

## Effect of ZnO addition on the electrical resistance of 2.6 mol%-Y<sub>2</sub>O<sub>3</sub> stabilized zirconia ceramic

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Zirconia (ZrO<sub>2</sub>)-based ceramics modified by the addition of stabilizing dopants, such as MgO, CaO, Y<sub>2</sub>O<sub>3</sub>, and CeO<sub>2</sub>, have been utilized as advanced materials, and the development of such materials has been receiving significant attention because of their excellent mechanical, thermal, chemical, and electrical properties [1–3]. Among them, Y<sub>2</sub>O<sub>3</sub>-doped tetragonal zirconia polycrystals (Y-TZP) are well known to possess a high strength and high fracture toughness [4]. Knives and grinding tools are being commercialized by taking advantage of these properties. However, Y-TZP is electrified during grinding since it is an insulator at room temperature. Therefore, the grinding chips adhere to the grinding tool. In order to reduce this problem, the technique of adding conductive materials, such as zinc oxide (ZnO), indium oxide (In<sub>2</sub>O<sub>3</sub>), and tin (IV) oxide (SnO<sub>2</sub>) to Y-TZP, has been considered [5]. It is ideally expected that the added conductive material exists at the grain boundary of Y-TZP and produces the conducting property. However, In<sub>2</sub>O<sub>3</sub> and ZrO<sub>2</sub> are known to form a solid solution, while the sinterability of SnO<sub>2</sub> is poor [6–9]. In the present study, the addition of ZnO to Y-TZP (ZrO<sub>2</sub>-2.6 mol%Y<sub>2</sub>O<sub>3</sub>) was investigated in order to increase the conduction.

HSY-2.6 grade powders prepared by the coprecipitation method at Daiichi Kigenso Kagaku Kogyo, Co., Ltd., were used as the base material which is hereafter represented by TZP, ZrO<sub>2</sub> containing 2.6 mol%Y<sub>2</sub>O<sub>3</sub>. Reagent-grade ZnO powders were purchased from Wako Pure Chemical Industries, Ltd. Samples for the present purpose were prepared by the following procedure: The component oxide mixture as the starting raw material was ball-milled with deionized water and PVA binder. After drying, these powders were isostatically pressed at 100 MPa and sintered in ZnO powder at a given temperature of 1250–1350 °C for 2 hr.

The density was calculated using Archimedes method. The amount of Zn after sintering and the powder X-ray diffraction (XRD) pattern were measured using a

Shimadzu EDX-700 X-ray fluorescence spectrometer (XRF) and a Rigaku MiniFlex diffractometer, respectively. After carrying out grinding to about 0.2 mm and mirror-polishing of the sample's surface, the electron probe X-ray microanalyzer (EPMA) measurement was carried out using a JEOL JXA-8900 electron probe microanalyzer. The sheet resistance and the volume resistivity at room temperature was calculated by the three-probe method (Advantest TR8652 electrometer) using Ag electrodes, according to JIS C2141. The three-point bending test was carried out according to the JIS R 1601 using samples of 3×4×40 mm.

The densities of Y-TZP-*x* wt.%ZnO sintered at 1250–1350 °C are shown in Fig. 1. The densities of the TZP-*x* wt.%ZnO samples significantly increased at the sintering temperatures of 1250–1300 °C. The magnitude of the increases decreased at 1300–1350 °C, but the densities were constant above 1350 °C. Therefore, the densification is estimated to be completed near 1350 °C. On the other hand, the samples were deformed by sintering above 1400 °C. Based on the XRF results, the amount of Zn in the samples sintered at 1350 °C in air significantly decreased due to the evaporation of ZnO. However, evaporation of

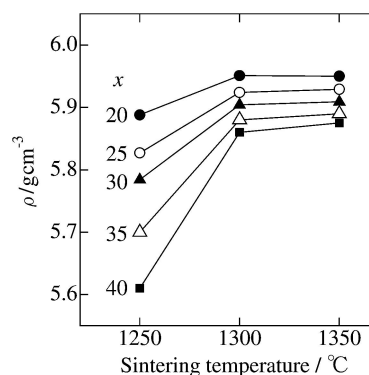


Fig. 1 Relationship between sintering temperature and density ( $\rho$ ) for TZP-*x*wt.%ZnO.

