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The effect of TiO_2 additives on the structural stability and thermal properties of yttria fully-stabilized zirconia

Hidetoshi Miyazaki

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Abstract TiO_2(0–20 mol%)-8 mol% YSZ (8YSZ) ceramics were synthesized by a traditional solid-state reaction method. A cubic single phase was observed for 8YSZ, 4 mol% TiO_2-8YSZ and 8 mol% TiO_2-8YSZ. Tetragonal and cubic mixed phases were observed for 12–20 mol% TiO_2-8YSZ ceramics. The sintering temperature was 1,700 °C for 8YSZ and 4 mol% TiO_2-8YSZ ceramics, whereas it was 1,500 °C for 8–20 mol% TiO_2-8YSZ. The thermal conductivity at room temperature decreased in proportion to increasing TiO_2 content, from 3.0 to 2.3 W/m K. The specific heat of TiO_2-8YSZ ceramics was unaltered as the TiO_2 content changed.

Keywords Solid state reaction · TiO_2-YSZ ceramics · Thermal diffusivity · Thermal conductivity

Introduction

Yttria-stabilized zirconia (YSZ) is one of the most commonly used high performance ceramic materials. Because of its high ionic conductivity, thermal stability and excellent mechanical properties, YSZ ceramics are used in high temperature electronic devices, such as oxygen sensors [1], solid oxide fuel cells [2], and thermal barrier coatings [3]. The high temperature cubic phase of zirconia is stabilized down to room temperature by a cation solid solution [4, 5].

TiO_2–ZrO_2 solid solution ceramics have been reported with TiO_2 contents less than 40 mol% [6]. In addition, previous studies have reported on TiO_2 doped YSZ ceramics [7–11]. The crystallographic, electrical, and optical properties of TiO_2-YSZ ceramics were evaluated in these reports. On the other hand, there have been few investigations into the thermal properties of TiO_2-YSZ ceramics [12].

In a previous report, the author evaluated the structural, thermal, and electrical properties of the TiO_2-3YSZ (yttria partially stabilized zirconia) ceramic [12]. This article describes the synthesis of TiO_2-doped 8YSZ ceramics by the solid-state reaction method, and the effect of TiO_2 on the crystal structure, microstructure, thermal stability, and thermal conductivity of TiO_2-8YSZ ceramics.

Experimental procedure

The starting material was 8 mol% yttria-stabilized zirconia (8YSZ, Tosoh, Japan) and TiO_2 (Wako, Japan) powders. The 8YSZ and TiO_2 powders were mixed with TiO_2 in amounts up to 20 mol% in ethanol. The mixture was dried in air and then die-pressed by uniaxial pressing at 100 MPa. The resultant pellet was calcined at 1,100 °C for 36 h in air. The calcined pellet was ground, and the powder was again die-pressed by uniaxial pressing at 100 MPa. The pellet was sintered at 1,500–1,700 °C for 12–96 h, and a TiO_2 solid-soluted 8YSZ specimen was synthesized. Throughout the sintering process, the heating and cooling rates were kept at 200 °C/h.

The crystal structure was determined by X-ray diffraction (XRD) using Rigaku RAD-C (Japan) at room temperature with CuKα radiation. The sample microstructure was observed by scanning electron microscopy (SEM) (Hitachi S-3100H, Japan) and the density of the sintered specimen measured by an Archimedean technique using

H. Miyazaki (✉)
Department of Material Science, Interdisciplinary Faculty of Science and Engineering, Shimane University, 1060, Nishikawatsu, Matsue, Shimane 690-8504, Japan
e-mail: miya@riko.shimane-u.ac.jp

toluene. The specific heat, thermal diffusivity, and thermal conductivity were evaluated by the laser flash method (Ulvac-Riko: TC-7000, Japan).

Results and discussion

TiO_2-doped 8YSZ (hereinafter, TiO_2-8YSZ) ceramics were prepared by traditional solid-state reaction at a sintering temperature of 1,500 °C for 24 h, and the structure of the products was characterized by XRD. Figure 1 shows the XRD patterns of the resultant TiO_2-8YSZ. To precisely characterize the cubic and tetragonal phases of YSZ, the precise XRD pattern between the angles of 70°–80° was also indicated, as shown in Fig. 2. A TiO_2 phase was not observed in all samples, confirming that TiO_2 could be doped in 8YSZ up to 20 mol%. Cubic single phase (JCPDS 27-0997) was identified for 8YSZ, 4 mol% TiO_2-8YSZ, and 8 mol% TiO_2-8YSZ ceramics. Tetragonal (JCPDS 17-0923) and cubic phases were observed for 12–20 mol% TiO_2-8YSZ. These results suggested that a tetragonal phase of 8YSZ was stabilized by the existence of TiO_2.

