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Short communication

Lowering the sintering temperature of Gd-doped ceria by mechanochemical activation

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Abstract

Two kinds of $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ pellets were synthesized by a solid-state reaction using two types of commercial CeO_2 and Gd_2O_3. In contrast to previous reports, pellets with a sintered density of 99% at 1300 °C were obtained regardless the powder used. Mechanochemical activation of the starting materials by 7 h of high energy milling, which resulted in particles several tens of nanometer in size, was effective in reducing the sintering temperature. $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ pellets could be synthesized by direct sintering without calcination due to the homogeneous distribution of fine starting materials. The final phase was confirmed by the ionic conductivity, X-ray diffraction patterns and lattice parameters.

Keywords: A. Milling; A. Powders: solid state reaction; D. CeO_2; E. Fuel cells

1. Introduction

The high operating temperature of yttria-stabilized ZrO_2 (YSZ), which leads to the restriction in materials selection and maintenance problems in solid oxide fuel cells (SOFCs), is the main impediment to its more widespread use as an electrolyte. Therefore, it is essential to reduce the operating temperature to intermediate temperatures of 500–700 °C. Gd-doped CeO_2 (GDC) is an ideal material for this purpose because it exhibits 4–5 times higher ionic conductivity than YSZ at these intermediate temperatures [1]. However, being a refractory material, CeO_2-based materials generally require high sintering temperatures of 1400–1600 °C for densification [2].

Many attempts have been made to decrease the sintering temperature of GDC, including the use of nano-sized powder produced by various wet-chemical routes [3–5] and the addition of sintering aids [6–10]. For practical application, it is important to achieve a sintered density $\geq$95% at temperatures $\leq$1300 °C. Although the solid-state reaction route is the most economical powder synthetic method, it is generally associated with a coarse particle size, requiring a high sintering temperature. For example, Torrens et al. [3], who examined the sintering behavior of GDC powders prepared by different routes, reported that a solid-state reacted powder showed an inferior sintering density. Therefore, few have attempted to decrease the sintering temperature of GDC derived by a solid-state reaction. On the other hand, a few researchers recently succeeded in synthesizing ultrafine ceramic powders, such as $BaTiO_3$, at relatively low temperatures using this method [11]. The use of fine starting materials and mechanochemical activation by efficient milling are the key steps in this process. Therefore, this study examined whether mechanochemical activation of the starting materials using high energy milling can reduce the sintering temperature of solid-state reacted GDC. In addition, this study also examined whether the calcination process can be omitted due to the homogeneous distribution of fine staring materials obtained by heavy milling.

2. Experimental procedure

Two kinds of $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ were synthesized using two types of commercial CeO_2 (>99.99%, D_{mean} = 197 nm, Kanto Chemicals, and >99.9%, D_{mean} = 150 nm, Wako Chemicals, Japan) and Gd_2O_3 (>99.95%, D_{mean} = 4500 nm, Uranus Chemicals, Taiwan) by a solid-state reaction. The formulated powders were named as K- and W-powder according to the first

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initial of the CeO_2 suppliers' name. 100 g of each formulated powder mixed with 200 g of ethanol was milled in a high-energy mill (MiniCer, Netzsch, Germany) for 7 h at a rotor speed of 3000 rpm with 0.1 mm ZrO_2 beads after adding 1 wt.% of a dispersant (BYK-103, BYK Chemie, USA). A commercial $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ powder (GDC 20-TC, Fuel Cell Materials, USA), and K- and W-powder, which were mixed by ball-milling for 4 h using 5 mm ZrO_2 balls, were also prepared for comparison. After drying the slurry, the obtained powders were pressed uniaxially at 120 MPa into pellets with a 10 mm diameter without calcination. The pellets were sintered at 1300 °C for 3, 5 and 15 h in air at different heating rates of 5 and 10 °C/min.

The evolution of the mean particle size upon high energy milling was estimated from the SEM images by measuring the maximum and minimum diameter of 100 particles using image analysis software (SigmaScan, Systat Software, USA). The density was measured using the Archimedes method. The crystal structure of the sintered pellets was analyzed by X-ray diffraction (XRD: RINT 2200, Rigaku using Cu K_α line, 40 kV and 40 mA). The sample morphology and phase distribution was determined by scanning electron microscopy (SEM; Hitachi S-4800) equipped with an energy dispersive X-ray spectrometer (EDX: Horiba EX-250). The ionic conductivity of the sintered pellets was measured over 300–800 °C in air by two-probe impedance spectroscopy (HP4192a, Hewlett-Packard, USA) over the frequency range, 5 Hz to 13 MHz.

