Journal of the Ceramic Society of Japan 117 [4] 449-451 2009 Paper

Change of phase compositions in calcia stabilized zirconia ceramics using a boric acid additive

Qiang SHEN, Changlian CHEN, Fei CHEN, Junguo LI and Lianmeng ZHANG†

State Key Lab of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Wuhan 430070, China

Dense calcia-stabilized zirconia (CSZ) ceramics were prepared by using a small amount of boric acid (H_3BO_3) as the sintering additive at the sintering temperature of 1700°C. The effect of H_3BO_3 content on the sintering behavior, the change of phase composition and mechanical properties of the CSZ ceramics were mainly investigated. The results showed that, due to the reaction between B_2O_3 and CaO, borate liquid was formed during the sintering, which promoted the the densification of CSZ ceramics. Meanwhile, the depletion of the CaO from the lattice of CSZ ceramics resulted in the phase transformation of ZrO_2. The content of tetragonal ZrO_2 phase increased with increasing the H_3BO_3 content. So the phase composition of CSZ ceramics could be well controlled by adjusting the amount of H_3BO_3. The bending strength and fracture toughness of the sintered CSZ ceramics also increased with increasing the H_3BO_3 content, namely the content of tetragonal ZrO_2 phase, which had better mechanical properties, and the highest value reached 267 MPa and 3.35 MPa·m$^{1/2}$, respectively.

Key-words : Calcia stabilized zirconia (CSZ), Phase composition, H_3BO_3, Mechanical properties

[Received December 1, 2008; Accepted February 19, 2009]

1. Introduction

Calcium oxide (CaO) is one of the most common used oxides, which can form a solid solution with ZrO_2,[1] and calcia-stabilized zirconia (CSZ), therefore, can be used as a refractory and excellent insulation material. Moreover, because of its high thermochemical stability, it is also one of the best candidates for oxygen sensor application.[2)–6)]

Usually, tetragonal phase ZrO_2 has better mechanical properties than partially stabilized zirconia or fully stabilized zirconia, whereas partially stabilized zirconia has better thermal shock resistance.[7] Phase composition plays an important role in zirconia ceramics properties. Previous researches focused rather limited on preparation of CSZ ceramics composed of both cubic and tetragonal phases. It has been proved that B_2O_3 could react with CaO to extract CaO from the cubic ZrO_2[2] and resulted in the destabilization of cubic zirconia and the formation of monoclinic ZrO_2.[8] The amount of monoclinic phase increased linearly with increasing the B_2O_3 content and the presence of monoclinic ZrO_2 phase enhanced the thermal shock resistance but reduced the bending strength of the sintered CSZ ceramics.

In the present study, attempts were made to prepare the CSZ ceramics with both tetragonal and cubic ZrO_2 phases by using H_3BO_3 as the sintering additive at the sintering temperature of 1700°C. The effect of H_3BO_3 content on the phase composition and mechanical properties of the obtained CSZ ceramics were mainly investigated.

2. Experimental procedure

2.1 Starting materials

The 7 wt% CSZ powder with an average particle size of ~0.5 μm was used as the starting powder, which was produced by Yixing Ultra-Fine Powder Co. (Jiangsu, China). The H_3BO_3 powder, used as the sintering additive, was in analytical purity, the purity of which was greater than 99.5%.

2.2 Samples preparation

The 7 wt% CSZ powder with 0 wt%, 0.5 wt%, 1.0 wt% and 1.5 wt% of H_3BO_3 were mixed uniformly. The mixtures were loaded by the steel die (Φ50 mm) and pressed using a uniaxial pressure of 30 MPa to get the green bodies. Then, the green bodies were sintered at 1700°C in air by an electric furnace with a heating rate of 10°C/min, holding for 2 h. The samples were finally cooled down with the furnace.

2.3 Samples characterizations

The density and the porosity of the sintered CSZ ceramics were measured by using the Archimedes' method. Microstructure of the samples was observed by the scanning electron microscopy (SEM; Model JSM–5610LV, Japan). The Raman spectra of sintered samples were tested by the Laser Confocal Raman Microscope of RENISHAW, the wave number was in the range of 100 cm^{-1} to 700 cm^{-1}, and spectral width and time constant were 1.4 cm^{-1} and 0.3 s, respectively. The phase compositions were determined by XRD, using a Rigaku D/Max-RB with Cu target, 2θ range of 20–80°. The content of cubic and tetragonal phase of the samples was calculated from the XRD by Rietveld refinement method.[9),10)] The bending strength was tested by the three-point method, with a span length of 30 mm and crosshead speed of 0.5 mm/min on a universal testing machine (MTS–810, USA) and the fracture toughness was tested by the single edge notched beam technique.