Since the cubic phase was confirmed as a main phase in all samples, the lattice constant of the cubic phase was calculated for the TiO_2-doped 8YSZ specimens from the observed XRD patterns. Figure 3 shows the effect of TiO_2 content on the lattice constant and the lattice volume of the resultant specimen. To evaluate the lattice constant, silicon powder (JCPDS 27-1402) was used as an internal standard sample. The lattice constant and the lattice volume decreased with increasing TiO_2 content. Ti ions are smaller than Zr ions, and we assume that the Ti ion substitutes for the Zr site. Thus, the lattice constant and the cell volume decreased with an increase in TiO_2 content.

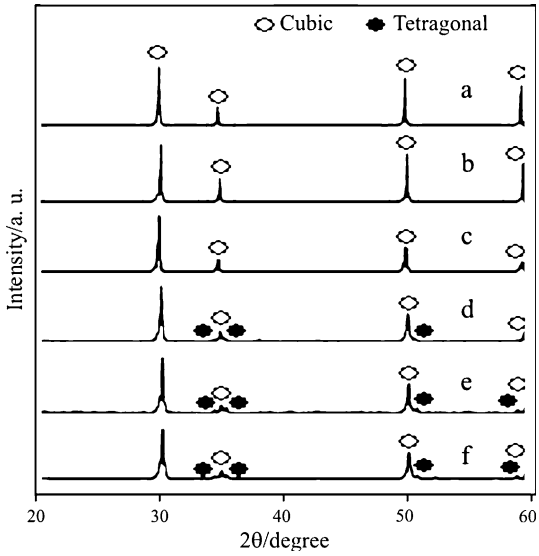

Fig. 1 XRD patterns for TiO_2-8YSZ ceramics with a measurement angle of 20°–60°. (a) Non-doped, (b) 4 mol% TiO_2, (c) 8 mol% TiO_2, (d) 12 mol% TiO_2, (e) 16 mol% TiO_2, and (f) 20 mol% TiO_2

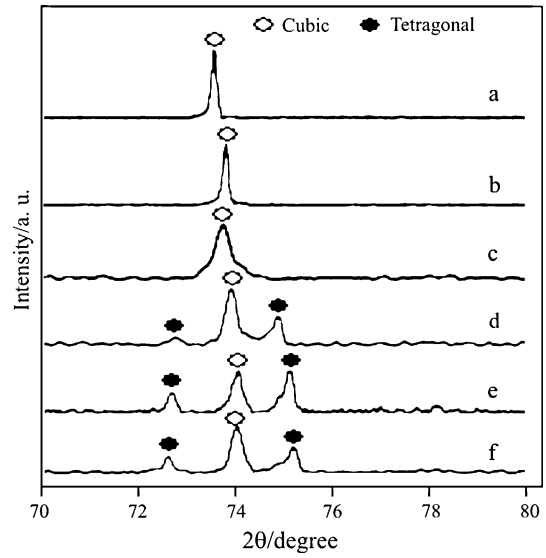

Fig. 2 XRD patterns for TiO_2-8YSZ ceramics with a measurement angle of 70°–80°. (a) Non-doped, (b) 4 mol% TiO_2, (c) 8 mol% TiO_2, (d) 12 mol% TiO_2, (e) 16 mol% TiO_2, and (f) 20 mol% TiO_2

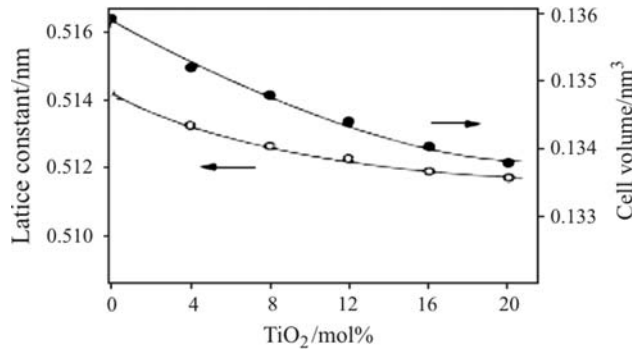

Fig. 3 The lattice parameters and cell volume of TiO_2-8YSZ as a function of the TiO_2 content

