JOURNALOF

Ceramic Processing Research

Correlation between the powder properties and sintering behaviors of nano-crystalline gadolinium-doped ceria

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Nano-crystalline gadolinium-doped ceria ($Ce_{0.9}Gd_{0.1}O_{1.95}$ (GDC)) powders prepared by different routes such as a co-precipitation method (COP), a glycine-nitrate-process (GNP) and a sol-gel thermolysis process (STP) resulted in different powder properties. In order to find out the effect of powder properties on sinterability, dilatometric studies were carried out on these powders. Dilatometric studies revealed a pronounced correlation between powder properties and the sintering behavior. Along with crystallite size and surface area, agglomerate size also played an important role in achieving a high sintered density at relatively low sintering temperature.

Key words: Powders-chemical preparation, Sintering, Sol-gel processes, CeO₂, Fuel Cells.

Introduction

Solid oxide fuel cells (SOFCs) have been attracting great attention as a promising technique for electrical power generation due to their higher efficiency, high waste-heat utilization, environmental friendliness and greater fuel flexibility [1]. A conventional SOFC electrolyte, 8 mol% yttria-stabilized zirconia (YSZ), operates at a high temperature (800-1000 °C) and results in a high cost, physical and chemical degradation of the component materials. Therefore, it becomes particularly important to reduce the operating temperature of the SOFC and the development of low/intermediate temperature (400-800 °C) SOFCs (LT/IT-SOFCs) is the key to commercialization. Among the various doped ceria, gadolinia-doped ceria has particularly been given more attention and 10 mol% of gadolinia-doped ceria $(Ce_{0.90}Gd_{0.1}O_{1.95})$ is being extensively researched for electrolyte applications in SOFCs due to its higher ionic conductivity below 800 °C and good compatibility with electrodes [2-4].

The ceria-based electrolytes are commonly synthesized by a solid state route, where a very high temperature sintering (~1500 °C) is required to achieve high densities. However, such a high sintering temperature results in the reduction of CeO₂ to Ce₂O₃ (valance changes from Ce⁺⁴ to Ce⁺³), which may produce micro-cracks [5, 6]. Moreover such a type of reduction may cause an increase in electronic conductivity and results in a short across the cell components. This eventually leads to an efficiency loss and a drop in open-circuit voltage [7]. This makes it necessary to develop a low-temperature sinterable doped ceria. Nano-crystalline powders promote the sintering at a low temperature and give a fully dense material when compared to their microcrystalline counterparts. Thus, the synthesis of doped ceria powder with controlled powder characteristics is of practical importance to get a dense sintered product at a lower sintering temperature. Various approaches for synthesizing nano-crystalline ceria powders have been reported, such as homogeneous precipitation [8-11], room temperature solution precipitation [12], hydrothermal crystallization [13, 14], a microwave-assisted hydrothermal route [15], thermal hydrolysis [16], solvothermal synthesis [17], flame spray pyrolysis [18, 19], azeotropic distillation [20] and electrochemical method [21]. Among them, the co-precipitation method at room temperature is widely adopted in laboratories not only because of its low preparation cost and that it has simple process but also due to the synthesis of nano-crystalline powders with a narrow particle size distribution. There are several reports describing solution processing techniques to yield ceria powders which can be sintered at lower temperatures [22-26]. The major driving force for sintering in these cases is the nano-crystalline nature of the powders associated with the high surface area and lower agglomeration which enhances the sintering [27].

In our present study, firstly, an attempt was made to prepare GDC powders with a range of varying characteristics and then the role of these powder properties on the sintering behavior was investigated. Thus, solution methods such as co-precipitation (COP) [28], a sol-gel thermolysis process (STP) [29] and a glycine nitrate process (GNP) [30] were used to prepare GDC nano-powders. Due to the difference in synthesis temperatures, where COP was prepared at room temperature [28], for STP the combustion temperature

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was below 1000 °C [29] and for GNP the combustion temperature was above 1000°C [30], different powder properties can be expected for these synthesis methods. Each of these synthesis methods resulted in powders with different characteristics in terms of crystallite size, particle size, agglomeration, etc., which in turn were expected to affect the sinterability of these powders. The sinterability of these powders was monitored by a dilatometer. Here, we have made an effort to correlate and compare the powder characteristics viz., crystallite size, surface area, agglomerate size with the sintering behavior of GDC prepared by the different synthesis methods.

