceria; Nanostructured materials; Solution combustion

1. Introduction

CeO_2 is a potential candidate for a variety of high-technology applications, which can be summarized as follows: It is the most superior glass-polishing material because of its abrasive nature [1]. It has remarkably similar physico-chemical and thermochemical properties to plutonia. Therefore, it can be used as a surrogate material for plutonia to simulate its thermophysical properties [2]. It has also been found to have applications in automobile exhaust formulations [3]. It is used as a minor additive in silicon nitride [4] and it is also used as an additive to increase the toughness of sintered zirconia [5]. Doped ceria is used as an oxide-ion electrolyte in a solid-oxide fuel cell (SOFC) [6]. All these applications demand high-purity cerium oxide in the finest-particulate form.

The nanoparticles, in general, show higher catalytic activity, better sinterability and other unusual properties in contrast to the bulk material. The synthesis of nanostructured ceria powder with controlled powder characteristics is of practical importance to get dense sintered product at a lower sintering temperature, in particular when problem of change of valence state of cerium ($Ce^{4+} \rightarrow Ce^{3+}$) is associated during sintering at the higher temperature (>1300 °C) [6].

Ceria powder has been reported to be synthesized by different techniques including hydrothermal [7], precipitation [8] and combustion [9,10]. These wet chemical processes provide an intimate blending of the constituents. However, success for getting the desired powder characteristics by the wet chemical processes is usually governed by the kind of solution chemistry during the process [11,12]. Among the available solution chemistry routes, the combustion technique is capable of producing nanostructured powders of oxide ceramics at lower calcination temperatures in a surprisingly shorter time [13,14]. The combustion technique involves an exothermic decomposition of a fuel-oxidant precursor which results in either the finely divided powder with required phase or semi-decomposed precursor having a considerable carbonaceous residue depending on the nature of fuel and fuel-to-oxidant ratio used in the process [15].

Citric acid has three carboxylic and one hydroxyl group for coordinating the metal ions, which facilitate the formation of viscous gel [16]. In this manuscript, we report

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on the influence of powder properties on sinterability studies and sintered microstructure of ceria, prepared by the citrate–nitrate combustion and hydroxide or oxalate decomposition processes.

2. Experimental work

AR grade cerium nitrate [$Ce(NO_3)_3 \cdot 6H_2O$], and citric acid ($C_6H_8O_7 \cdot H_2O$) were mixed in the required molar ratios in a minimum volume of de-ionized water to obtain transparent aqueous solutions. These solutions after thermal dehydration (at ≈80 °C on a hot plate to remove the excess solvent) resulted in highly viscous yellowish liquids, hereafter termed as precursors. As soon as the viscous liquids were formed, the temperature of the hot plate was increased to ≈200 °C. At this stage, the viscous liquids swelled and auto-ignited, with the rapid evolution of large volume of gases to produce voluminous powders. In order to investigate the suitability of the combustion synthesized powder for sintering, the ceria powders were also prepared through hydroxide and oxalate routes. In order to obtained ceria powders through these routes, the aqueous solution of cerium nitrate was precipitated using a sufficient quantity of ammonia and oxalic acid, respectively. Then they were washed for the unwanted nitrates and excess ammonia and oxalic acid using de-ionized water. The as-prepared precipitates were dried and calcined at 600 °C for 1 h to obtain pure ceria powders. X-ray diffraction studies were carried on these powders for phase identification and the crystallite size estimation using Cu Kα radiation on a Philips X-ray diffractometer, model PW 1927. Silicon was used as an external standard for correction due to the instrumental broadening. The synthesized ceria powders were cold pressed in the form of 12 mm diameter pellets at a compaction pressure of 200 MPa using a uni-axial hydraulic press. Stearic acid was used as a lubricant. Sintering was performed in air at 1250 °C for 1 h with a heating rate of 10 °C/min. The sintered densities were determined using the Archimedes' principle. The microstructure studies on the sintered pellets were carried out by scanning electron microscopy using a JEOL scanning microscope, model JSM-T330A. The extent and nature of agglomeration was studied by a particle size analyzer. The equipment used was Horiba, model LA-500 (Japan), particle size analyzer based on laser diffraction, which covers the particle size range of 0.20–200 μm.