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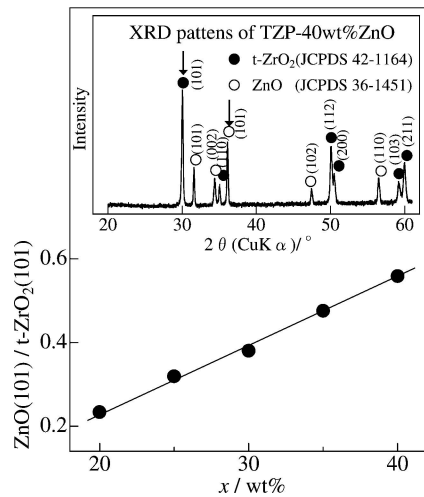


Fig. 2 Relationship between the amount of ZnO and the ratio of XRD peak (ZnO(101) / t-ZrO<sub>2</sub>(101)) for TZP-*x*wt.%ZnO.

ZnO from the samples sintered in the ZnO powders was not observed.

The XRD patterns of the TZP-40 wt.%ZnO samples are shown in Fig. 2. Only tetragonal-ZrO<sub>2</sub> (*t*-ZrO<sub>2</sub>, JCPDS No. 42–1164) and ZnO (JCPDS No. 36–1451) peaks were observed. The peaks of the impurities, which consisted of ZrO<sub>2</sub>, Y<sub>2</sub>O<sub>3</sub>, and ZnO, were not observed. Fig. 2 shows the relationship between the amount of the ZnO additive and the XRD peak ratio (ZnO(101)/*t*-ZrO<sub>2</sub>(101)) of the strongest peaks of ZnO and *t*-ZrO<sub>2</sub> on the surface in the

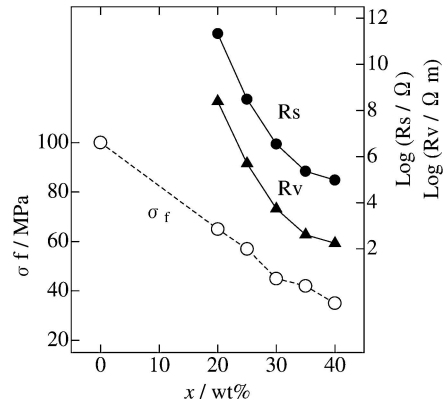


Fig. 4 Relationship between amount of ZnO and sheet resistance (*R<sub>s</sub>*), volume resistivity (*R<sub>v</sub>*) and three-point bending strength ( $\sigma_f$ ) for TZP-*x*wt.%ZnO sintered at 1350 °C.

samples. The ZnO(101)/*t*-ZrO<sub>2</sub>(101) linearly increased with an increase in the amount of ZnO. From Fig. 2, it is estimated that the ZnO does not dissolve into the TZP grains.

The SEM image of the mirror-polished surface of TZP-25 wt.%ZnO sintered at 1350 °C and the EPMA results of Zr, Y, and Zn are shown in Fig. 3. The Zn elements were observed only at the grain boundary of the TZP grains and the presence of elemental Zn was not observed in the TZP grains. This result is in good agreement with the above XRD results.

