

# Fabrication of Porous Yttria-Stabilized Zirconias Controlled by Additives

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## ABSTRACT

To fabricate a thick, porous yttria-stabilized zirconia without cracking and warping, a method for the simultaneous control of the porosity and shrinkage was designed. As a pore former, a potato starch was used. For the control of shrinkage, the oxidation of Al metal particles was used. For the sintering of the above powder mixtures, a partial sintering technique was used at 1300°C for 10 min in air. Upon adding the additives, high open porosity above 53% and a low shrinkage level were obtained. As a result, cracking and warping of the sintered body were deterred. This outcome most likely resulted from the compensation of sintering shrinkage due to the volume expansion caused by oxidation of the Al metal particles during heat-treatment.

**Key words :** Porosity, Shrinkage, Warping, Starch, Zirconia

## 1. Introduction

Of late, porous ceramics have been intensively developed owing to favorable qualities such as their high temperature stability, catalytic activity, corrosion or erosion resistance, and light weight.<sup>1)</sup> Among these ceramics, porous yttria-stabilized zirconia (YSZ) ceramics are becoming increasingly important due to their potential for various applications in membranes for filtration processes, thermal insulators and sensors. Especially, the characteristics of YSZ with significant oxygen ionic conductivity at high temperatures has led to extensive investigation into uses as electrolytes for a solid oxide fuel cell (SOFC), oxygen separation membranes, oxygen sensors and other electrochemical devices.<sup>2-4)</sup>

There are several methods for fabricating porous ceramics, according to the applications. The most common techniques are the partial sintering of initially porous powder compacts or the sintering of powder mixtures which undergo solid state reactions that lead to pore formations. In this approach, a porous network is formed by the spaces between the necked particles, and it is difficult to achieve porosities greater than ~50%. These porosities can be increased through the use of various pore formers.<sup>1,3,5,6)</sup> Currently, various starch particles as a fugitive material have been used for the fabrication of porous ceramics.<sup>7-10)</sup> The main advantages of this approach are its simplicity, low-cost, environmental friendliness, easy burn-out, the ready availability of starch particles of various morphologies and sizes (2-170  $\mu\text{m}$ ), and the fact that it can be applied to any material that can be dispersed in an aqueous suspension.<sup>1,10)</sup>

Using this technique, however, irregular shrinkage can be produced in the matrix material,<sup>9,10)</sup> which causes warping and cracking in the sintered body.

Several years ago, a low-shrinkage process based on the oxidation of aluminum powder was presented. This process is known as the reaction-bonded aluminum oxide (RBAO) process. In the method, it is possible to fabricate low-shrinkage alumina because the volume expansion by the oxidation of aluminum powder during heat-treatment can compensate for the sintering shrinkage in an Al-Al<sub>2</sub>O<sub>3</sub> powder compact.<sup>11,12)</sup> In the case of thick Al-Al<sub>2</sub>O<sub>3</sub> compacts, however, Al tends to remain in the bulk, as the oxidation of Al by conventional heating proceeds inward from the surface.<sup>11)</sup> The problem can be mitigated somewhat using a slow heating process.

In the present investigation, therefore, to prevent warping and cracking in a thick, sintered porous body, the simultaneous control of the porosity and shrinkage was the aim. As a pore former, potato starch (20 wt%) was used. To control shrinkage, the oxidation of Al powder (5 wt%) and slow heating were also used. As a result, a porous YSZ without cracking or warping was obtained.

## 2. Experimental Procedure

Zirconia powder (TZ-8Y, Tosoh, Tokyo, Japan), Al powder (Kojundo Chemical Co., Japan), and potato starch (Kanto Chemicals Co., Japan) were used as starting materials for the fabrication of porous yttria-stabilized zirconia. For porosity control alone, mixed powders (100 g) of the zirconia (80 g) and starch (20 g: 20 wt%) were ball-milled at 150 rpm for 24 h. For both porosity and shrinkage control, mixed powders (50 g) of the zirconia (37.5 g), Al (2.5 g: 5 wt%) and starch (10 g: 20 wt%) were ball-milled at 150 rpm for 24 h. Approximately 5 g of the mixed powder was uniaxially

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pressed into a rectangular bar under 0.5 MPa. A CIP process was omitted. Burnout of the starch as a pore former was performed with slow heating to 400°C. Following the burnout, oxidation of the Al particles was carried out via very slow heating to 500°C. Finally, sintering was carried out through conventional heating in a MoSi<sub>2</sub> resistance box furnace. All samples were sintered at 1300°C for 10 min in air. Heating and cooling rate in the final sintering process were 5°C/min, respectively.