3. Results and discussion

Since high energy milling was performed at 3000 rpm by adopting a continuous circulation method, the coarse and non-uniform starting materials for both of K- and W-powder were milled into fine particles, as shown in Fig. 1. The mean particle size of the K- and W-powders decreased from 248 and 227 nm to 64 and 78 nm, respectively, after 7 h of milling. The particle size decreased considerably at the initial milling stage, i.e. up to 1 h of milling. In order to minimize contamination during milling, the mill chamber had a ZrO_2 lining, which was filled with 80 vol.% of 0.1 mm ZrO_2 beads.

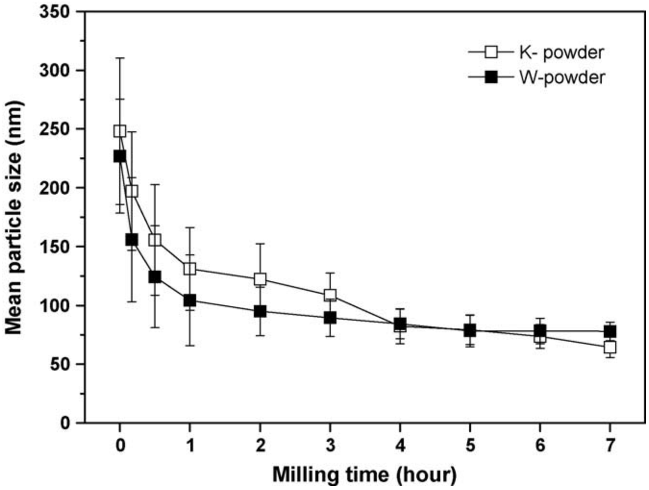

Fig. 1. Evolution of the mean particle size upon high energy milling for the formulated K- and W-powder.

Fig. 2 shows the distribution of Gd in the ball-milled, high energy-milled and commercial GDC powder. 4 h of ball milling