3. Results and discussion

According to the principle of propellant chemistry [9] for stoichiometric redox reaction between a fuel and an oxidizer, the ratio of the net oxidizing valency of the metal nitrate to the net reducing valency of the fuel should be unity. During the combustion reaction, Ce^{3+} oxidizes into Ce^{4+} using atmospheric oxygen. The combustion reactions with citric acid are less violent and more controllable compared to urea or glycine due to its weak exothermic nature. The total oxidizing valency of $Ce(NO_3)_3$ works out to be 15− whereas the total reducing valency of $C_6H_8O_7 \cdot H_2O$ is 18+. Hence, in order to achieve stoichiometric combustion reaction, theoretically 1 mol of cerium nitrate needs 15/18 (or 5/6) mol of citric acid. Details of these experiments are reported elsewhere [17]. It was found [17] that the combustion of fuel deficient ratio of citric acid and cerium nitrate yields ceria powder with best powder properties (surface area 127 m^2/g and crystallite size 6 nm), which is expected to be highly sinter active. The sintering was performed on the powder obtained through fuel-deficient precursor, whose green density was found to be ≈52% of its theoretical density. Sintering at 1250 °C for 1 h in static air resulted in ≈96% of its theoretical density. The ultra-fine nature with very high surface area of the starting powder is responsible for producing such a high sintered density at a low temperature in a very short time duration. Hence, due to suppression of grain growth, fine grain microstructure is obtained after sintering. Fig. 1a shows the microstructure of the well-sintered pellet with sub-micron grain size. The ceria powders prepared from the oxalate and hydroxide decompositions were also sintered under identical conditions, which resulted in 90 and 84% sintered densities. The SEM micrographs of the sintered pellets show the presence of considerable porosity (Fig. 1b and c). The difference in sinterability of ceria powder prepared through citrate–nitrate combustion route vis-à-vis that from oxalate and hydroxide routes could be attributed to their powder properties (Table 1). It can be seen that the ceria powder obtained through citrate–nitrate route has got the best powder properties (127 m^2/g surface area and 6 nm crystallite size) compared to the other two powders. Thus, the highest sintered density is obtained for this powder, which can be attributed to its superior powder properties. There is a higher deriving force, in this case, for sintering, and therefore even despite of achieving high sintered density, ultra-fine grains are retained.

In order to further understand the different sintering behaviour of oxalate and hydroxide derived ceria powder, they were studied by a particle size analyzer based on laser diffraction. The technique is used as an indication for particle size distribution of powders. However, the success of the technique depends on dispersion of the powder. Since, the combustion synthesized powders are agglom-

Table 1
Comparison of properties of ceria powders prepared by various routes

Process	Surface area (m^2/g)	Crystallite size (nm)	Sintered density (percent of theoretical density)
Citrate–nitrate route	127	6	96
Oxalate decomposition	83	16	90
Hydroxide decomposition	28	13	84