The bulk densities of the sintered samples were measured using the Archimedes method with distilled water as an immersion medium. A value of 5.90 g/cm<sup>3</sup> was used as the theoretical density of YSZ. The pore size distribution was characterized by mercury porosimetry (Thermo Finnigan, Pascal 140+440). For this measurement, the pressure was increased to 200 MPa. The flexural strength was determined using a three-point bending method. Test bars with a dimension of 6.0×6.5×25 mm were polished to 1200 grit SiC paper and the long edges were chamfered. The bars were then annealed at 600°C for 30 min to remove machining stresses. The strength measurement was carried out by universal test machine (Hounsfield, H10KS) with a 20 mm span at room temperature. The crosshead speed was 5 mm/min. Unnotched bars were used for the strength measurement. All the data of strength were obtained from the samples with failures originating from the center of test bar. All strength data were also determined using an average of five specimens. The photo of sintered samples was taken using commercial digital camera. The microstructures of the samples were analyzed on the fracture surface by SEM (Jeol, JSM-6300, Japan) after being coated with gold.

### 3. Results and Discussion

#### 3.1. Porosity Control

Porous materials are defined as solids containing pores. Pores are classified into two types: open pores connected to the outside of the material, and closed pores isolated from the outside of the material. For most industrial applications of porous materials, open pores are required. Closed porous materials are used mainly for sonic and thermal insulators or low-specific-gravity structural components.<sup>13)</sup> For porous materials, thus, several pore-related factors, such as the porosity, pore type, pore size, pore size distribution, and specific surface area, are important.

Table 1 shows the bulk density measured using the Archimedes method. The porosity of the partially sintered

**Table 1.** Density and Porosity Measured by the Archimedes Method

Specimen	Relative density (%)	Total porosity (%)	Open porosity (%)
TZ-8Y (pure)	68	32	32
TZ-8Y+Starch (20)	47	53	53
TZ-8Y+St.+Al (5)	39	61	61

YSZ was 32%. The addition of starch increased the porosity of partially sintered YSZ, as expected. A high open porosity of 53% was obtained, owing to the starch addition. The additional porosity appeared to have resulted from the site that remained at the original starch site after the burn-out of the starch. The addition of Al also increased the sample porosity, as seen in Table 1, as a volume expansion of 28% was evidently caused by the oxidation of Al particles during sintering.<sup>12)</sup> All samples had only open pores. In general, it is known to be difficult to obtain a porosity level above 50% by partial sintering.<sup>1,3)</sup> Regarding this result, however, it is believed that this can be achieved by adding additives for use as pore formers.

Table 2 shows the specific surface area, open porosity and average pore diameter measured by mercury porosimetry. For the open porosity, slightly different values between the two methods were obtained. The difference, however, is likely to be insignificant and was most likely a measurement problem. Therefore, the open porosities measured by the Archimedes method seem to be supported by the data obtained from the mercury porosimetry measurement. In terms of the pore size, the whole samples were macroporous (>50 nm). The average pore diameter and specific surface area increased with increasing porosity or with adding additives.

