Mechanical Characterizations of Boron Oxide Doped Yttria-stabilized Tetragonal Zirconia Electrolyte for High-temperature Solid Oxide Fuel Cell Operated

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Abstract—The aim of this work is to estimate the effect of doping boron oxide to yttria-stabilized tetragonal zirconia (B$_2$O$_3$-Y-TZP) as electrolyte for solid oxide fuel cell operated at high temperature. Nanoindentation has been performed to investigate mechanical properties of doping and pure electrolyte, whereas scanning electron microscopy has been used for morphology studies of the sintered specimens, and X-ray diffraction used for identifying phase and microstructure of electrolyte. The crystallite size of B$_2$O$_3$ doped Y-TZP and Y-TZP estimated to be 137 nm and 895 nm, respectively. The grain size of B$_2$O$_3$ doped Y-TZP and Y-TZP was estimated to be 426 nm and 1225 nm, respectively. B$_2$O$_3$ doped Y-TZP specimens exhibited elastic modulus (E) 115E+15 Pa with yield stress t (N/m$^2$) as much as 327.198 MPa, hardness as much as 948.623 kg/mm$^2$, and fracture strength as much as 3.421 MPa. Mechanical properties of doping and pure electrolyte, whereas scanning electron microscopy has been used for morphology studies of the sintered specimens, and X-ray diffraction used for identifying phase and microstructure of electrolyte. The crystallite size of B$_2$O$_3$ doped Y-TZP and Y-TZP estimated to be 137 nm and 895 nm, respectively. The grain size of B$_2$O$_3$ doped Y-TZP and Y-TZP was estimated to be 426 nm and 1225 nm, respectively. B$_2$O$_3$ doped Y-TZP specimens exhibited elastic modulus (E) 115E+15 Pa with yield stress t (N/m$^2$) as much as 327.198 MPa, hardness as much as 948.623 kg/mm$^2$, and fracture strength as much as 3.421 MPa.

Index Terms—Boron oxide High-temperature Solid oxide fuel cell operated, Mechanical properties, Nanoindentation, Yttria-stabilized tetragonal zirconia.

I. INTRODUCTION

Nanoindentation is recognized as a technique to characterize the mechanical properties of materials at very small scales or ultralow applied load indentation [1]. Y$_2$O$_3$-stabilized zirconia is well known for its high hardness, toughness, and strength [2]. Previous experimental results show that boron oxide (B$_2$O$_3$) facilitated phase transformation from cubic to monoclinic phase [3]. In the current work, sintered 2 mol% B$_2$O$_3$ doped Y-TZP pellets have been manufactured and its mechanical properties have been estimated by nanoindentation examination with a diamond cube-corner indenter.

II. EXPERIMENTAL PART

About 3 mol% TZP nanopowder supplied by Hongwu International Group Ltd., China, B$_2$O$_3$ and stearic acid supplied by Merck used as raw materials. The X-ray diffraction (XRD) and scanning electron microscopy (SEM) of raw materials analyzed to determine their phases and particle size.

The XRD pattern of raw materials and sintered specimens was taken using Philips analytical XRD type PW1930 with cobalt $\lambda_{co}$ = 1.78901 Å radiation tube operating at 40 kV and 30 mA. The particle size determined by SEM TESCAN Vega III Czech Republic used 5 KV to get the image in Fig. 1. Doped specimens prepared by mixing 2 mol% B$_2$O$_3$ in 99.987 purity with Y-TZP in Spex 6000 Mixer/Miller with zirconia jars and zirconia balls with different sizes in diameter range from 10 to 18 mm, respectively. The mixtures were compacted by cold pressing at 27.50 MPa in stainless steel die 20 mm in diameter and 0.6 mm thick. Green specimens sintered in air using a Retsch box furnace at 1923°C. To make sure that specimens undergo slow heating and to avoid thermal stress during sintering the heating rate kept at 2°C/min. The heating profile depicted in Fig. 2. The specimens kept for 1 h at 673°C to make sure of removed binder and kept for 1 h at 1100°C and finally sintered at 1923°C for 180 min as shown in Fig. 2. The morphology of specimens examined by SEM Cambridge with 10.0X resolution after polishing and 15 min thermal etching at 1673°C and sputter coating with Au. XRD used to identify the phase, crystal structure, and crystallite size of sintered specimen. The mechanical properties of sintered specimens estimated by nanoindentation tester type Triboscope system; model Hysitron at room temperature carried out with International Standards Organization (ISO) 14577 with a cube-corner indenter with average radius of curvature <50 nm. The tip of the testing instrument was calibrated by Oliver-Pharr method (ISO 14577) [5,6]. The procedure performed done with applied indenter tip with increasing normal load.
on the surface of the tester specimen. When the penetration depth of tip indenter reached a preset maximum value, the normal load will be gradually reduce until partial or complete relaxation occurs [7]. In the current work, the $P_{\text{max}}$ load ranges from 908.8 to 984.5 $\mu$N, which applied at fixed rate of about 196.9 $\mu$N/S. The nanomechanical properties of the B$_2$O$_3$ doped Y-TPZ such as reduced elastic modulus and hardness, evaluated from the load-displacement nanoindentation data using the widely accepted Oliver and Pharr method [8,9]. The young modulus calculated using eq. (1):