Fig. 4 shows the sheet resistance (*R<sub>s</sub>*) and the volume resistivity (*R<sub>v</sub>*) of TZP-*x* wt.%ZnO (*x*=20–40) sintered

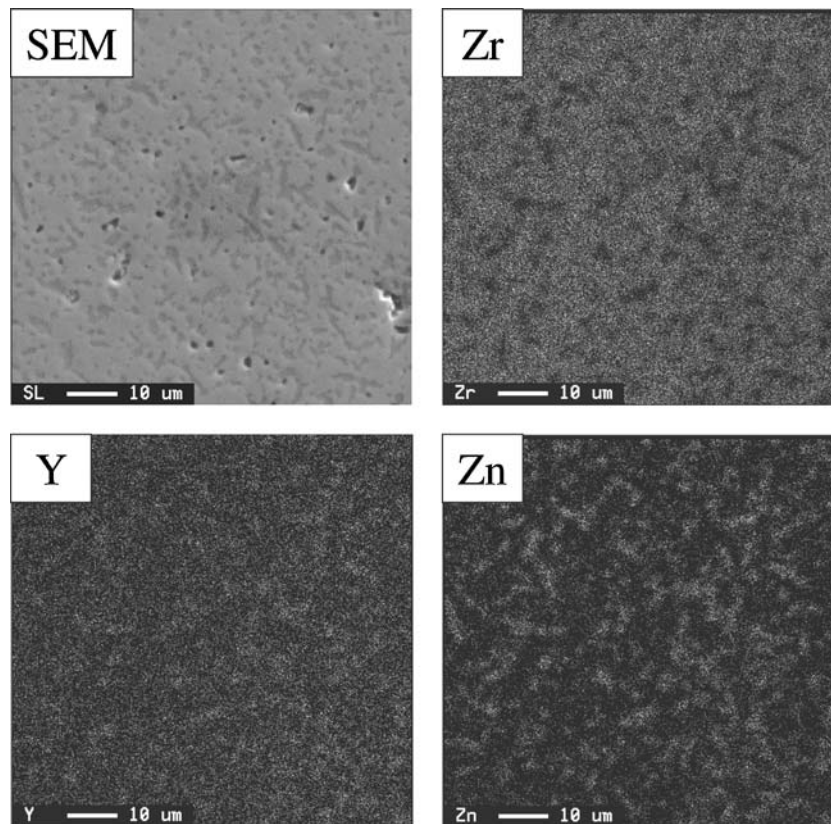


Fig. 3 EPMA results for the mirror-polished surface of TZP-25wt.%ZnO sintered at 1350 °C.

at 1350 °C. It was seen that both the  $R_s$  and  $R_v$  linearly decreased with an increase in the amount of ZnO, i.e., the conduction increased. The results of the three-point bending test for TZP- $x$  wt.%ZnO sintered at 1350 °C are shown in Fig. 4. It was found that the three-point bending strength ( $\sigma_f$ ) monotonically decreased with an increase in the amount of ZnO, and the  $\sigma_f$  value of TZP-40 wt.%ZnO (40 MPa) was less than half that of TZP-0 wt.%ZnO (100 MPa). In order to remove the static electricity, which is generated during the grinding process, the sheet resistance ( $R_s$ ) and the volume resistivity ( $R_v$ ) should be below  $10^8 \Omega$  and  $10^6 \Omega\text{m}$ , respectively. It is necessary to add more than 25 wt.%ZnO, and then the  $\sigma_f$  value of TZP-25 wt.%ZnO is 58 MPa.

TZP ( $\text{Y}_2\text{O}_3$ -doped tetragonal zirconia polycrystals,  $\text{ZrO}_2$ -2.6 mol% $\text{Y}_2\text{O}_3$ )- $x$  wt.%ZnO ( $x=20$ – $40$ ) were fabricated by sintering at 1250–1350 °C and then their microstructure, electrical resistance, and mechanical properties were investigated. These results are summarized as follows:

1. The identification of TZP- $x$  wt.%ZnO was completed at around 1350 °C.
2. ZnO did not evaporate from TZP- $x$  wt.%ZnO when sintering in the ZnO powder was carried out.
3. According to the XRD and EPMA results of TZP- $x$  wt.%ZnO, it was observed that compounds except for

TZP and ZnO were not formed and the solid solution of ZnO into TZP was not formed.

4. Although the conduction of TZP- $x$  °Cwt.%ZnO increased with an increase in the amount of ZnO, their mechanical properties significantly decreased.

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