3. Results and discussion

3.1 Effect of the H_3BO_3 content on the densification of the CSZ ceramics

Figure 1 shows the porosity and the density of sintered CSZ samples as a function of the H_3BO_3 content. It is obviously

† Corresponding author: L. Zhang; E-mail: lmzhang@whut.edu.cn

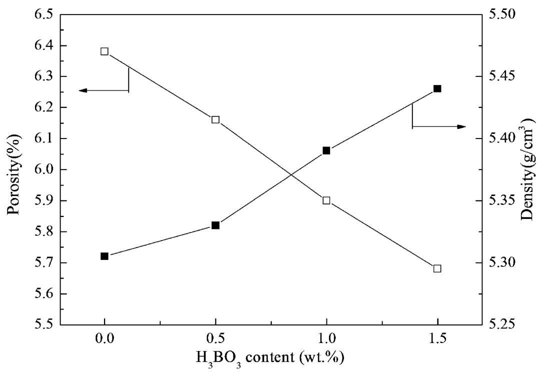


Fig. 1. Effect of the H_3BO_3 content on the porosity and density of the sintered CSZ ceramics.

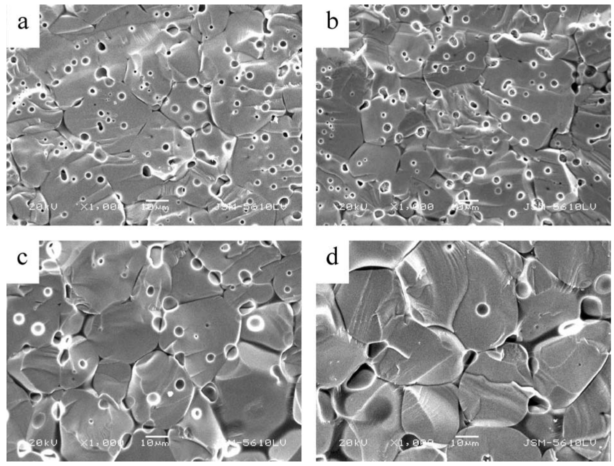


Fig. 2. SEM images of the sintered CSZ samples with H_3BO_3 content of: (a) 0 wt%, (b) 0.5 wt%, (c) 1.0 wt% and (d) 1.5 wt% H_3BO_3.

observed that the porosity of the sintered CSZ ceramics is rather low and almost shows no variation with the H_3BO_3 content. The porosity is in the range of 5.7% to 6.4%, correspondingly the density is from 5.31 g/cm^3 to 5.44 g/cm^3, when the H_3BO_3 content is increased from 0 to 1.5 wt%. The porosity and density of the sintered samples are believed to have a significant relationship with the phase compositions of the obtained CSZ ceramics.

Figure 2 presents the SEM images of the sintered CSZ ceramics with H_3BO_3 content in the range of 0–1.5 wt%. It is seen clearly that the pores are composed of nearly all closed pores with pore size of less than 10 μm. The ZrO_2 grains are well grown and compacted to a relative high density, which is in agreement with the results shown in Fig. 1. It is also observed that the grain size of ZrO_2 and the pore size are apparently increased with increasing the H_3BO_3 content. It is indicated in the Ref. [11] that H_3BO_3 is not stable existing and decomposes when enhancing the temperature, which can be described by Eq. (1):

$$2H_3BO_3 \rightarrow 3H_2O + B_2O_3 \quad (1)$$

According to the phase diagram of B_2O_3 and CaO,[12] four kinds of borate composites with different melting points can be formed at different B_2O_3 and CaO contents, as shown from Eq. (2) to (5).

$$2B_2O_3 + 3CaO \rightarrow CaB_4O_7 \quad \text{(melting point ~1000°C)} \quad (2)$$

$$B_2O_3 + CaO \rightarrow CaB_2O_4 \quad \text{(melting point ~1160°C)} \quad (3)$$