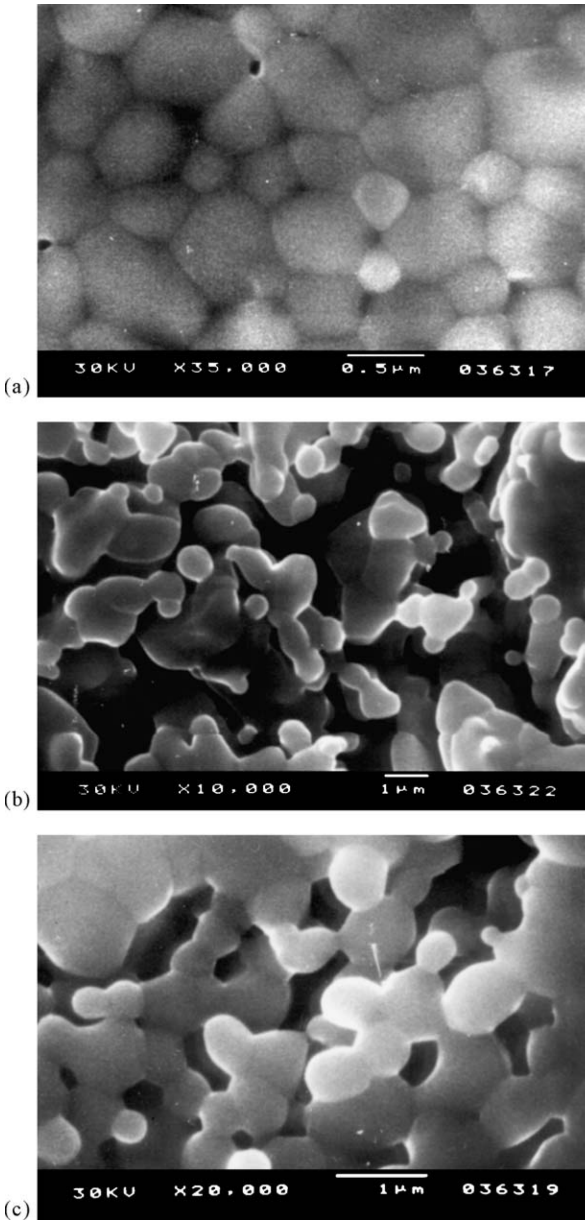

Fig. 1. SEM micrograph of sintered pellets obtained from: (a) combustion product; (b) hydroxide decomposition; and (c) oxalate decomposition.

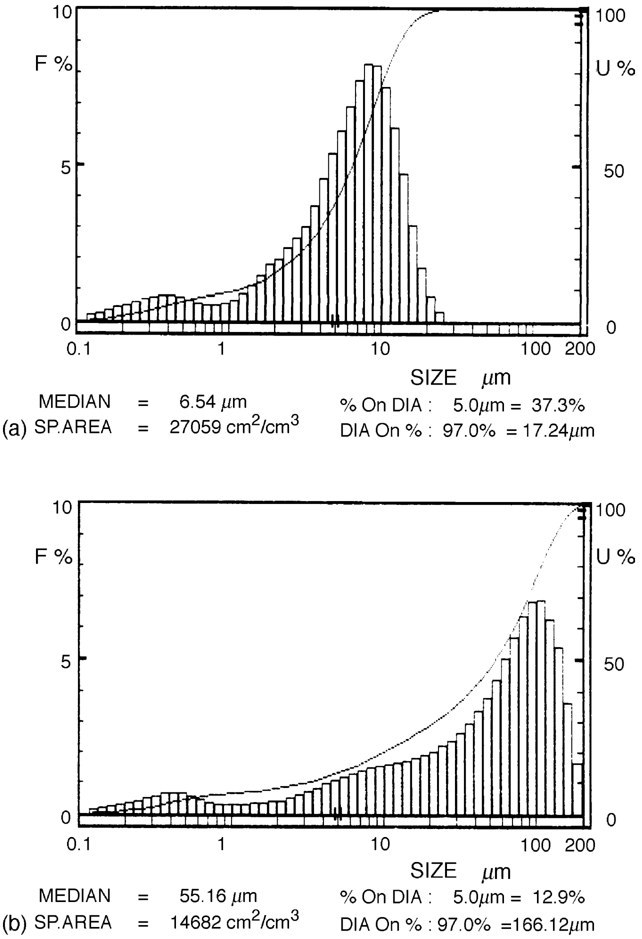

Fig. 2. Particle size distribution of ceria powders derived from: (a) oxalate and (b) hydroxide decomposition.

erates of primary nanoparticles, it is difficult to disperse them as individual particles and hence in spite of their true particle size, the results are merely indicative of the size of agglomerates. However, due to instrumental limitation, the particle size distribution analyzer based on laser diffraction is not capable of giving the true size of the nanaoparticles produced by combustion synthesis. Fig. 2a and b shows the curves for particle size distribution of ceria powders derived from the hydroxide and oxalate decomposition. The agglomerates in case of ceria powder obtained by hydroxide decomposition was about 55 μm, whereas for that obtained by oxalate decomposition was about 6.5 μm. Therefore, it appears that the poor sintered density obtained in the case of ceria powder obtained from hydroxide decomposition is due to the presence of large agglomerates.

The results obtained for the powder characteristics and sinterability of the ceria powders prepared through different routes indicate that achieving nanocrystalline nature of the powder alone is not sufficient to govern the sinterability of the powder. The nature and extent of agglomeration among nanocrystallites have a great influence on the sinterability of the powder. In comparison to hydroxide and oxalate routes, combustion synthesized powder, resulted [17] into less extent of agglomeration and soft nature of the agglomerates, which in turn produced the highest sintered density under similar sintering conditions.

4. Conclusions

Nanocrystalline ceria powders were prepared by different chemical processes, which yielded varying powder properties. The sintering behaviour was correlated with powder properties. It was found that the powder with the highest surface area and smallest particle size is the most sinter active. Due to its high deriving force for sintering, it achieved high sintered density without any appreciable grain growth, which is a noteworthy result.

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