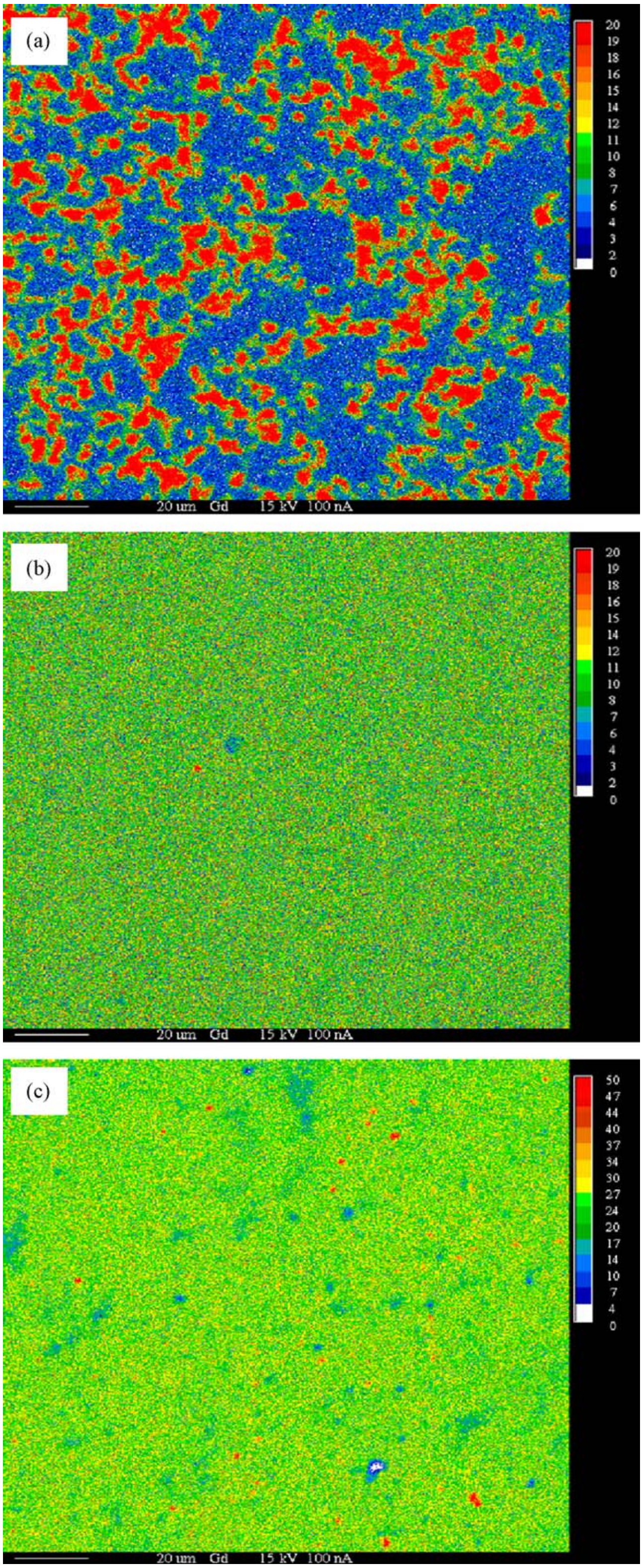

Fig. 2. Energy dispersive X-ray (EDX) mapping results, showing the distribution of Gd in (a) ball-milled, (b) high energy-milled and (c) commercial $Ce_{0.8}Gd_{0.2}O_{2-\delta}$.

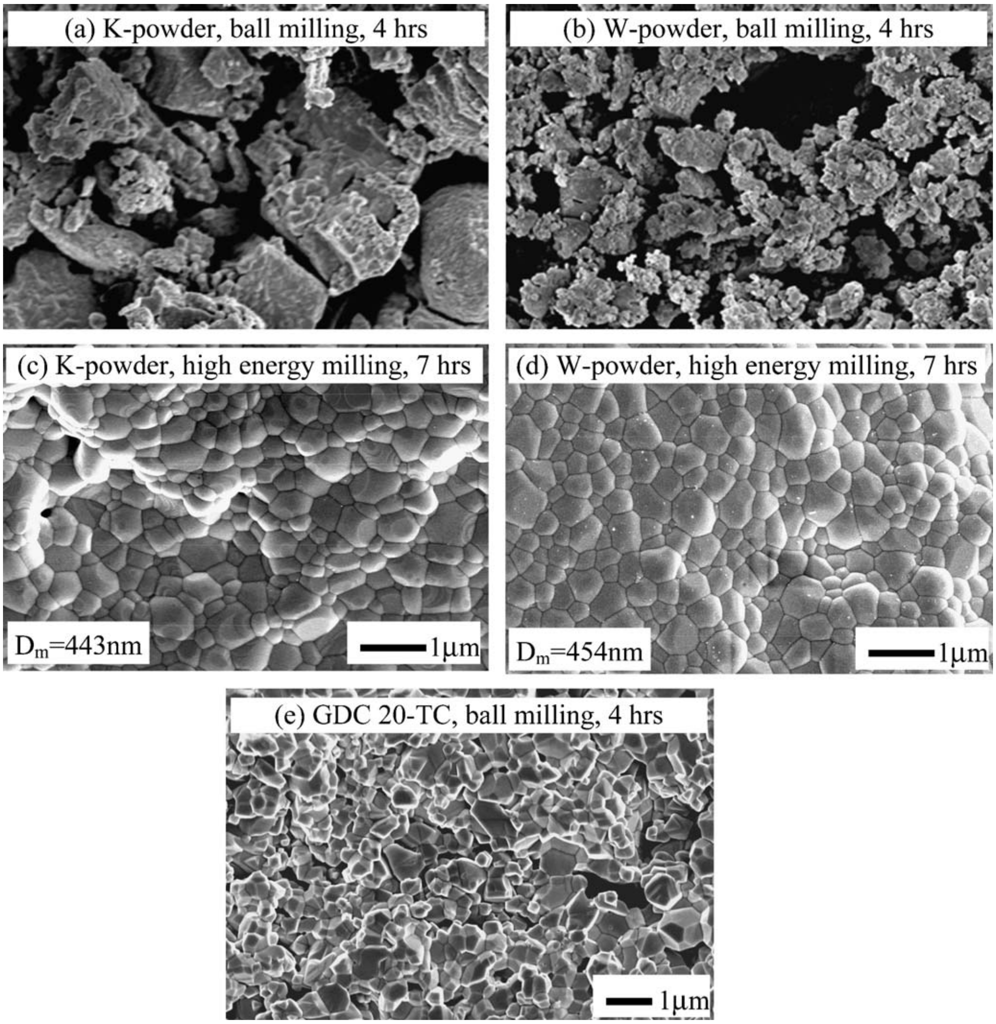

Fig. 3. SEM image of the fractured surface of $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ sintered at 1300 °C using the K-, W- and commercial GDC 20-TC powder with different milling methods.

results in segregation of the Gd_2O_3 phase, where the coarse initial particles remained almost unchanged. On the other hand, the high energy-milled powder shows a very uniform distribution of starting material, which was more homogeneous than that of the calcined commercial one.

