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Improvements in microstructural and mechanical properties of ZrO_2 ceramics after addition of BaO

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Abstract

The effects of the addition of BaO on the sinterability, phase balance, microstructure, and mechanical properties of 8 mol% yttria-stabilized cubic zirconia (8YSZ) were investigated using scanning electron microscopy, X-ray diffraction (XRD) analyses, and micro-hardness testing. The 8YSZ powder was doped with 0–15 wt% BaO using a colloidal process. The undoped and BaO-doped 8YSZ specimens were sintered at 1550 °C for 1 h. The XRD analyses results showed that the specimens doped with up to 1 wt% BaO did not exhibit BaO-related peaks, indicating that BaO was completely solubilized in the 8YSZ matrix. However, when more than 1 wt% BaO was added, $BaZrO_3$-related peaks appeared, suggesting that the overdoped BaO did not dissolve in the 8YSZ matrix but formed a secondary phase of $BaZrO_3$ at high temperatures. Grain size measurements showed that the grain size of 8YSZ decreased with an increase in the amount of BaO added. The decrease in the grain size was owing to the fact that the grains of $BaZrO_3$, which precipitated at the grain boundaries and grain junctions of 8YSZ, increased the grain boundary cohesive resistance because of the pinning effect. This resulted in a decrease in the grain boundary mobility, and an increase in the grain boundary energy. Furthermore, while the addition of BaO to 8YSZ caused a slight decrease in the hardness of 8YSZ, the fracture toughness of 8YSZ increased from 1.64 MPa $m^{1/2}$ to 2.08 MPa $m^{1/2}$, owing to the resulting decrease in the grain size.

Keywords: 8 mol% yttria-stabilized cubic zirconia; BaO; $BaZrO_3$; Fracture toughness

1. Introduction

ZrO_2 exhibits monoclinic, tetragonal, and cubic crystal structures, depending on the temperature and amount of stabilizer used. Further, 8 mol% yttria-stabilized cubic zirconia (8YSZ), which has a fluorite-like structure, exhibits high oxygen-ion conductivity and chemical stability over a wide range of temperatures and oxygen partial pressures. Therefore, 8YSZ is used widely in oxygen sensors and heat barriers and as an electrolyte in solid oxide fuel cells (SOFCs) [1–3]. Yttria ions (+3) replace zirconia ions (+4) in the ZrO_2 crystal structure, and oxygen lattice vacancies are formed to create pole neutrality. The oxygen ions, which are activated at high temperatures, are transported by means of these vacancies. As a result, the material exhibits ionic conductivity [4–6].

8YSZ, which has a high oxygen-ion conductivity, undergoes grain growth at approximately 1000 °C, the temperature at SOFCs work most efficiently [7]. As a result, it loses its mechanical strength. Therefore, the electrolytes in the SOFCs have to be replaced frequently. This, in turn, makes generating energy more difficult and increases the cost. In order to overcome these problems, various metal oxides and chemical compounds are being explored for use as dopants for 8YSZ [8]. For these reasons, it is essential to improve the mechanical properties of 8YSZ, which is used as a solid electrolyte in SOFCs. A number of studies have been reported on the ionic

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conductivity and mechanical properties of 8YSZ ceramics. Carvalho et al. have investigated the solidification and oxide ionic conductivity of ZrO_2–$BaZrO_3$ composites. They reported that when yttrium is used as a dopant, it remains predominantly in the fluorite-ZrO_2 lattice, owing to the high thermodynamic stability of $BaZrO_3$ and that oxide vacancies or electron–hole pairs are the dominant charge carriers [9]. Angle et al. have investigated the thermal shock resistance, mechanical properties, and ionic conductivity of 8YSZ doped with small amounts of alumina or mullite to form cubic 8YSZ for use in fuel cells and oxygen sensors. They found that doping with small amounts of alumina or mullite increases the hardness, fracture toughness and room-temperature flexural strength of 8YSZ, owing to a decrease in the grain size and crack deflection through second-phase blocking. They have also reported that the specific grain boundary conductivity of alumina-doped 8YSZ was almost the same as that of undoped 8YSZ. On the other hand, they showed that the grain size of 8YSZ decreased with the addition of alumina, owing to pinning effect of the alumina nanoparticles in the 8YSZ. Furthermore, this caused a decrease in the total ionic conductivity of 8YSZ, owing to the blocking of the grain boundaries by the alumina nanoparticles. They also reported that the addition of 10–20 vol% mullite reduced the grain boundary conductivity of 8YSZ significantly and increased the activation energy for ionic conduction, even though the grain size of the mullite-containing samples was larger than that of the alumina-containing ones. This was because of the formation of a non-conductive intergranular silicate phase that wet and segregated along the grain boundaries [10]. The mechanical properties of 1–15 wt% La_2O_3-doped 8YSZ were investigated using the Vickers hardness test by Aktas et al. They reported that the fracture toughness of 8YSZ increased with an increase in the amount of La_2O_3 doped, because of crack deflection by the existing secondary pyrochloric $La_2Zr_2O_7$ phase at the grain boundaries [11].