$$\frac{1}{E_r} = \frac{1-v_i^2}{E_i} + \frac{1-v_r^2}{E_r}$$

Where, $E_r$ is reduced elastic modulus, $v$ is Poisson ratio for the endurance material, and $E_i$ and $v_i$ are the elastic modulus and Poisson ratio of the indenter, respectively. The hardness was evaluated from eq. (2):

$$H = \frac{P_{\text{max}}}{A}$$

Where, $A$: Contact area at that load, $P_{\text{max}}$: Maximum load, and the stiffness ($S$) was estimated from eq. (3) [10]:

$$E_r = \frac{\sqrt{v_i} S}{\frac{\sqrt{A}}{2}}$$

158

Fig. 1. Scanning electron microscopy of yttria-stabilized tetragonal zirconia powder.

Fig. 4. X-ray diffraction pattern of yttria-stabilized tetragonal zirconia powders.

Fig. 2. Heating profile for sintering pellets

Fig. 5. X-ray diffraction pattern of HBO2 powders.

Fig. 3. Particle size analysis of boron oxide.

Fig. 6. X-ray diffraction date for sintered yttria-stabilized tetragonal zirconia.

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III. Results and Discussion

Fig. 3 shows the particle size of B₂O₃, while in Fig. 1, the particle size of Y-TZP can be seen. In Fig. 4, XRD pattern of Y-TZP powders is shown. In addition to Y-TZP phase, a small amount of ZrO₂ impurity phases is also present. Fig. 5 shows the XRD pattern of as received B₂O₃ powders which exhibit HBO₃ phase. This could be as a result of humidity of the powder during delivery for the XRD analysis.

Williamson-Hall analysis showed that the peak broadening is mostly due to the crystallite size [11]. Based on this analysis, the crystallite size of Y-TZP was estimated to be around 137 nm.

\[ B \times \cos(\theta) = \frac{K \times \lambda}{\text{Size}} + 4 \times \text{Strain} \times \sin(\theta) \]  

(4)

In Figs. 8 and 9, SEM micrographs of sintered Y-TPZ and B₂O₃ to yttria-stabilized tetragonal zirconia (B₂O₃-Y-TZP) were shown. It can be noticed that the doped Y-TZP shows grain growth in comparison to pure Y-TPZ due to the effect of 2% mol B₂O₃. The average grain size of sintered Y-TPZ is about 426 nm, while the B₂O₃ doped Y-TZP is about 1225 nm.

The elasticity modulus of Y-TPZ and B₂O₃-Y-TPZ can be calculated using eq. (1) in load-displacement curve for both Figs. 10 and 11 as listed in Table I.
From Table I, it can be observed that $B_2O_3$ caused reduction in elastic modulus, hardness, and yield stress, while resulted in improvement in stiffness fracture strength.

IV. Conclusion

The influence of $B_2O_3$ content on the densification, tetragonal phase stability, young modulus, hardness, and fracture toughness was investigated using nanoindentation technique. Morphology of the sintered specimens was obtained through SEM, whereas the phases of both mixtures and sintered doping Y-TZP specimens were characterized by XRD.

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REFERENCES


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<table>
<thead>
<tr>
<th>Specimen code</th>
<th>Elastic modulus (E) (Pa)</th>
<th>Hardness (H) (kg/mm$^2$)</th>
<th>Yield stress $\sigma$ (N/m$^2$)</th>
<th>Fracture strength (MPa.M$^{1/2}$)</th>
<th>Crystal size (nm)</th>
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<tr>
<td>Y-TZP</td>
<td>759E+15</td>
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<td>2823.656</td>
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<tr>
<td>$B_2O_3$-Y-TZP</td>
<td>115E+15</td>
<td>948.623</td>
<td>327.198</td>
<td>3.421</td>
<td>895</td>
</tr>
</tbody>
</table>

$B_2O_3$-Y-TZP: Boron oxide to yttria-stabilized tetragonal zirconia