#### 3.2. Shrinkage Control

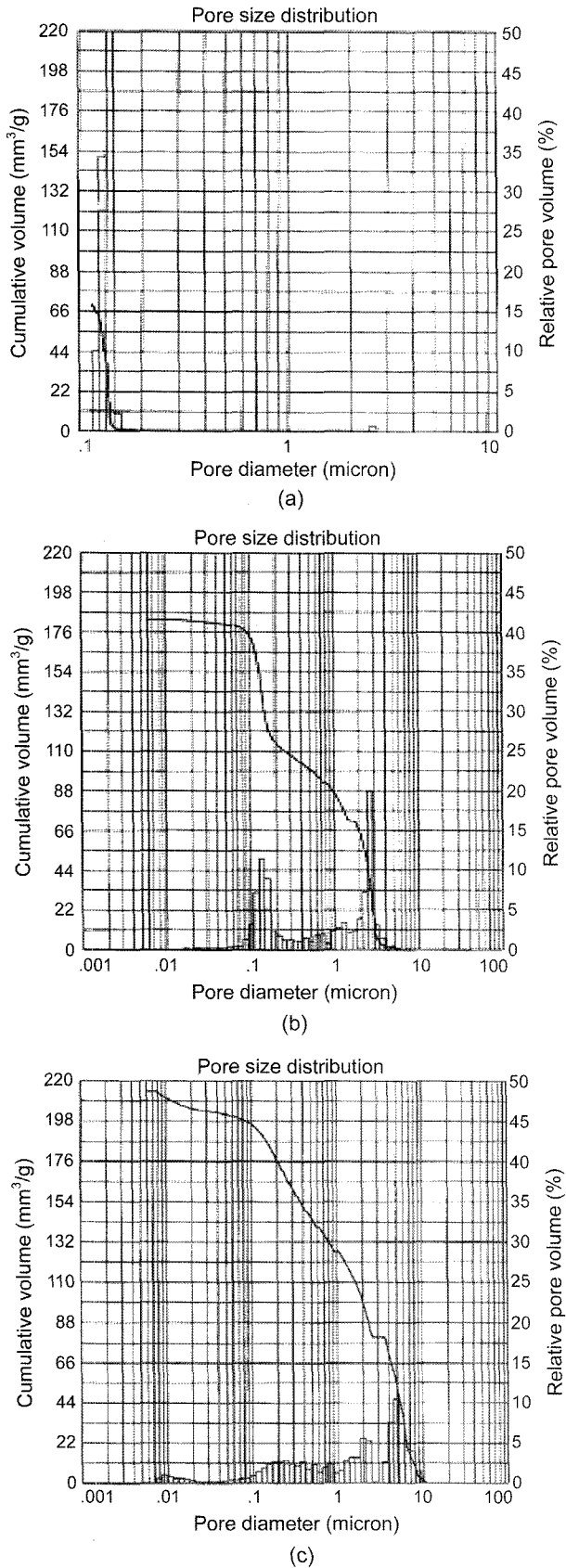
Table 3 shows the shrinkage, porosity, and flexural strength of samples. The shrinkage was determined by measuring the dimensions of the samples. Upon adding the additives, the shrinkage of the sintered samples reduced, and thereby the porosity increased. The decrease in the shrinkage with the addition of starch is inconsiderable, compared to the effect of the starch on the porosity. In reaction-bonded aluminum oxide ceramics, the volume expansion associated with the oxidation of Al metal partially compensates for the sintering shrinkage.<sup>12)</sup> The oxidation of Al metal would thus be able to be used for a low-shrinkage process even in other oxide ceramics. As seen in Table 3, the

**Table 2.** Specific Surface Area, Open Porosity and Pore Size Measured by Mercury Porosimetry

Specimen	Specific surface area (m <sup>2</sup> /g)	Open porosity (%)	Average pore diameter (μm)
TZ-8Y (pure)	2.08	31	0.14
TZ-8Y+Starch (20)	2.88	53	2.66
TZ-8Y+St.+Al (5)	5.27	55	4.84

**Table 3.** Shrinkage, Total Porosity and Flexural Strength

Specimen	Volumetric shrinkage (%)	Total porosity (%)	Flexural strength (MPa)
TZ-8Y (pure)	46	32	68 (±9.9)
TZ-8Y+Starch (20)	41	53	13 (±0.3)
TZ-8Y+St.+Al (5)	21	61	6 (±0.2)

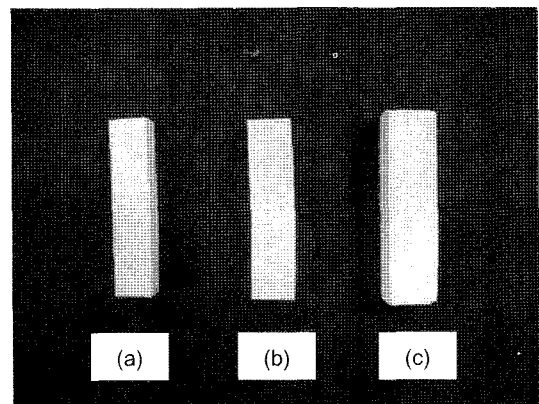


**Fig. 1.** Pore size distributions obtained from an YSZ; (a) pure, (b) with starch alone, and (c) with both starch and Al metal powder, sintered at 1300°C for 10 min in air.

shrinkage of YSZ with Al was nearly two times smaller than that of YSZ without Al. Therefore, the volume expansion associated with oxidation of Al is likely to highly contribute to the decrement of the shrinkage by sintering.

