ELSEVIER

Ceramics International 26 (2000) 207–211

CERAMICS INTERNATIONAL

# Mechanical properties of ytterbia stabilized zirconia ceramics (Yb-TZP) fabricated from powders prepared by co-precipitation method

Susumu Nakayama [a,*], Sachihiko Maekawa [b], Tetsuji Sato [b], Yoshio Masuda [b], Shinji Imai [c], Masatomi Sakamoto [d]

[a] *Department of Applied Chemistry and Biotechnology, Niihama National College of Technology, Niihama 792-8580, Japan*
[b] *Daiichi Kigenso Kagaku Kogyo Co., Ltd., Osaka 541-0043, Japan*
[c] *Sharp Takaya Electronics Industry Co., Ltd., Asakuchi 719-0301, Japan*
[d] *Department of Material and Biological Chemistry, Faculty of Science, Yamagata University, Yamagata 990-8560, Japan*

Received 17 November 1998; received in revised form 6 January 1999; accepted 21 February 1999

**Abstract**

2.0, 2.4, 2.6, 3.0 and 3.5 mol% $Yb_2O_3$-doped tetragonal zirconia polycrystals (Yb-TZP) were fabricated and their mechanical properties [three-points bending strength ($\sigma_f$), Vickers hardness ($H_v$) and fracture toughness ($K_{1C}$)] were measured. The value of $\sigma_f$ was the highest for the 2.6 mol% $Yb_2O_3$-doped sample. The $H_v$-value increased and the $K_{1C}$-value decreased, as the $Yb_2O_3$ content increased. The comparison of these mechanical properties with those of the corresponding $Y_2O_3$-doped zirconia (Y-TZP) revealed the excellence of Yb-TZP, though slight. 

*Keywords:* Ytterbia stabilized zirconia; Co-precipitation method; Mechanical property; Ball-milling medium

## 1. Introduction

Zirconia-based ceramics modified by the addition of stabilizing dopants such as MgO, CaO, $Y_2O_3$ and $CeO_2$ have been utilized as advanced materials or have received much attention for the development of such materials because of their excellent mechanical, thermal, chemical and electrical properties [1–3]. Among them, yttria-doped tetragonal zirconia polycrystals (Y-TZP) are well known to possess the high strength and the high fracture toughness [4]. The studies about mechanical properties of Y-TZP has been carried out by many researchers and that of a series of Y-TZP samples fabricated from commercial sources produced by the co-precipitation method was reported by Gross and Swain [5]. On the other hand, although there are a few reports about mechanical properties of other rare-earth oxide doped tetragonal zirconia polycrystal [Ln-TZP (Ln = Dy, Er and Yb, etc)], the mechanical properties of a series of Ln-TZP samples fabricated from powders prepared by the co-precipitation method has been little investigated [6,7].

In the present work, five kinds of $ZrO_2$ containing 2.0, 2.4, 2.6, 3.0 and 3.5 mol% $Yb_2O_3$ as an additive (Yb-TZP) were fabricated by sintering powders prepared by the co-precipitation method, and their mechanical properties were compared with those of Y-TZP ($ZrO_2$ containing 2.0, 2.6 and 3.0 mol% $Y_2O_3$).

## 2. Experimental

### 2.1. Materials

Yb-TZP and Y-TZP powders (HSYb and HSY grades, respectively) produced by the co-precipitation method were received from Dai-ichi Kigenso Kogyo, Co., Ltd. Chemical analysis, specific surface area and particle size of each powder are listed in Table 1. These raw materials without binders were isostatically pressed at 100 MPa and sintered in air at a given temperature of 1400 to 1550°C for 2 h. Hereafter, the sample thus fabricated

* Corresponding author. Fax: +81-897-37-1245.
*E-mail address:* nakayama@chem.niihama-nct.ac.jp (S. Nakayama).