Experimental Details

GDC nano-crystalline powders were successfully prepared by COP, GNP and STP methods [28-30]. Formation of single phase nano-crystalline GDC powders was observed by using an X-ray diffractometer (PW 3830 X-ray generator, Netherlands). The specific surface area of the GDC powders was measured by BET (Quantachrome Corporation Autosorb, USA). The average equivalent particle size is calculated from the BET surface area of the powders using the equation: $D_{BET} = 6000/(\rho. S_w)$, where D_{BET} is the average diameter of a spherical particle (nm); S_w represents the BET surface area of the powder (m^2/g) ; and ρ is the theoretical density (g/cm³). The morphology of the powders was observed using a transmission electron microscope (TEM, Technai G2 F20, USA). A scanning electron microscope (EDS/SEM, XL-30 FEG ESEM, Netherlands) was used for both compositional and microstructural analyses. A particle size analyzer (PSA) (Microtrac UPA 150, USA) was used to determine the average value of the apparent particle size.

To observe the sintering behavior, uni-axially formed pellets were pressed at 200 MPa using cold isostatic pressing (CIP). Shrinkage of the green bodies was measured with a dilatometer (Netsch Dil 402C/3/G, Germany) up to 1500 °C in air with a heating rate of 3 K·minute⁻¹. The relative density of the prepared samples was estimated by using the relation: relative density (%) = $(d_m/d_{th}) \times 100$, where d_m is the density of the samples measured using Archimedes method and d_{th} is the theoretical density of the GDC sample.

Results and Discussion

Fig. 1 depicts the XRD patterns of the GDC powders synthesized by various synthesis methods. All the powders prepared showed the main reflections of GDC with a typical cubic fluorite structure (JCPDS No 75-0161). Crystallite size was calculated by X-ray line broadening using Scherrer's formula [29].The crystallite size of GDC prepared by COP was 8.7 nm and it was smaller than the GDC prepared by STP (10.1 nm) and GNP (17 nm). The reason for larger crystallite sizes of GDC for GNP was due to the higher flame temperature during the synthesis process [30]. From the results of the XRD analysis it can be observed that the order of the crystallite size showed good agreement with the synthesis temperature of the GDC powders (COP < STP < GNP).

Fig. 2 shows the TEM images of the GDC samples which showed the average particle sizes were around 8-10 and 17-25 nm for COP and GNP samples, respectively. For the STP sample prepared by GNP the average particle size was around 10-11 nm. The BET surface area equivalent particle size of GDC powders prepared by COP, GNP and STP were around 12.2, 21.9 and 15.6 nm, respectively. The order of the particle size obtained from TEM and BET is COP < STP < GNP which is similar to the order of the crystallite size and synthesis temperature of the GDC nano-powders.



Fig. 1. XRD patterns of the prepared GDC powders.



Fig. 2. TEM images of the prepared GDC powders obtained by (a) COP (b) GNP and (c) STP.



Fig. 3. Agglomerate particle size distribution of GDC powder obtained by various synthesis routes; (a) COP (b) GNP and (c) STP.

It can be observed from TEM, BET and XRD analyses that the particle size of GDC powders obtained from TEM and BET were somewhat larger than those calculated from Scherrer's equation. Thus, it can be said that a bunch of one or two crystallites are grouped to form primary particles.

Fig. 3 shows the agglomerate size distribution of the GDC powders synthesized by COP, GNP and STP after an ultrasonication of 15 minutes. Fig. 3 clearly shows that the particle size observed by the particle size analyzer is much higher than the primary particle size and crystallite size observed from TEM, BET and XRD results. This shows that the primary particles are grouped together to form large agglomerates. From Fig. 3, it can be observed that the GDC prepared by COP resulted in a uni-modal agglomerate size distribution where as the GDC prepared by GNP and STP resulted in a bi-modal agglomerate size distribution. It can be noticed that the GDC prowders synthesized by COP showed a smaller agglomerate size (245 nm) when compared to GDC powders synthesized by STP (990 nm) and GNP (626 nm).

