

Microstructural and electrical conductivity properties of cubic zirconia doped with various amount of titania

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Materials

ABSTRACT

Purpose: A dopant concentration higher than the optimum may reduce the number of mobile oxygen ions because of defect association causing conductivity degradation. In this study, the effect of TiO₂ addition on the microstructure and electrical conductivity of cubic zirconia was investigated.

Design/methodology/approach: The cubic zirconia powders with 0-10 wt% TiO₂ were prepared by a colloidal processing and pressureless sintering. The effect of TiO₂ addition on the microstructure and electrical conductivity of cubic zirconia was investigated. Sintered specimens were characterized by XRD, SEM and impedance spectroscopy.

Findings: The experimental results showed that when the TiO₂ amount was less than 5 wt %, the specimens were entirely single cubic phase; further addition of TiO₂ (5 wt% or more) destabilized cubic zirconia phase and caused the formation of tetragonal phase. Grain size measurements for undoped and TiO₂ doped cubic zirconia specimens showed that grain size decreased with increasing TiO₂ content. The electrical conductivity of TiO₂ doped cubic zirconia decreased with increasing TiO₂ content and increased with increasing test temperature.

Research limitations/implications: The measurement of electrical conductivity is one of the important requirements for the electrolyte in solid oxide fuel cells. Generally, the ac impedance of an ionic conductor contains the contributions from grain, grain boundary and electrode-electrolyte interface at high, intermediate and low frequencies, respectively, which can be reflected in a complex plane by three successive arcs[6].

Originality/value: Determination of the microstructural and electrical conductivity properties of cubic zirconia doped with various amount of titania.

Keywords: Ceramics; Electrical properties; Cubic zirconia; Titania; SOFC

1. Introduction

A fuel cell is an electrochemical device where the chemical energy of a fuel is converted into electricity by electrochemical oxidation of the fuel[1]. Fuel cells typically have a pair of electrodes (anode and cathode) and an electrolyte. The working principal of a fuel cell is similar that of a battery. However, unlike

a battery, a fuel cell does not run down or require recharging. A fuel cell operates as long as both fuel and oxidant are supplied to the electrodes[2]. Various types of fuel cells (polymer electrolyte fuel cell, methanol fuel cell, solid oxide fuel cell etc.) are being developed as power sources for a large number of applications. Solid oxide fuel cell (SOFC) offers several advantages over other types of fuel cells such as high efficiency, low emission, high power density and fuel flexibility[1].

The 8 mol% yttria-stabilized cubic zirconia is widely used as electrolyte in solid oxide fuel cells and oxygen sensors because of its good stability and high temperature ionic conductivity[3]. The microstructure is of vital importance and critical for ionic conductivity of the electrolyte. The ionic conductivity of a stabilized zirconia depends upon concentration and mobility of oxygen vacancies, which in turn are closely linked to the dopant concentration. A dopant concentration higher than the optimum may reduce the number of mobile oxygen ions because of defect association causing conductivity degradation. In this study, the effect of TiO₂ addition on the microstructure and electrical conductivity of cubic zirconia was investigated.

2. Experimental procedure

The materials used in the present work were 8 mol% yttria-stabilized cubic zirconia (c-ZrO₂) (Tosoh, Japan) and high purity TiO₂ (Rare Metallic, Japan) powders. The average particle sizes were 0.3 μm for c-ZrO₂ and 0.2 μm for TiO₂. The chemical composition of c-ZrO₂ was 13.6 wt.% Y₂O₃ (equivalent to 8 mol%), 85.9 wt.% ZrO₂ and the following impurities (in wt.%), Al₂O₃ 0.25, SiO₂ 0.10, TiO₂ 0.12, Fe₂O₃ 0.003, Na₂O 0.002 and CaO 0.02. Different amounts of TiO₂ corresponding to 0, 5 and 10 wt% were doped with c-ZrO₂.

A colloidal processing route was used for the preparation of specimens for phase content, microstructure and electrical conductivity measurements. The slurry was prepared by dispersing the designated amounts of cubic zirconia and TiO₂ powders in ethanol and then ball milled for 24 hours to obtain a good dispersion in a plastic container using zirconia balls. The mixed powders were dried by rotary distillation, sieved through a 60-mesh screen to remove hard agglomerate particles and then die-pressed into disks by uniaxial pressing at 40 MPa in a steel die followed by cold isostatic pressing (CIP) at 100 MPa.