0272-8842/00/$20.00 
PII: S0272-8842(99)00042-5

Table 1
Chemical analyses, specific surface areas and particle sizes of Yb-TZP and Y-TZP powders

| Grade | Ignition loss | $ZrO_2$ | $Yb_2O_3$ or $Y_2O_3$ | $Na_2O$ | CaO | $Al_2O_3$ | $H_2O$ | Surface area ($m^2\ g^{-1}$) | Particle size (μm) |
|---|---|---|---|---|---|---|---|---|---|
| | | | | (wt%) | | | | | |
| HSYb-2.0 | 0.36 | 92.77 | 6.11 | 0.005 | 0.007 | 0.24 | 0.11 | 7.5 | 0.41 |
| HSYb-2.4 | 0.39 | 95.76 | 7.11 | 0.006 | 0.004 | 0.25 | 0.09 | 7.7 | 0.43 |
| HSYb-2.6 | 0.39 | 91.18 | 7.70 | 0.004 | 0.005 | 0.25 | 0.08 | 8.0 | 0.29 |
| HSYb-3.0 | 0.37 | 90.13 | 8.91 | 0.003 | 0.006 | 0.22 | 0.05 | 7.3 | 0.44 |
| HSYb-3.5 | 0.31 | 88.75 | 10.21 | 0.003 | 0.005 | 0.25 | 0.08 | 7.3 | 0.31 |
| HSY-2.0 | 0.24 | 95.21 | 3.57 | 0.006 | 0.007 | 0.25 | 0.15 | 7.8 | 0.37 |
| HSY-2.6 | 0.26 | 94.81 | 4.66 | 0.010 | 0.007 | 0.24 | 0.17 | 8.2 | 0.37 |
| HSY-3.0 | 0.10 | 93.24 | 5.34 | 0.010 | 0.010 | 0.24 | 0.12 | 7.3 | 0.47 |

from HSYb-n powder which is $ZrO_2$ containing n mol% $Yb_2O_3$ is represented as Ybn. For instance, the sample fabricated from HSYb-3.0 powder in Table 1 is represented as Yb3.0.

### 2.2. Microstructure

Sintered sample was ground using a #600 diamond wheel and then further polished using diamond grains of 1–5 μm until a flat mirror face is obtained. X-ray diffraction analysis (XRD, $2\theta/\mathrm{Cu}K_\alpha$ scan between 27 and 33°) of such sample was carried out for the estimation of ratio of the monoclinic phase to the sum of tetragonal and cubic phases. The ratio of tetragonal phase to cubic phase was estimated from X-ray diffraction analysis in the range of 72 to 75°. When $X_m$, $X_{(t+c)}$, $X_t$ and $X_c$ are defined as the intensity ratios of monoclinic peaks (111) and (11-1), (tetragonal and cubic) peak (111), tetragonal peaks (004) and (400) and cubic peak (400) after correcting for the background counts to the sum of all phases, respectively, these ratios are expressed as follows:

$$X_m = (I_m(111) + I_m(11\text{-}1))/(I_m(111) + I_m(11\text{-}1) + I_{(t+c)}(111))$$

$$X_{(t+c)} = I_{(t+c)}(111)/(I_m(111) + I_m(11\text{-}1) + I_{(t+c)}(111))$$

$$X_t = X_{(t+c)} \times (X_t(004) + X_t(400))/(X_t(004) + X_t(400) + X_c(400))$$

$$X_c = X_{(t+c)} \times X_c(400)/(X_t(004) + X_t(400) + X_c(400))$$

where $I$ denotes the peak intensity, and subscripts m, (t+c), t and c denote the monoclinic, (tetragonal + cubic), tetragonal and cubic phases, respectively.

The microstructures were evaluated by thermal etching of samples polished in the way described above. The fine grain sizes were observed by scanning electron microscopy (SEM).

### 2.3. Mechanical properties

The three-points bending test was carried out according to the JIS R 1601, using the sample of 3×4×40 mm. The Vickers hardness and the fracture toughness were determined according to the JIS R 1610 (load: 98.07 N) and the JIS R 1607 by the indentation microfracture method.

### 2.4. Abrasion and grinding efficiency tests

Samples, Yb3.0 and Y3.0, were used for these tests. Each powder was molded into a ball designed so that the ball of 1 cm diameter can be obtained through sintering. This molding was sintered at 1500°C for 2 h to produce ball-milling media. The abrasion and grinding efficiency tests were carried out using these ball-milling media. 3600 g of the media were placed in a 2 l alumina based ball-mill pot, together with water (800 ml) and fused alumina powders (# 325). After the pot was rotated at 100 rpm for 48 h, the weight decrease of mediam and the particle size distribution of alumina powders were measured. Here, the particle size distribution was analyzed with a laser diffraction particle size analyzer.