The aim of this study was to improve the mechanical properties of 8YSZ, which is used in SOFCs as an electrolyte, by adding BaO to it. The effects of the addition of different amounts of BaO on the sinterability, phase balance, microstructure, and mechanical properties of cubic zirconia (8YSZ) were investigated.

2. Experimental procedure

The raw materials used in this study were 8YSZ (Tosoh, Japan) and BaO (Taimei Japan) powders. The average particle sizes of the powders were 0.3 μm and 0.4 μm, respectively. The chemical compositions of the powders are listed in Table 1.

The specimens for the microstructural and mechanical investigations were prepared by means of colloidal processing. Doping was carried out in a plastic container by mechanically mixing the 8YSZ and BaO powders (BaO content of up to 15 wt%) in ethanol using zirconia balls. The mechanical mixing was done in a “speks” type mixer at 200 rpm for 12 h. The prepared slurries were left to dry for 24 h in air by simply removing the lid of the mixer. The resultant agglomerated powders, which exhibited moderately high hardnesses, were then ball milled for 10 min to ensure homogeneity and to break up any agglomerates. The thus-obtained powders were sieved through a 60 μm screen and then pressed at 200 MPa in a single-axis die with a radius of 10 mm and height of 4 mm. The inner surface of the steel die was cleaned after each dry-pressing process, and stearic acid was applied on the side walls of the die as a lubricant.

Sintering was performed in a box-type furnace under normal atmospheric conditions. The pressed pellets were first subjected to a presintering treatment at 1000 °C and then sintered at temperatures of 1200–1550 °C for 1 h at heating and cooling rates of 5 °C/min. The densities of sintered specimens with perfect shapes were calculated using the rule of mixtures and from the weight/volume ratio, which was determined by the geometrical method. The relative densities were estimated based on the assumption that the sintered samples were of the cubic phase and that the theoretical densities of 8YSZ and BaO are 5.68 and 5.72 g/cm^3, respectively.

After the sintering process, the surfaces of the specimens were ground and polished by conventional metallographic techniques, and the specimens were thermally etched by being heated in a furnace at 50 °C below the sintering temperature for 1 h. The microstructures of the sintered specimens were investigated using scanning electron microscopy (SEM) (JEOL Lv 6060). The grain sizes were measured using the mean linear intercept method. The average grain sizes of the specimens were determined using the following equation:

$$D = \frac{L_i}{N_i \cdot M} \quad (1)$$

where L_i is the length of the line, N_i is the number of grain-boundary intercepts, and M is the magnification corresponding to the photomicrograph of the specimen.

X-ray diffraction (XRD) analyses (Shimadzu XRD 6000, CuK_α, $\lambda = 1.5405$ Å) were performed to determine the changes induced in the crystal structure and lattice parameters of 8YSZ after the addition of various amounts of BaO. The specimens

Table 1
Chemical compositions of the powders used in this study as the starting materials.

Powder	wt%									
	ZrO_2	Y_2O_3	BaO	La_2O_3	TiO_2	FeO_2	Na_2O_3	CaO	Al_2O_3	SiO_2
8YSZ	85.9	13.6	–	–	0.1	0.003	0.01	0.02	0.25	0.1
BaO	–	–	99.9	–	–	0.02	–	–	0.01	0.07