The green compacts of the mixed powders were pressureless sintered at 1450 °C for an hour in air. The density of as-sintered specimens was measured using Archimedes' method in distilled water. After sintering, the specimens were sectioned, ground, polished to 1 μm surface finish and thermally etched in air for 30 min. at a temperature 50 °C lower than sintering temperature. Scanning electron microscopy (Jeol 6060 Lv) equipped with an energy dispersive x-ray spectrometer attachment was used to characterize the microstructure of as-sintered specimens. Grain sizes were measured by the mean linear intercept method. X-ray diffraction patterns of the specimens were obtained using a Siemens D-5000 Diffractometer and monochromated high intensity Cu Kα radiation. A scan speed of 0.02 2θ/s was employed.

The electrical conductivity measurements were carried out with pellet specimens of 10 mm diameter and about 3 mm thick. The two surfaces of each sintered pellet were slightly polished with abrasive paper and platinum paste was applied to both sides of the specimens. The specimens were then dried in an oven at 100 °C to eliminate the solvent and annealed at 1000 °C for 30 min. to avoid an excessive shrinkage of the platinum electrodes. The temperature dependence of electrical conductivity was measured using a frequency response analyzer (Solartron Model 1260) in the frequency range of 5-13 MHz. Measurements were made in air and in the temperature range of 300-800 °C at an interval of 100 °C. The AC impedance diagrams were analyzed by Zview software.

3. Experimental results and discussion

An earlier XRD results showed that the specimens containing up to 5 wt% TiO₂ revealed only cubic zirconia structure. However, when the TiO₂ concentration increased to 5 wt% or more, the additional reflections from tetragonal zirconia structure started to appear. Therefore, the addition of more than 5 wt% TiO₂ destabilized the cubic phase and induced the formation of the tetragonal phase. The amount of tetragonal phase increased with increasing TiO₂ in the c-ZrO₂ matrix. No TiO₂ or TiZrO₄ phases were observed, even when the dopant amount was 10 wt%[4,5]. The mole percentage for the cubic and tetragonal zirconias in the 5 wt% TiO₂ doped c-ZrO₂ was calculated to be 89% and 11%, respectively. When the dopant amount increased to 10 wt% TiO₂, the percentage of the tetragonal zirconia phase increased to 37%. These results were also confirmed by measuring the lattice parameter change of cubic zirconia with TiO₂ content. The average lattice parameter of c-ZrO₂ decreased with increasing TiO₂ content. The decrease in lattice parameter with increasing TiO₂ content in the c-ZrO₂ showed that Ti goes into solid solution. The lower values of the lattice parameter found for the TiO₂ doped c-ZrO₂ could be due to the dissolution in the cubic phase of TiO₂ and the substitution of smaller Ti⁴⁺ ions for Zr⁴⁺ and Y³⁺ ions in the cubic lattice, (the ionic radii of Ti⁴⁺, Y³⁺ and Zr⁴⁺ for 8 fold coordination are 0.74, 1.015 and 0.84 Å, respectively). These results showed that the TiO₂ up to 10 wt% could be accommodated in solid solution in the cubic zirconia matrix.

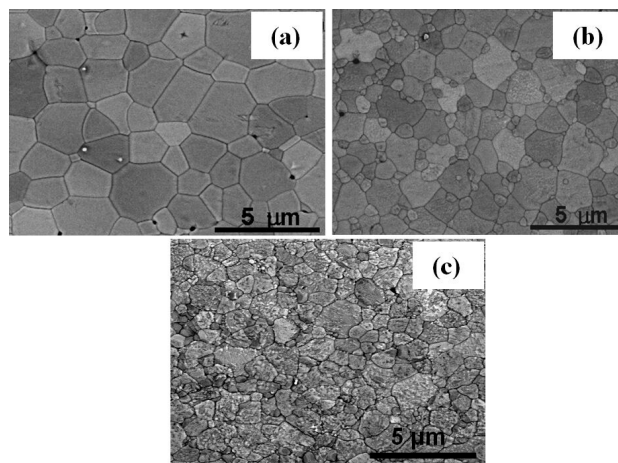


Fig. 1. Microstructural evolution of the compositions (a) undoped c-ZrO₂, (b) 5 wt% TiO₂ doped c-ZrO₂ and (c) 10 wt% TiO₂ doped c-ZrO₂, sintered at 1450 °C for 1 h