Fig. 3 shows SEM image of the fractured surface of $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ sintered at 1300 °C using the K-, W- and commercial GDC 20-TC powder with different milling methods. Both the K- and W-powders treated by ball milling show a highly porous microstructure with 60–62% of the theoretical density after 3 h sintering, as shown in Fig. 3(a) and (b), respectively. The ball-milled commercial GDC 20-TC powder also shows porous microstructure with the density of 77%. On the other hand, the pellets prepared by high energy-milled K- and W-powder showed an almost fully densified microstructure with a sub-micron grain size, as shown in Fig. 3(c) and (d), respectively.

Fig. 4 compares the density of the high energy-milled K- and W-powder at two different heating rates of 5 and 10 °C/min and ball-milled K-, W- and commercial powder at 5 °C/min after sintering at 1300 °C as a function of the keeping time. Compared to the density of approximately 60% for the ball-milled powder and 77% of commercial powder, the high energy-milled powder shows a significantly higher density of 92–99% regardless of the type of powder used. The sintered density increased with increasing keeping time for all samples. The sintered density of the high energy-milled K- and W-

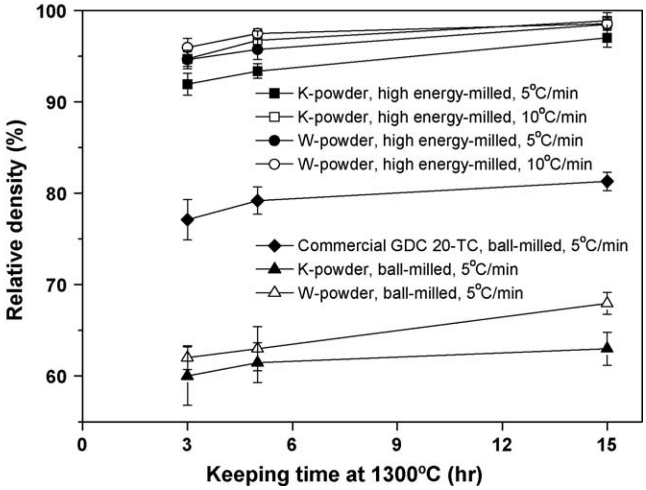

Fig. 4. Density of the $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ pellets sintered at 1300 °C for 3, 5 or 15 h with different heating rates using various powders.

powder increased from 92% and 95% to 97 and 99%, respectively, with increasing keeping time at 1300 °C from 3 h to 15 h. The sintered density was also increased slightly using a faster heating rate, as shown in Fig. 4. The higher sintered density with the faster heating rate can be explained in connection with the fast firing, which provides a higher density than that after slower firing. Fast firing has been used successfully for many types of materials, including alumina, soft ferrites and lead zirconate titanate [12,13]. Although the mechanism of fast firing is not completely understood, it is known that the temperature gradient is extremely important in driving densification for certain ceramic systems. Fast firing can be applied only to fine particle systems, where high energy-milled GDC may belong to this category.

Since the calcination process was skipped for the starting materials in this study, the formation of $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ was confirmed by a comparison of the XRD patterns (not shown here) using the pellets prepared from high energy-milled K- and W-powder after calcination at 1000 °C for 5 h. All pellets showed identical peaks regardless of calcination, indicating that the calcination process can be skipped for these homogeneously distributed fine particles prepared by high energy milling. The lattice parameter calculated from the XRD patterns of $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ was 0.5411 ± 0.0002 nm regardless the type of powder used, which is in good agreement with previous reports [10,14,15]. Moreover, the logarithmic grain conductivity ($\log \sigma$) of the sintered pellets was approximately -2.03 and -1.40 S/cm at 500 and 700 °C, respectively, for both the high energy-milled K- and W-powder, which cannot be achieved when the GDC phase is not formed [8,9,16].

4. Conclusions

$Ce_{0.8}Gd_{0.2}O_{2-\delta}$ pellets with a density $\geq 95\%$ could be synthesized by a solid-state reaction at 1300 °C via 7 h of high energy milling for the starting materials. On the other hand, 4 h of ball-milled powder showed only 60% and a commercial one showed 77% of density at the same sintering condition. The mechanochemical activation by heavy milling and the resultant fine starting materials helped to reduce the sintering temperature because of the short diffusion length and enhanced solid-state reaction rate. In addition, direct sintering without calcination was possible for the same reason. The final phase was confirmed by ionic conductivity, XRD and lattice parameter measurements.

Acknowledgements

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