Densities of the resultant specimens were measured by an Archimedean technique, and the relative densities were calculated using the measured density and the ideal density. Where the ideal lattice of TiO_2-8YSZ was formed (Ti was substituted perfectly to the Zr site in 8YSZ), ideal density was calculated with the ideal lattice of TiO_2-8YSZ. The calculated relative density is shown in Table 1. All samples were sintered at 1,500 °C for 24 h. The specimens of 8YSZ and 4 mol% TiO_2-8YSZ had low relative densities compared to specimens with more than 8 mol% of TiO_2 content. To improve the relative densities of 8YSZ and 4 mol% TiO_2-8YSZ specimens, these specimens were sintered under other sintering conditions. The 8YSZ was

Table 1 Relative density of the sintered TiO_2-8YSZ ceramics

TiO_2 content/mol%	0	4	8	12	16	20
Relative density/%						
1,500 °C for 24 h	94.5	93.3	99.0	98.8	99.8	98.8
1,700 °C for 12 h	99.4	–	–	–	–	–
1,700 °C for 96 h	–	97.0	–	–	–	–

sintered at 1,700 °C for 12 h, and the 4 mol% TiO_2-8YSZ was sintered at 1,700 °C for 96 h. The relative densities of the resultant 8YSZ and 4 mol% TiO_2-8YSZ were 99.4% and 97.0%, respectively. Hereinafter, these high density specimens were employed as the specimens of 8YSZ and 4 mol% TiO_2-8YSZ to evaluate the thermal properties. From these results, an increase of TiO_2 content in 8YSZ decreased the sintering temperature of 8YSZ.

Figure 4 depicts the surface morphology of the resultant specimens observed by SEM. From the micrographs, all the resultant TiO_2-8YSZ ceramics were very dense and well sintered; hence, it is assumed that the microstructures of these ceramics did not affect the thermal properties. In addition, increasing the TiO_2 content in 8YSZ decreased the grain size of the resultant specimens. The sintering temperatures and sintering times of the specimens of 8YSZ and 4 mol% TiO_2-8YSZ differed from those of the other samples, and these specimens should not be considered in terms of the tendency to change the grain size of TiO_2-8YSZ.

Figure 5 illustrates the thermal conductivity of the TiO_2-8YSZ ceramics at room temperature. The thermal conductivity decreased in proportion to an increasing TiO_2 content from 3.0 to 2.3 W/m K. This suggested that the thermal conductivity of the TiO_2-8YSZ decreased with an increasing TiO_2 content. In addition, Ti ions are lighter than the Y and Zr ions. This caused a mass defect at the cation sites, generated by Ti substitution at the Y or Zr site in YSZ. This defect was a phonon-scattering center, and hence, thermal conductivity decreased due to the substitution of Ti for 8YSZ.

Figure 6 shows the thermal conductivity of the TiO_2-8YSZ specimens as a function of temperature. The thermal conductivity of the non-doped-8YSZ specimen was almost unaltered above 200 °C, and the thermal conductivity of the other samples increased with temperature. This suggests that a solid solution of Ti ion to Zr site in 8YSZ created a temperature dependence for thermal conductivity above 200 °C.

At temperatures lower than 200 °C, the thermal conductivity of 8YSZ tended to decrease with increasing TiO_2 content in 8YSZ. On the other hand, at temperatures higher than 200 °C, the thermal conductivity of the specimens did not depend much on the TiO_2 content in 8YSZ.