Typical SEM micrographs of undoped and TiO₂ doped c-ZrO₂ specimens are shown in Figure 1. Fully densified bodies were obtained for 5 and 10 wt% TiO₂ doped c-ZrO₂s in contrast to undoped c-ZrO₂, which exhibited a small amount of intergranular porosity. The grain boundaries for the undoped specimen were fairly regular. However, the 5 and 10 wt% TiO₂ doped specimens developed more irregular grain boundaries with a large number of small grains present at grain junctions and grain boundaries, indicating that the grain growth of the large grains was inhibited by the small grains during sintering. EDS analysis indicated that the small grains were tetragonal zirconia in which the yttria

concentration is much lower than that in large grains. Therefore, the small grains are the yttria deficient tetragonal phase and the large grains are the yttria rich cubic zirconia phase. In addition, the surface of the TiO_2 doped specimens (Fig.1 (b and c)) is not as smooth as that in undoped one (Fig.1 (a)). Grain size measurements for undoped and TiO_2 doped c-ZrO_2 specimens sintered at 1450°C showed that grain size decreased with increasing TiO_2 content. The grain size distribution for undoped is normal (Fig. 1 (a)). However, a bimodal grain size distribution is observed for 5 and 10 wt% TiO_2 doped c-ZrO_2 (Fig. 1 (b-c)).

The measurement of electrical conductivity is one of the important requirements for the electrolyte in solid oxide fuel cells. As reported earlier, generally, the ac impedance of an ionic conductor contains the contributions from grain, grain boundary and electrode-electrolyte interface at high, intermediate and low frequencies, respectively, which can be reflected in a complex plane by three successive arcs[6].

In the present study, the electrical measurements were carried out on undoped and TiO_2 doped c-ZrO_2 specimens sintered at 1450°C for which the densification level of the specimens was higher than 95% theoretical density and, therefore the effect of porosity on the conductivity can be considered as negligible. As

an example, the ac impedance spectroscopies of 5 wt% TiO_2 doped c-ZrO_2 specimens at different temperatures are shown in Figure 2. As can be seen from this figure, three arcs can be identified clearly at temperatures of $300, 400$ and 500°C at high and low frequencies. Whereas, when the temperature is higher than 500°C , the high frequency semicircle disappeared and only the low frequency semicircle was observed. This showed that the breakdown of grain happened at high temperatures. As mentioned above, the grain size of the TiO_2 doped c-ZrO_2 is smaller than the undoped c-ZrO_2 . Hence, the effective area of the grain boundary per unit of the TiO_2 doped c-ZrO_2 is larger than the undoped c-ZrO_2 , and the breakdown of grain boundary of the TiO_2 doped c-ZrO_2 is not easy to happen in contrast to undoped c-ZrO_2 at high temperature. With increasing temperature, it became difficult to analyze the impedance data in terms of grain and grain boundary contributions due to poorly developed semicircles. It was also seen that the resistances of the grain and grain boundaries decreased significantly with increasing temperature. This decrease was mainly a result of the increased grain size and the consequent reduction in the total grain boundary area. The temperature dependences of grain (σ_g), grain boundary (σ_{gb}) and the total conductivities ($\sigma_T = \sigma_g + \sigma_{gb}$) of 5 wt% TiO_2 doped c-ZrO_2 at