Table 2
Each phase ratio in Yb-TZP and Y-TZP estimated from XRD peak intensities

| | Monoclinic phase ($X_m$) | Tetragonal phase ($X_t$) | Cubic phase ($X_c$) |
|---|---|---|---|
| Yb2.0 | 0.07 | 0.93 | – |
| Yb2.4 | 0.02 | 0.98 | – |
| Yb2.6 | – | 1.00 | – |
| Yb3.0 | – | 1.00 | – |
| Yb3.5 | – | 0.94 | 0.06 |
| Y2.0 | 0.05 | 0.95 | – |
| Y2.6 | – | 1.00 | – |
| Y3.0 | – | 0.92 | 0.08 |

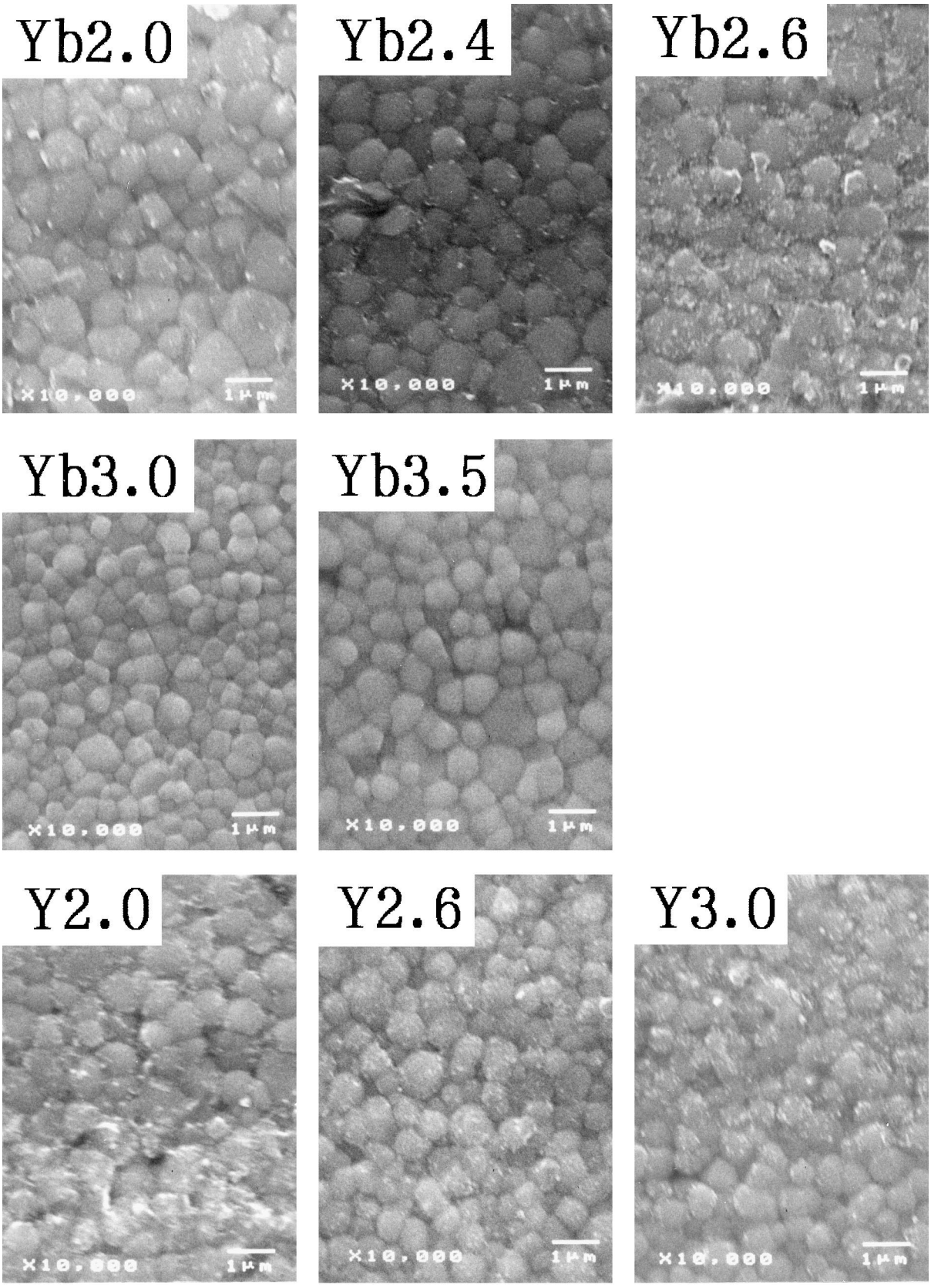


Fig. 1. SEM photographs of the polished and thermally etched samples (bar = 1 μm).