The linear shrinkage as a function of temperature for the different GDC samples is shown in Fig. 4. It can be observed from the figure that the linear shrinkage of the GDCs prepared by COP and STP starts at a lower temperature (~400 °C) when compared to the GDC prepared by GNP (~700 °C). The reason for such phenomena can be due to the smaller crystallite and primary particle size of GDCs prepared by COP and STP when compared to GNP. Multi-shrinkage behavior is observed for the GDCs prepared by STP and GNP due to different agglomerate sizes. From the results of the agglomerate size distributions it can be observed that both the GDC samples prepared by STP and GNP showed a bi-modal agglomerate size distribution with varied agglomerate sizes. The smaller agglomerates can be sintered at lower temperatures whereas the larger agglomerates can be sintered at higher temperatures. From the linear shrinkage behavior, it can be observed that the GDC powders prepared by COP can be sintered



Fig. 4. Linear shrinkage behavior of GDC samples as a function of temperature.

at a lower temperature (< 1000 °C) than the GDC powders prepared by STP and GNP where a higher sintering temperature is required to obtain a full dense body. In order to find out the minimum sintering temperature (> 95%relative density) of the GDC powders prepared, a sintering test was performed. GDCs prepared by each synthesis process were sintered at two different temperatures selected by the shrinkage behavior of the different GDC samples. GDCs prepared by COP, GNP and STP were first sintered at a lower temperatures of 900 °C, 1200 °C and 1400 °C, respectively, and this did not result in fully-dense bodies. GDCs prepared by COP, GNP and STP were sintered at temperatures of 950 °C, 1300 °C and 1500 °C, respectively, and this resulted in fully- dense bodies. Therefore, it can be observed that the minimum sintering temperature to obtain fully-dense bodies (>95% relative density) for the GDCs prepared by COP, GNP and STP was around 950 °C, 1300 °C and 1500 °C, respectively.

It becomes very important to study the role of crystallite size, particle size and agglomerate size on the sintering behavior of the GDC powders synthesized by COP, STP and GNP. Fig. 5 shows the powder characteristics and sintering properties of the GDCs prepared. It can be observed from the figure that the GDC sample prepared by COP consists of the finest crystallites, has a relatively high surface area and most importantly a smaller agglomerate size (245 nm). This can be the driving force for the maximum shrinkage of the green pellet which was able to fully sinter below 1000 °C. The poor sintering behavior observed for the GDC samples prepared by GNP and STP can be correlated to the larger agglomerate size and fully- dense bodies were obtained at 1300 °C and 1500 °C, respectively. Although the GDC sample prepared by STP has a smaller crystallite size and particle size than the GDC sample prepared by GNP, the sintering temperature of the STP sample is much higher than that of the GNP sample which is mainly due to larger agglomerate size. Thus, it can be said conclusively that the agglomerate size plays a very



Fig. 5. Powder and sintering properties of GDC obtained by various synthesis routes.

important role in governing the sintering behavior along with the crystallite size and primary particle size. This type of behavior where the larger agglomerate size results in a higher sintering temperature irrespective of the order of the crystallite and primary particle size was also observed for other ceria-based materials prepared by various combustion fuels [31-32]. Another important conclusion which can be made from the present investigation is that at a lower sintering temperature, a fully-dense body can be obtained by COP which has a lower crystallite size, higher surface area and most importantly lower agglomerate size when compared to the other GDC samples that were prepared.

Conclusions

Nano-crystalline GDC powers prepared by different chemical processes yielded varying powder properties. The sintering behavior has been correlated with the powder properties. The variation in the properties such as surface area and agglomerate size appears to be characteristic features of the synthesis process. The dilatometric studies revealed that the sintering behavior was a cumulative function of various powder morphologies and, in particular, strongly influenced by the agglomeration. It may be suggested that in order to enhance the sinterability one has to optimize the initial powder characteristics by means of selecting suitable synthesis methods. The GDC powder prepared by COP resulted in a higher sintering density at a lower sintering temperature mainly due to the smaller agglomerate size when compared to the GDCs prepared by GNP and STP.

Acknowledgements

This work was supported by the Institutional Research Program of KIST.

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