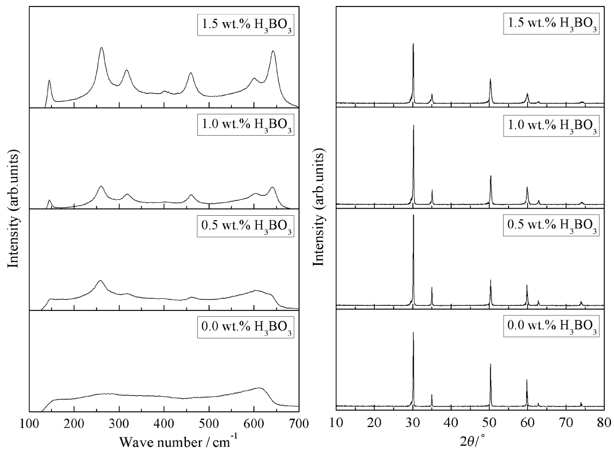
$$B_2O_3 + 2CaO \rightarrow Ca_2B_2O_5 \quad \text{(melting point ~1300°C)} \quad (4)$$

$$B_2O_3 + 3CaO \rightarrow Ca_3B_2O_6 \quad \text{(melting point ~1470°C)} \quad (5)$$

The above reactions occur during the sintering of the CSZ ceramics at 1700°C and the borate liquid can be formed, which promotes the ZrO_2 grains growth and rearrangement. On the other hand, a little amount of the volatilization of the borate liquid can introduce some porosity to the sintered samples, which reduces the density of the CSZ ceramics. Moreover, it is significantly found that during the reaction between B_2O_3 and CaO, the depletion of CaO can efficiently improve the phase transformation of ZrO_2 from cubic to tetragonal phase, which can be used to control the phase composition of CSZ ceramics by adjusting the H_3BO_3 content.

3.2 Effect of the H_3BO_3 content on the phase composition of the CSZ ceramics

Figure 3 presents the Raman spectra and the XRD patterns of the sintered CSZ ceramics with different H_3BO_3 contents. For



(a) (b)

Fig. 3. Raman spectra and XRD patterns of the sintered CSZ ceramics with different H_3BO_3 contents: (a) Raman spectra, (b) XRD patterns.

CSZ samples sintered at 1700°C, no monoclinic ZrO_2 phase is detected, which is the major difference from those samples sintered at 1400°C.[2] When the H_3BO_3 content is 0 wt%, no peaks are detected from Raman spectra, indicating the phase of the ZrO_2 in the sintered CSZ ceramic is cubic phase. When the H_3BO_3 content is increased from 0.5 wt% to 1.5 wt%, the peaks of the characteristic tetragonal ZrO_2 phase are observed and the intensity of the peaks increases gradually, indicating an increased tetragonal ZrO_2 phase content.

In order to quantify the effect of the H_3BO_3 content on the phase composition of ZrO_2 in the sintered CSZ ceramics, the quantitative analysis for the sintered CSZ ceramics with various H_3BO_3 contents was carried out by the XRD Rietveld refinement method. The initial parameters of the crystal cells of c-ZrO_2 and t-ZrO_2 for Rietveld refinement were acquired by the references.[13)–16)] The refinements were completed until the R_p figure of merit and the R_{wp} figure of merit was respectively below 10%.

Table 1 lists the results of quantitative analysis for the phase composition. It is seen clearly that when the H_3BO_3 content is increased from 0 wt% to 1.5 wt%, the content of cubic CSZ decreases from 100% to 62% and the content of tetragonal CSZ

Table 1. Content of the c-CSZ and t-CSZ in the Sintered CSZ Ceramics

H_3BO_3 (wt%)	0.0	0.5	1.0	1.5
c-CSZ (wt%)	100	85	72	62
t-CSZ (wt%)	0	15	28	38

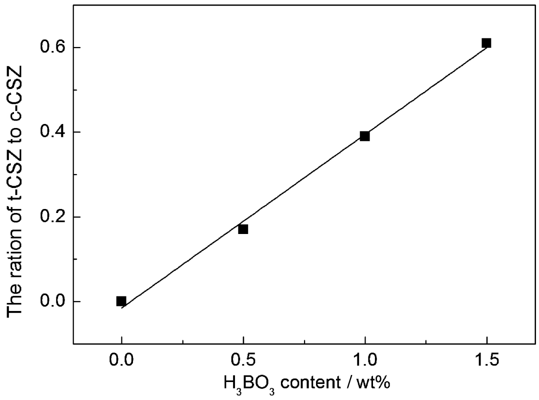


Fig. 4. Ratio of t-CSZ to c-CSZ as a function of the H_3BO_3 content.