The pore size distribution is an important property, because most porous materials do not have uniform pores. As a rule, the large pores mainly contribute to a high level of porosity, while the small pores mainly offer a large surface area. A narrow pore size distribution, i.e. a uniform pore size is required for many applications such as filters and bioreactor beds.<sup>13</sup> In contrast, both a high level of porosity and a large surface area are required for the application of molten aluminum filter.<sup>14</sup> Fig. 1 shows pore size distributions of the above three samples measured by mercury porosimetry. With adding additives, the pore size distribution was changed. The result is closely correlated to the pore size and specific surface area of the sintered samples, as shown in Table 2. In terms of the cumulative small pore volume (Fig. 1), the number of small pores below 0.1  $\mu\text{m}$  increased with adding additives, resulting in the large specific surface area. The pore size also increased with the addition of the additives, leading to the higher level of porosity. Considering the shape of the pore size distribution curve, a uniform size distribution was shown in YSZ without additives (Fig. 1(a)), while a broad and irregular size distribution appeared in YSZ with starch (Fig. 1(b)). Upon adding additional Al metal particles, the degree of irregularity in the size distribution decreased (Fig. 1(c)). It is thus believed that the irregularity in the size distribution occurred due to an irregular shrinkage with adding starch particles and that the volume expansion caused by the oxidation of Al during sintering relaxed the irregular shrinkage caused by the starch particles.

As aforesaid, using a starch particle as a fugitive material for the fabrication of porous ceramics, irregular shrinkage can be produced in a matrix material,<sup>9,10</sup> which causes warping and cracking in a thick, sintered body. Fig. 2 shows a photo of the as-sintered samples. Both YSZ samples with/



**Fig. 2.** Effect of an additive as a pore former on the warping and cracking of the thick, porous YSZ; (a) pure, (b) with starch alone, and (c) with both starch and Al metal powder, sintered at 1300°C for 10 min in air.

without starch slightly revealed cracking and warping, while YSZ sample with both starch and Al particles did not show any cracking and warping. The result is therefore thought of as the effect of the compensation of sintering shrinkage by the volume expansion caused by an oxidation of Al particles during sintering.

### 3.3. Flexural Strength

On the whole, introducing porosity into materials results in decreased density, which degrades the mechanical strength of the materials. For nearly all applications of porous materials, a high mechanical strength is desirable along with high porosity.<sup>13)</sup> With adding additives, the flexural strength of YSZ decreased, while its porosity increased, as shown in Table 3. Given that the mechanical strength for porous materials depends on many parameters, including the grain size, grain bond area, pore size distribution and porosity,<sup>13)</sup> it is difficult to simply estimate the fracture strength of porous materials. Considering the present results, however, higher level of porosity and a broad pore size distribution seem to be responsible for the degradation of the fracture strength of YSZ with additives. Although the addition of Al particles degraded the flexural strength of porous YSZ, it is noteworthy that sintering shrinkage compensation by a volume expansion caused by oxidation of Al prevents cracking and warping of porous YSZ.

### 3.4. Microstructure

Fig. 3 shows the microstructures of partially sintered YSZ

with/without additives. Typically, long-chain open pore structures and neck growths between  $ZrO_2$  particles are shown in Fig. 3(a) and (b). With adding the starch particles, the microstructure was composed of a continuous  $ZrO_2$  matrix with large spherical-shaped pores, corresponding to the original starch particles in shape and size (Fig. 4), as shown in Fig. 3(c) and (d). Small pore volume and its size were also different between samples with/without starch particles, as seen in Fig. 1. With adding the Al particles, a typical change in the microstructures between Fig. 3(c) and (d) was not likely to occur at a glance. Based on the pore size distribution (Fig. 1), however, the small pore volume increased.