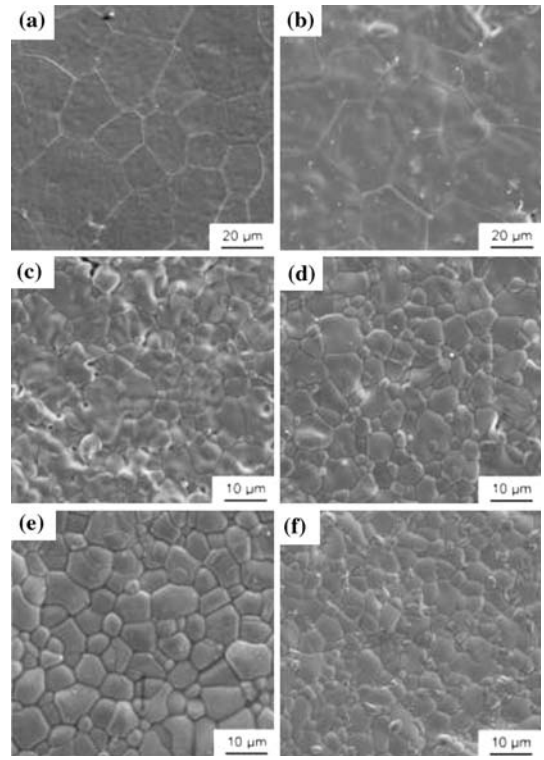

Fig. 4 Surface morphology of TiO_2-8YSZ ceramics. **a** 4 mol% TiO_2-8YSZ sintered at 1,700 °C for 12 h, **b** 4 mol% TiO_2-8YSZ sintered at 1,700 °C for 96 h, **c** 8 mol% TiO_2-8YSZ sintered at 1,500 °C for 24 h, **d** 12 mol% TiO_2-8YSZ sintered at 1,500 °C for 24 h, **e** 16 mol% TiO_2-8YSZ sintered at 1,500 °C for 24 h, and **f** 20 mol% TiO_2-8YSZ sintered at 1,500 °C for 24 h

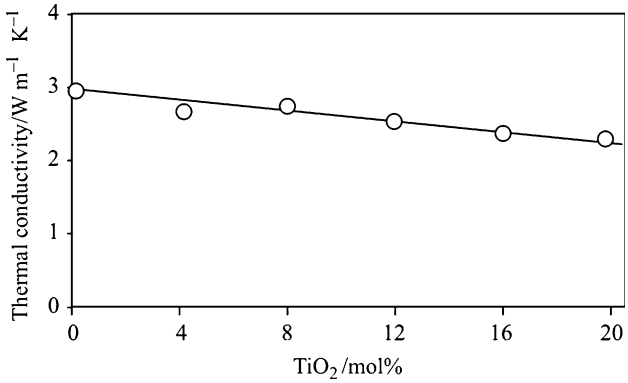

Fig. 5 Thermal conductivity of TiO_2-8YSZ ceramics at room temperature, as a function of TiO_2 content. The *solid line* is a visual guideline

In the previous reports, the Debye temperature of YSZ was reported to be about 200 °C [13, 14]; hence, it is assumed that thermal conductivity behavior changed much around that temperature.

Figure 7 illustrates the specific heat of the TiO_2-8YSZ specimens as a function of temperature. The specific heat of all specimens increased slightly with temperature. The

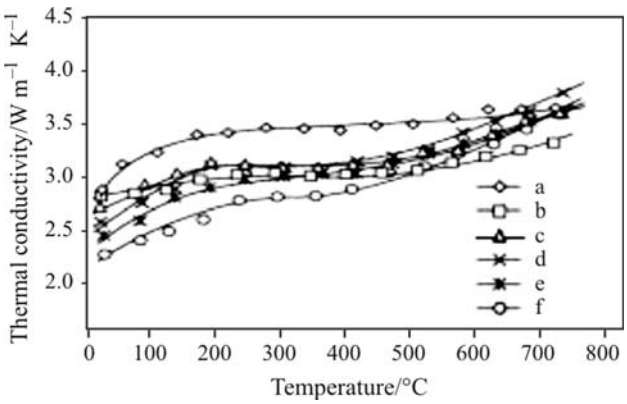

Fig. 6 Temperature dependence of the thermal conductivity of TiO_2-8YSZ ceramics. The *solid line* is a visual guide. (a) Non-doped, (b) 4 mol% TiO_2, (c) 8 mol% TiO_2, (d) 12 mol% TiO_2, (e) 16 mol% TiO_2, and (f) 20 mol% TiO_2