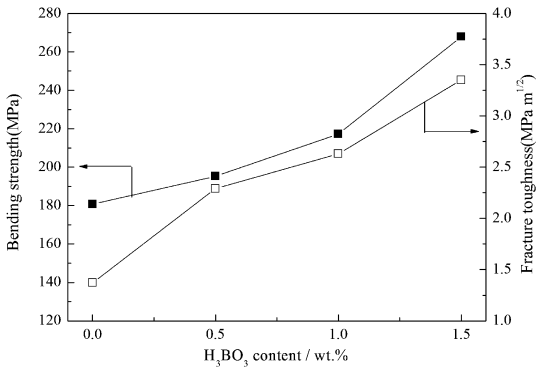


Fig. 5. Bending strength and fracture toughness as a function of the H_3BO_3 content.

increases from 0% to 38%. The ratio of t-CSZ to c-CSZ almost exhibits a linear variation with the H_3BO_3 content, as shown in **Fig. 4**. So it is believed that the fraction of cubic CSZ and tetragonal CSZ can be well controlled by adjusting the H_3BO_3 content.

3.3 Effect of the H_3BO_3 content on the mechanical properties of the CSZ ceramics

Figure 5 shows the bending strength and fracture toughness of the sintered CSZ ceramics as a function of H_3BO_3 content. It is obviously observed that for samples without H_3BO_3, the bending strength is 184 MPa and the fracture toughness is 1.37 $MPa{\cdot}m^{1/2}$. When the H_3BO_3 content is increased to 1.5 wt%, the bending strength and fracture toughness are 267 MPa and 3.35 $MPa{\cdot}m^{1/2}$, respectively. It is known that tetragonal ZrO_2 has better mechanical properties than cubic phase and monoclinic phase, as a result, the increased tetragonal ZrO_2 phase with increasing the H_3BO_3 content shown in Table 1 contributes to the mechanical properties enhancement.

4. Conclusions

CSZ ceramics was successfully prepared at 1700°C by using 0–1.5 wt% H_3BO_3 as a additive. During the sintering, CaO could react with B_2O_3 to form borate liquid, which promoted the densification of the sintered CSZ ceramics, but the volatilization of a little amount of borate might introduce some porosity at the same time.

When the H_3BO_3 content was increased from 0 wt% to 1.5 wt%, the content of cubic CSZ decreased from 100 wt% to 62 wt% and the content of tetragonal CSZ increased from 0 wt% to 38 wt%. The ratio of t-CSZ to c-CSZ almost exhibited a linear variation with the H_3BO_3 content. This enabled us to control the phase composition of the sintered CSZ ceramics.

The bending strength and fracture toughness were increased with increasing the H_3BO_3 content, namely the content of tetragonal ZrO_2 phase, which had better mechanical properties, and the highest value reached 267 MPa and 3.35 $MPa{\cdot}m^{1/2}$, respectively.

References

1) S. Colin, B. Dupre, C. Gleitzer, X. L. Coq, M. C. Kaerle and C. Guenard, *J. Eur. Ceram. Soc.*, 9, 389–395 (1992).
2) R. C. Buchanan and A. Sircar, *J. Am. Ceram. Soc.*, 66, C20–C21 (1983).
3) C. G. Kontoyannis and G. Carountzos, *J. Am. Ceram. Soc.*, 77, 2191–2194 (1994).
4) R. Steven, "An Introduction to Zirconia (Publication No. 113)," Magnesium Elektron Ltd., Sherwin Rivers, Ltd., Stoke-on-Trent, UK (1983).
5) M. Zhou and A. Ahmad, *Int. J. Appl. Ceram. Technol.*, 3, 218–224 (2006).
6) M. Zhou and A. Ahmad, *Mater. Res. Bull.*, 41, 690–696 (2006).
7) C. T. Yang, H. J. Cho and W. J. Wei, *J. Eur. Ceram. Soc.*, 22, 199–207 (2002).
8) D. Z. de Florio and R. Muccillo, *Mater. Res. Bull.*, 39, 1539–1548 (2004).
9) W. Pyda and A. Pyda, *J. Eur. Ceram. Soc.*, 27, 769–773 (2007).
10) K. Matsui, H. Horikoshi, N. Ohmichi and M. Ohgai, *J. Am. Ceram. Soc.*, 86, 1401–1408 (2003).
11) X. Guo, *J. Mater. Sci. Lett.*, 15, 38–39 (1996).
12) H. Yu, Q. Chen and Z. P. Jin, *Coupling Phase Diagrams Thermochem.*, 23, 101–111 (1999).
13) M. Morinaga and J. B. Cohen, *Acta Crystal. A*, 35, 789–795(1979).
14) A. M. Geprge, M. A. Vaidya and A. B. Phadnis, *J. Mater. Sci.*, 26, 4194–4195 (1991).
15) D. G. Lamas and N. E. Walsoe de Reca, *J. Mater. Sci.*, 35, 5563–5567 (2000).
16) P. Wang, Y. Jia, D. Wang and Y. Luo, *J. Inorg. Mater.*, 12, 551–555 (1997).