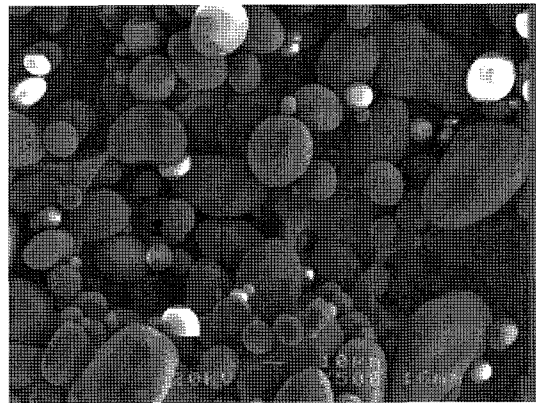


Fig. 4. SEM micrograph of potato starch particles used as a pore former. Note that the particles have nearly spherical shapes.

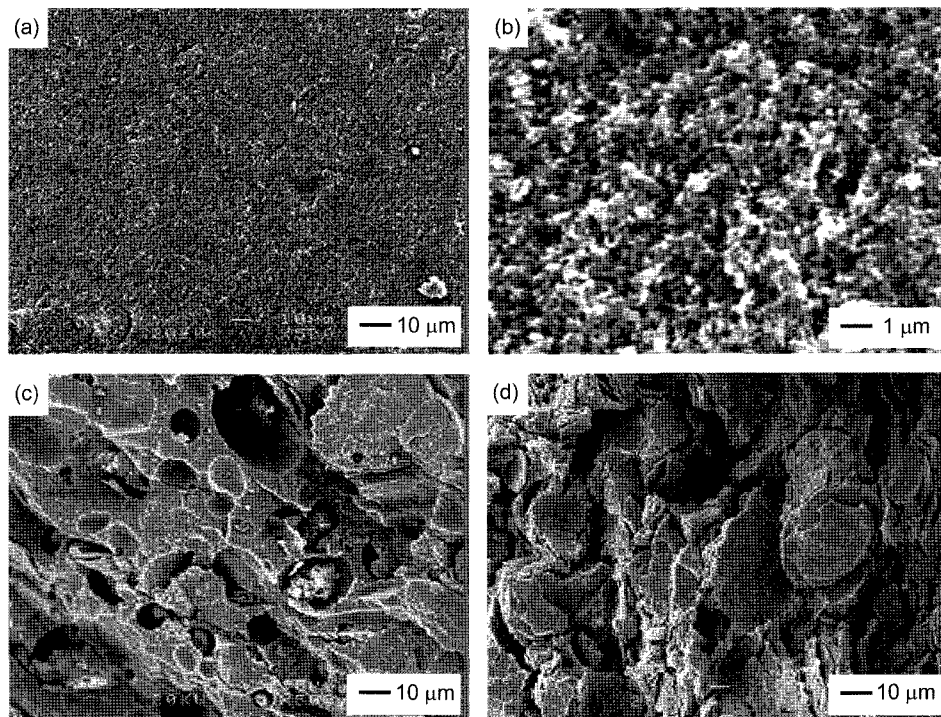


Fig. 3. SEM microstructures showing the fractured surface of a porous YSZ; (a) pure under low magnification, (b) pure under high magnification, (c) with starch alone, and (d) with both starch and Al metal powder, sintered at 1300°C for 10 min in air.

Generally, in the case of a partially sintered body with high porosity, stress concentrations occur at necks between matrix particles. If there is a remarkably large pore in a porous material, it also leads to a stress concentration.<sup>13)</sup> In the present investigation, all samples were partially sintered at the same temperature for the same time. The decrease in the fracture strength with adding starch particles, therefore, appears to have resulted primarily from the stress concentrations around the large pores formed by starch particles.

#### 4. Conclusions

In order to fabricate porous YSZ ceramics without warping and cracking in a thick, sintered body, simultaneous control of porosity and shrinkage was carried out. For the purpose, potato starch was used as a pore former and Al metal particles were added to an YSZ powder along with starch particles. With adding these additives, a higher level of porosity and a larger specific surface area were obtained, while a lower flexural strength was obtained. The decrement of the fracture strength appears to mainly result from the stress concentrations around the large pores produced by the starch particles. In particular, the addition of Al metal particles hindered the irregular shrinkage by starch particles and prevented warping and cracking in the sintered, porous body as well. This can be attributed to the volume expansion caused by the oxidation of Al, compensating for the sintering shrinkage.

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