## 3. Results and discussion

Densities were the highest for all samples (Yb2.0, Yb2.4, Yb2.6, Yb3.0, Yb3.5, Y2.6 and Y3.0), when the sintering temperature was 1500°C or above. Mechanical properties such as three-points bending strength, Vickers hardness and fracture toughness were also the most superior for all samples sintered at 1500°C. Therefore, the discussion will be, hereafter, made on the data of samples sintered at 1500°C.

### 3.1. Microstructure

Table 2 summarizes the ratio of each phase experimentally estimated from the XRD measurements. The major phase is tetragonal for all samples. The monoclinic and cubic phases are slightly observed for Yb2.0, Yb2.4, Yb3.5, Y2.0 andY3.0.

Fig. 1 shows SEM photographs of samples polished and etched in the way described in experimental Section 2.2. For all samples, uniform structures are observed and grain sizes are within 1.5 μm. Gross and Swain reported that the large size grains of cubic phase are observed for the sintered zirconia bodies with 4 mol% $Y_2O_3$ or more[5]. However, such large grains are not observed in all of the present samples, as can be seen from Fig. 1.

### 3.2. Mechanical properties

Three-points bending strength, Vickers hardness and fracture toughness of Yb2.0, Yb2.4, Yb2.6, Yb3.0 and Yb3.5 were determined and compared with those of Y2.0, Y2.6 and Y3.0.

Fig. 2 shows the three-points bending strengths and the densities. The strength of Ybn increases from Yb2.0 to Yb2.6 and decreases beyond Yb2.6 with increasing $Yb_2O_3$ content. It is also the case in the Yn. The density of Ybn gradually increases with increasing $Yb_2O_3$ content, whereas that of Yn gradually decreases with increasing $Y_2O_3$ content.

The Vickers hardness increases with increasing $Yb_2O_3$ content, whereas fracture toughness decreases with increasing $Yb_2O_3$ content, as shown in Fig. 3. Fig. 3 shows also that the behaviors of these two mechanical properties for Ybn are very similar to those for Yn fabricated from the commercially obtained Y-TZP powders in the way of Gross and Swain.

Here, it should be noted that the three-points bending strengths and the densities of Yb2.0, Yb2.6 and Yb3.0 are apparently higher, and the Vickers hardness and the fracture toughness are slightly higher, compared with those of the corresponding Y2.0, Y2.6 and Y3.0. Such superior mechanical properties of the present Yb-TZP may be related to its higher density than Y-TZP, though the clear interpretation cannot be obtained at present.

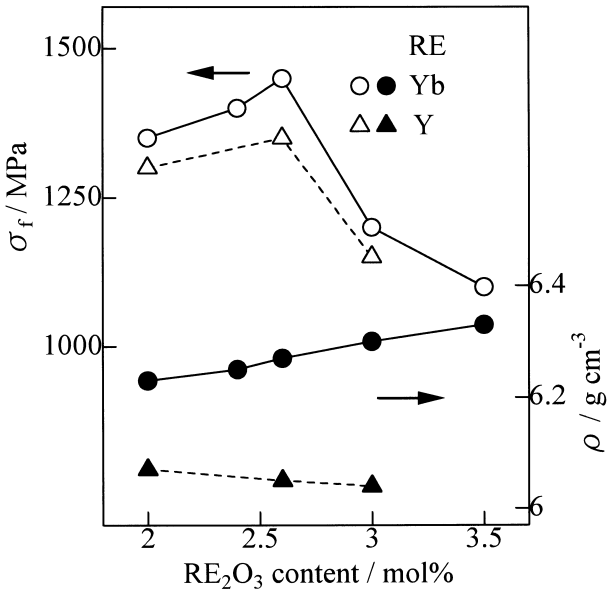


Fig. 2. Effects of $RE_2O_3$ content (RE = Yb or Y) on three-points bending strength ($\sigma_f$) and density ($\rho$).