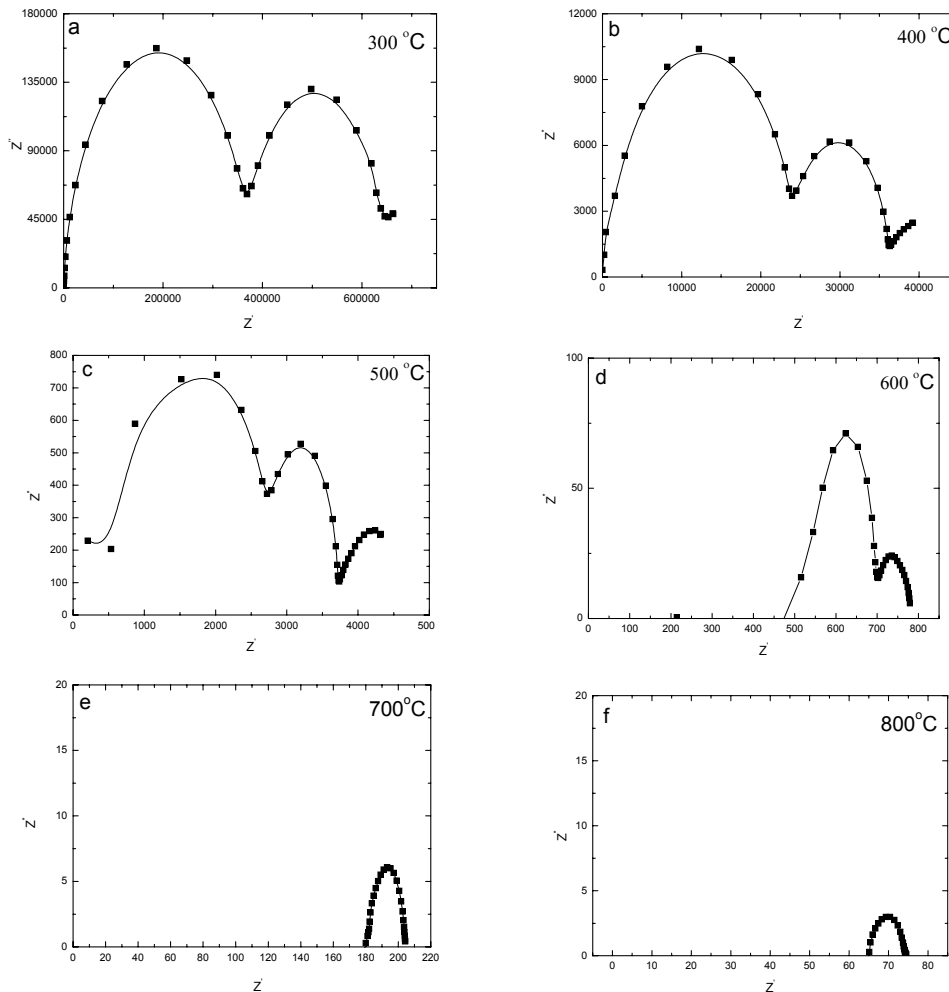


Fig. 2. The ac impedance spectroscopies of 5 wt% TiO_2 doped c-ZrO_2 specimens at different temperatures

temperatures from 300-800 °C is shown in Figure 3. All three conductivities slightly increased up to 600 °C and at higher temperatures a sharp increase was seen. Also at all temperatures, the grain boundary conductivity values were higher than the grain.

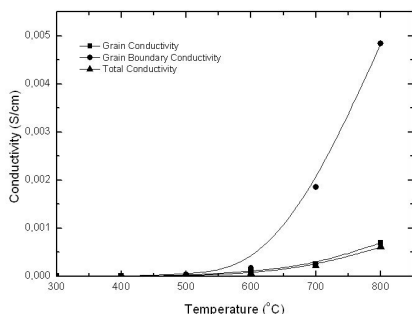


Fig. 3. The temperature dependence of grain, grain boundary and total conductivities of 5 wt% TiO₂ doped cubic zirconia at temperatures from 300-800 °C

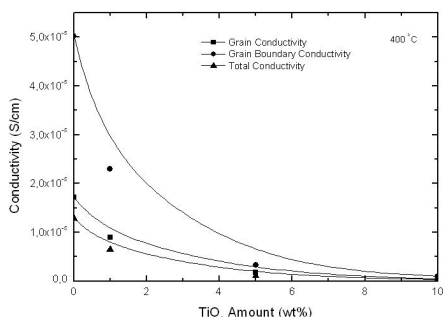


Fig. 4. The effect of TiO₂ content on the conductivity of cubic zirconia at 400 °C