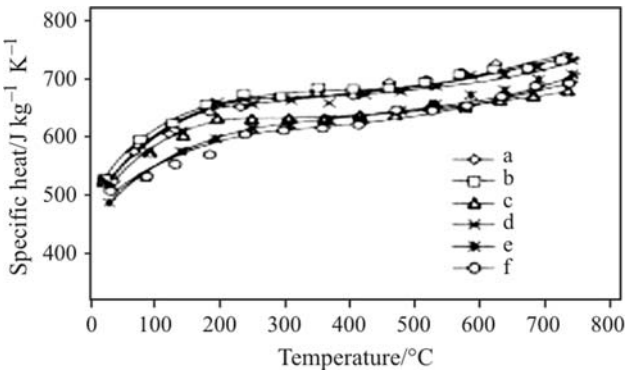

Fig. 7 Temperature dependence of the specific heat of TiO_2-3YSZ ceramics. The *solid line* is a visual guideline. (a) Non-doped, (b) 4 mol% TiO_2, (c) 8 mol% TiO_2, (d) 12 mol% TiO_2, (e) 16 mol% TiO_2, and (f) 20 mol% TiO_2

specific heat of TiO_2-8YSZ tended to decrease slightly with increasing TiO_2 content throughout the temperature range.

Conclusions

TiO_2 doped 8YSZ ceramics were prepared by solid state reaction, and the crystallographic structure, microstructure, and thermal properties were investigated for the resultant TiO_2-8YSZ ceramics.

TiO_2 could be dissolved into 8YSZ up to 20 mol%, and the phase of the 8YSZ matrix changed from cubic single phase to the tetragonal and cubic mixed phase with increasing TiO_2 content. Increasing TiO_2 content in 8YSZ ceramics caused decrease of the sintering temperature.

The thermal conductivity of the TiO_2-8YSZ ceramics decreased with increasing TiO_2 content below 200 °C. At temperatures above 200 °C, increasing TiO_2 content in 8YSZ decreased the thermal conductivity. On the other hand, thermal conductivity of the specimens was unaltered with changing TiO_2 ratio at temperatures much higher than 200 °C. The specific heat of TiO_2-8YSZ ceramics decreased slightly with an increase in TiO_2 content.

References

1. Park JS, Park CO, Kim HJ, Miura N. Low temperature oxygen sensor using YSZ‖ß-ß" alumina bielectrolyte. Solid State Ionics. 2005;176(15–16):1371–5.
2. Minh NQ. Ceramic fuel cells. J Am Ceram Soc. 1993;76:563–88.
3. Guo S, Kagawa Y. Isothermal and cycle properties of EB-PVD yttria-partially-stabilized zirconia thermal barrier coatings at 1150° and 1300°C. Ceram Int. 2007;33:373–8.
4. Scott HG. Phase relationships in the zirconia-yttria system. J Mater Sci. 1975;10:1527–35.
5. Yoshimura M. Phase stability of zirconia. Am Ceram Soc Bull. 1988;67:1950–5.
6. Brown FH, Duwez P. The zirconia-titania system. J Am Ceram Soc. 1954;37:129–32.
7. Zschech E, Kountouros PN, Petzow G. Synchrotron radiation Ti-K XANES study of TiO_2-Y_2O_3-stabilized tetragonal zirconia polycrystals. J Am Ceram Soc. 1993;76:197–201.
8. Duran P, Capel F, Moure C, Gonzalez-Elipe AR, Caballero A, Banares MA. Mixed (oxygen ion and n-type) conductivity and structural characterization of titania-doped stabilized tetragonal zirconia. J Electrochem Soc. 1999;146:2425–34.
9. Capel F, Moure C, Duran P, Gonzalez-Elipe AR, Caballero A. Structure and electrical behavior in air of TiO_2-doped stabilized tetragonal zirconia ceramics. Appl Phys A. 1999;68:41–8.
10. Capel F, Moure C, Duran P, Gonzalez-Elipe AR, Caballero A. Structure and electrical behaviour in air of TiO_2-doped stabilized tetragonal zirconia ceramics. J Eur Ceram Soc. 1999;19:765–8.
11. Capel F, Moure C, Duran P, Gonzalez-Elipe AR, Caballero A. Structure-electrical properties relationships in TiO_2-doped stabilized tetragonal zirconia ceramics. Ceram Int. 1999;25:639–48.
12. Miyazaki H. Influence of TiO_2 solid solution on the thermal property and ionic conductivity of partially stabilized zirconia. Int J Appl Ceram Technol. 2008;5:490–8.
13. Hasselman DP, Johnson LF, Bentsen LD, Syed R, Lee HL. Thermal diffusivity and conductivity of dense polycrystalline ZrO_2 ceramics: a survey. Am Ceram Soc Bull. 1987;66:799–806.
14. Lawless WN. Low-temperature specific heat of a ZrO_2:Y_2O_3 oxygen conductor. Phys Rev B. 1980;21:585–8.