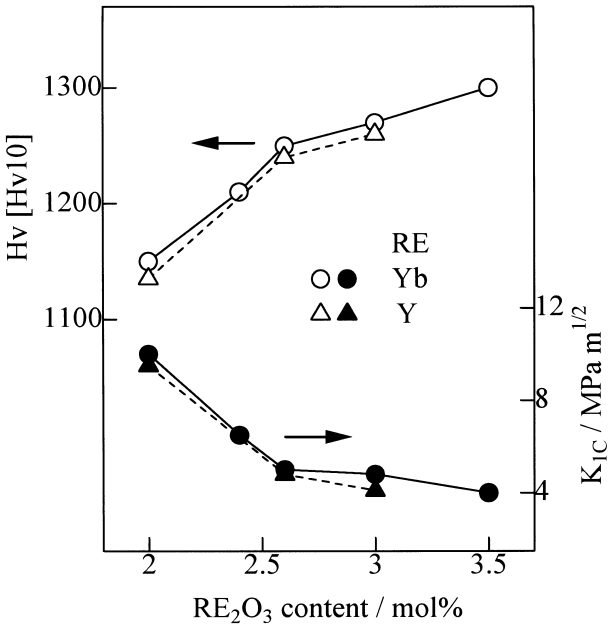


Fig. 3. Effects of $RE_2O_3$ content (RE = Yb or Y) on Vickers hardness ($H_v$) and fracture toughness ($K_{1C}$).

When the present Yb-TZP samples were subjected to the autoclave test in a deionized water at 250°C for 50 h, many microcracks occurred in all samples because of the tetragonal-to monoclinic phase transformation to lead to the breakage of sintered bodies. Such a low temperature degradation was observed also for the Y-TZP[8,9].

### 3.3. Possibilities as ball-milling media

Results of abrasion tests using Yb3.0 and Y3.0 as ball-milling media are summarized in Table 3. The

Table 3
Weight losses of Yb3.0 and Y3.0 as ball-milling media after abrasion test

| | Weight loss (%) | |
|---|---|---|
| | After 24 h | After 48h |
| Yb3.0 | 0.280 | 0.510 |
| Y3.0 | 0.265 | 0.490 |

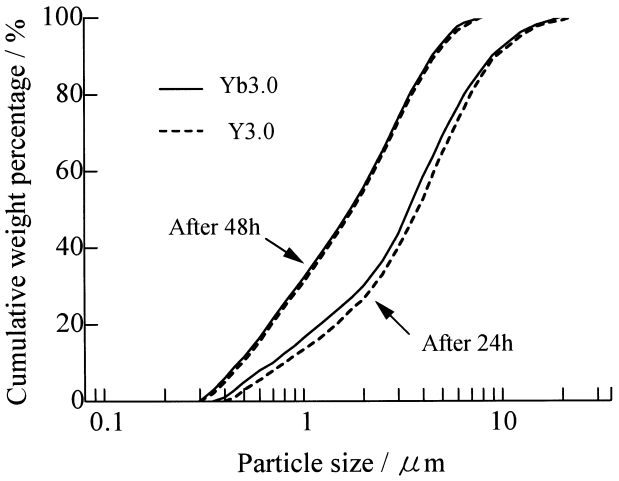


Fig. 4. Distribution curves of particle size of fused alumina powders after grinding test using Yb3.0 or Y3.0 as a ball-milling medium.

weight loss of Yb3.0 were found to be slightly larger than that of Y3.0. Fig. 4 shows the particle size distributions of fused alumina powders after the grinding efficiency tests using Yb3.0 and Y3.0 as ball-milling media. When the grinding time is 24 h, the distribution curve of alumina ground by Yb3.0 shifts to a smaller size side, compared with that of alumina ground by Y3.0, though the distribution curves are not almost different between two balling media when the grinding time is 48 h. Such a shift for the shorter grinding time may be due to the higher density of Yb3.0 (6.30 $g \cdot cm^{-3}$, see Fig. 2) than that of Y3.0 (6.05 $gcm^{-3}$, also see Fig. 2). Ohnishi and Sakuda used Y-TZP (6.0 $g \cdot cm^{-3}$), $TiO_2$ (4.0 $g \cdot cm^{-3}$), $Al_2O_3$ (3.8 $g \cdot cm^{-3}$) and glass (2.6 $g \cdot cm^{-3}$) as ball-milling media for the grinding tests of $BaTiO_3$ and found similar results that the grinding efficiency increases with increasing density of ball-milling medium[10].

