Sintering and mechanical properties of gadolinium-doped ceria ceramics

K Yasuda*, K Uemura and T Shiota

Ookayama 2-12-1-S7-14, Meguro-ku, Tokyo 152-8552, JAPAN

*E-mail: kyasuda@ceram.titech.ac.jp

Received 22 July 2011, Revised 21 November 2011

Abstract. Gadolinium-doped ceria (GDC) ceramics were made by sintering at various temperatures from 1000°C to 1400°C in air. The true density and apparent density were measured to calculate the relative density of GDC ceramics. The change in relative density revealed that densification of GDC ceramics increased up to 1200°C, and thereafter turned downward. It was suggested that pores were formed at 1300°C and 1400°C due to non-stoichiometry of ceria. JIS-type specimens were cut from the sintered body and tested by 4-point bending. Young’s modulus and bending strength decreased with increasing the sintering temperature from 1200°C to 1400°C, corresponding to the change in the relative density.

1. Introduction

Solid oxide fuel cell (SOFC) is one of the most promising power generators for high efficiency and multi-fuel compatibility; however, its working temperature is as high as 1000°C because yttria-stabilized zirconia is used as electrolyte. To attain long-term durability of this system, the lower working temperature is needed for next-generation SOFC, and 10-20mol% gadolinium-doped ceria (GDC) ceramics is considered to be one of new electrolytes.

GDC ceramics has good electrochemical properties even at 800°C; however, its sintering behavior and mechanical properties have not been fully investigated. Sammes et al. made 20 mol% Gd-doped ceria ceramics by sintering at 1600°C for 16 hours and obtained 96 % of relative density and 140 MPa of bending strength. Sameshima et al. reported that 20 mol% Sm-doped ceria ceramics (sintered at 1600°C) had the relative density from 86 to 98 % and fracture strength around 70 MPa. Thus, we do not have enough information on sintering behavior of GDC ceramics and also its fracture strength values are not consistent in the literatures.

In this paper, GDC ceramics were prepared by sintering Ce₉₀₋₅Gd₀佰₂O₂ powder compacts at 1000, 1100, 1200, 1300, 1400°C, respectively. The true density and apparent density were measured to calculate the relative density of GDC ceramics to make clear its sintering behavior. In addition to it, the bending specimens (4×3×36 mm³) were cut from the sintered body, and 4-point bending tests were carried out to discuss the relationship between relative density and mechanical properties of the GDC ceramics.

2. Experimental procedure
2.1. Sample preparation and density measurement

10mol% gadolinium-doped ceria powder was purchased from Anan Kasei Co. Ltd. because this powder is used as de facto standard of GDC powder. The GDC powder (grain size 0.46 µm) was compressed in uniaxial pressing at 7 MPa for 2 min, and then compressed again by cold isostatic pressing at 100 MPa for 2 min. The compacts were sintered in air at 1000, 1100, 1200, 1300, 1400 ºC, respectively. The holding time was 120 min, and heating and cooling rates were 5 ºC/min.

According to JIS standards, rectangular-sectioned specimens were made by cutting from GDC ceramics, and followed by mirror polishing with diamond slurry. The dimensions of the specimens were 4 mm in breadth × 3 mm in thickness × 36 mm in length. The apparent density was measured by Archimedes method. A small piece of sintered body was ground, and its true density was measured by pycnometry.

2.2. Bending test

4-point bending tests were conducted with universal materials testing machine (Shimadzu, Autograph DSC-R-10TS). The upper and lower spans were 10 mm and 30 mm, respectively. The crosshead speed was set to be 0.5 mm/min. Young’s modulus $E$ and fracture strength $\sigma_f$ were calculated from the equations below,

$$E = \frac{\Delta W(L-l)^2(2L+l)}{4bt^3\Delta u},$$

$$\sigma_f = \frac{3W_f(L-l)}{2bt^2},$$

where $L$ is lower span, $l$ is upper span, $b$ is breadth of the specimen, $t$ is thickness of the specimen, $\Delta u$ is the net displacement of the specimen after correction by displacement of loading train, $\Delta W$ is the load change against $\Delta u$, $W_f$ is the fracture load. The number of specimens was around 17 for each sintering condition.

3. Results and discussion

3.1. Sintering behaviour

The sintered body at 1000 ºC and 1100 ºC were still porous and weak, so that their bending specimens were not obtained due to breaking down during machining. However, true density and apparent density of these sintered bodies were measured.

Figure 1 and 2 show the true density and apparent density of GDC ceramics. The true density slightly decreases in the specimens sintered at 1300 ºC and 1400 ºC. This implies that oxygen vacancy increases from 1300 ºC. The apparent density also decreases in the specimens sintered at 1300 ºC and
1400°C. This means that pores are actually generated in these specimens.

Figure 3 shows the relative density defined as the ratio of apparent density divided by true density. Densification of GDC ceramics increases with increasing the sintering temperature, however, it turns downward at 1300°C and 1400°C. This means pore formation at high temperatures.

![Figure 3. Relative density of GDC ceramics.](image1)

Since the authors were anxious about that volatile matter evaporated from the GDC powder at high temperatures, differential thermo gravimetric analysis (TG/DTA) was carried out. As shown in Figure 4, TG curve does not change from 200°C to 1400°C. Its mass loss is less than 1 %, so that we cannot explain the change in relative density (around 3% from 1200°C to 1400°C) by using Figure 4. In addition to this, DTA curve is almost the same as that of a blank test.

As stated in section 3.1 the authors consider that this pore formation is caused by non-stoichiometric phases of ceria at high temperatures. The following defect reaction (in Kröger-Vink notation) was reported in these literatures,

![Figure 4. TG/DTA analysis of the GDC powder.](image2)
The authors have not had any direct evidence of this reaction yet, however, the reaction coincides well with the changes in the true density (viz. oxygen vacancy formation) and also in the relative density (viz. pore formation) at 1300°C and 1400°C.

3.2. Mechanical properties

Figure 5 and 6 show Young’s modulus and fracture strength of the GDC ceramics. The bending tests were conducted for the specimens sintered at 1200, 1300, 1400°C only. Young’s modulus and fracture strength slightly decrease with increasing the sintering temperature from 1200°C to 1400°C. This tendency can be explained by pore formation at high temperatures, corresponding to the change in the relative density.

4. Conclusion

Densification of GDC ceramics is advanced with increasing the sintering temperature, however, pore formation begins above 1300°C because non-stoichiometric phases of ceria is generated at these temperatures to release an oxygen gas. Therefore, dense GDC ceramics can be obtained by sintering at 1200°C. Young’s modulus and fracture strength slightly decrease with increasing the sintering temperature from 1200°C to 1400°C. This corresponds to the change in the relative density.

References

[1] Steele B C H and Heizel A 2001 Nature 414 345e52
[2] Leng Y J, Chan S H, Jiang S P and Khor K A 2004 Solid State Ionics 170 9
[3] Laukaitis G, Dudonis J and Milcias D 2007 Materials Science (Mendziagotyra) 13, 23
[4] Sammes N, Tomsett G and Zhang Y 1996 Denki Kagaku, 64 674
[5] Sameshima S, Ichikawa T, Kawaminami M and Hirata Y 1999 Materials Chemistry and Physics 61 31
[6] JIS R1601
[7] JIS R1602
[8] Greenwood N N 1968 Ionic Crystals, Lattice Defects and Nonstoichiometry (London : Butterworth & Co Ltd.) Chapter 5
[9] Bevan D J M and Kordis J 1964 J.Inorg. Nucl. Chem. 26 1509