Figure 4 shows the effect of TiO₂ content on the grain, grain boundary and total conductivity of c-ZrO₂ at 400 °C. As can be seen from this figure, all conductivities of c-ZrO₂ decreased with increasing TiO₂ content and grain boundary conductivity is always higher than the grain. The decreased conductivities can be explained as follows;

a) oxide vacancies increase with increasing yttria content in c-ZrO₂ and it is known that ionic conductivity of c-ZrO₂ increases with increasing oxide vacancy [7]. Since Ti ion (Ti⁴⁺) has the same charge number as Zr ion (Zr⁴⁺), no oxide vacancy would form by the solid solution of TiO₂. With increasing TiO₂ content, the Y₂O₃ content in TiO₂ doped c-ZrO₂ decreases and therefore the oxide vacancy decreases.

b) both a trapping of the oxygen ion vacancies by Ti ions and the formation of tetragonal phase (it is known that electrical conductivity of tetragonal zirconia is lower than cubic zirconia) which gives rise to a reduction in moving oxygen vacancies.

c) a blocking effect of the Ti⁴⁺ ions located at the grain boundaries on the oxygen ion transport.

d) the grain refinement. As mentioned above, the grain size of c-ZrO₂ decreased with increasing TiO₂ content. Consequently, the grain size of the TiO₂ doped c-ZrO₂ is smaller than undoped c-ZrO₂. The tendency for this effect is to decrease the conductivity.

e) the decrease in the volume fraction of the conducting phase in the TiO₂ doped c-ZrO₂ specimens.

4. Conclusions

1) XRD analysis of the c-ZrO₂ specimens containing less than 5 wt% TiO₂ revealed only cubic fluorite reflection, whereas XRD of the specimens with greater than 5 wt% showed the cubic fluorite and tetragonal phase. TiO₂ destabilized cubic zirconia phase and caused the formation of tetragonal phase.

2) The lattice parameter of the c-ZrO₂ decreased with increasing TiO₂ content. The decrease in lattice parameter with increasing TiO₂ content in the c-ZrO₂ showed that Ti goes into solid solution. The lower values of the lattice parameter found for the TiO₂ doped c-ZrO₂ could be due to the dissolution in the cubic phase of TiO₂ and the substitution of smaller Ti⁴⁺ ions for Zr⁴⁺ and Y³⁺ ions in the cubic lattice.

3) Grain size measurements for undoped and TiO₂ doped c-ZrO₂ specimens sintered at 1450 °C showed that grain size decreased with increasing TiO₂ content.

4) The grain, grain boundary and total conductivity of c-ZrO₂ decreased with increasing TiO₂ content. This decrease was due to both a trapping of the oxygen ion vacancies by Ti ions and the formation of tetragonal phase which gives rise to a reduction in moving oxygen vacancies.

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References

- [1] P. Bansal, D. Zhu, Thermal conductivity of zirconia-alumina composites, *Ceramics International* 31 (2005) 911-916.
- [2] A.B. Stambouli, E. Traversa, Solid oxide fuel cells (SOFCs): a review of an environmentally clean and efficient source of energy, *Renewable and Sustainable Energy Reviews* 6 (2002) 433-455.
- [3] J. Jiawen, C. Aimin, Y. Bangchao, Z. Yikang, *Science in China Ser. Engineering and Material science* 47/5 2004 569-576.
- [4] T. Chen, S. Tekeli, R. Dillon, M. Mecartney, *Ceramics International*, in press.
- [5] S. Tekeli, T. Chen, H. Nagayama, T. Sakuma, M.L. Mecartney, *Ceramics International*, in press.
- [6] M. Miyayama, H. Yanagida, A. Asada, Effects of Al₂O₃ Additions on Resistivity and Microstructure of Yttria-Stabilized Zirconia, *Am. Ceram. Soc. Bull.* 65/4 (1986) 660-664.
- [7] J.E. Bauerle, Study of solid electrolyte polarization by a complex admittance method, *Journal of Physics and Chemistry of Solids* 30 (1969) 2657-2670.
- [8] A.R. Gonzalez-Elipe, A.C. Martinez, F. Capel, C. Moure, P. Duran, Structure and Electrical Behavior in Air of TiO₂-Doped Stabilized Tetragonal Zirconia Ceramics, *Applied Physics A* 68 (1999) 41-48.
- [9] H. Miyazaki, J. Nakano, T. Kimura, T. Goto, *Journal of the Ceramic Society of Japan*, 112/5 (2004) 881-883.