## 4. Conclusion

2.0–3.5 mol% $Yb_2O_3$-doped tetragonal zirconia polycrystal samples (Yb-TZP) were fabricated at 1500°C from the commercial sources produced by the co-precipitation method and their mechanical properties were compared with those of $Y_2O_3$-doped zirconia samples, Y-TZP ($ZrO_2$-2.0, 2.6 and 3.0 mol% $Y_2O_3$). Results are summarized as follows: X-ray diffraction analyses revealed that tetragonal phase is almost completely formed in all samples, though the monoclinic phase for 2.0 and 2.4 mol% $Yb_2O_3$-doped samples and the cubic phase for 3.5 mol% $Yb_2O_3$-doped sample are observed as a minor phase.

The uniformity of microstructure was very high for all samples and their grain sizes were within 1.5 μm.

The 2.6 mol% $Yb_2O_3$ sample exhibited the highest three-points bending strength ($\sigma_f$). The Vickers hardness ($H_v$) increased and the fracture toughness ($K_{1C}$) decreased, with increasing $Yb_2O_3$ content. Mechanical properties such as $\sigma_f$, $H_v$ and $K_{1C}$ of Yb-TZP were superior, though slight in $H_v$ and $K_{1C}$, to those of the corresponding Y-TZP.

The particle size distribution of fused alumina powders ground by the 3.0 mol% $Yb_2O_3$ sample as a ball-milling medium shifted to the smaller size side, compared with that of alumina ground by the 3.0 mol% $Y_2O_3$ sample, when the grinding time was 24 h.

## Acknowledgements

Authors thank Mr. S. Kakita, Mr. T. Suzuki and Mr. K. Itoh of Daiichi Kigenso Kagaku Kogyo Co., Ltd. for their cooperations and Mr. R. Yajima, the former managing director of Shinagawa Refractories, Co., Ltd., for his valuable advice.

## References

[1] D.J. Green, R.H. Hannink, M.V. Swain, Transformation Toughening of Ceramics, CRC Press, Florida, 1989, pp. 133–212.
[2] R.H.J. Hannink, C.J. Howard, E.H. Kisi, M.V. Swain, Relationship between fracture toughness and phase assemblage in Mg-PSZ, J. Am. Ceram. Soc. 77 (1994) 571–579.
[3] K. Tsukuma, M. Shimada, Strength, fracture toughness and Vickers hardness of $CeO_2$-stabilized tetragonal $ZrO_2$ polycrystals (Ce-TZP), J. Mater. Soc. 20 (1985) 1178–1184.
[4] L. Ruiz, M.J. Readey, Effect of heat treatment on grain size, phase assemblage, and mechanical properties of 3 mol% Y-TZP, J. Am. Ceram. Soc. 79 (1996) 2331–2340.
[5] V. Gross, M.V. Swain, Mechanical properties and microstructure of sintered and hot isostatically pressed yttria-partially-stabilized ziconia (Y-TZP), J. Aust. Ceram. Soc. 22 (1986) 1–12.
[6] H. Watanabe, M. Chigasaki, Thermal shock resistance of $ZrO_2$ ceramics stabilized by rare earth oxides, Yogyo-Kyokai-Shi 94 (1986) 330–335.
[7] T. Log, R.A. Cutler, J.F. Jue, A.V. Virkar, Polycrystalline t′-$ZrO_2$ ($Ln_2O_3$) formed by displacive transformations, J. Mater. Soc. 28 (1993) 4503–4509.
[8] T. Sato, M. Shimada, Transformation of yttria-doped tetragonal $ZrO_2$ polycrystals by annealing in water, J. Am. Ceram. Soc. 68 (1985) 356–359.
[9] S. Nakayama, S. Imai, M. Sakamoto, Effect of $La_2O_3$ addition on Thermal-stability of Y-TZP, J. Mater. Sci. Lett., in press.
[10] H. Ohnishi, M. Sakuda, Zirconia grinding and dispersing media, New Ceramics 5 (1996) 31–36.