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Optimization of high-pressure sintering of transparent zirconia with nano-sized grains

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ABSTRACT

We show an optimum condition for high-pressure (400 MPa) spark-plasma-sintering (SPS) of transparent cubic (8 mol% yttria) zirconia. The obtained samples represent higher in-line transmittance compared to the existing SPSed zirconias, and maintain nano-grained structures. The role of oxygen defects in transparency of the zirconia is discussed.

1. Introduction

Transparent ceramics with high refractive index have attracted great interest in optical applications. According to the data of single crystal [1], titania, perovskite type oxides [$MTiO_3$ (M = Ca, Sr and Ba)] and cubic zirconia (8–12 mol% Y_2O_3–ZrO_2) possess a refractive index higher than 2.0. As one of the most versatile engineering ceramics, polycrystalline yttria-stabilized zirconia (YSZ) is highly expected to serve as a multifunctional material in optical applications provided it can combine transparency (high refractive index) with excellent mechanical/thermal properties [2–12].

For high transparency, it is necessary to achieve a full density or extremely low porosity because residual pores significantly scatter light and deteriorate light transmission. For yttria-stabilized zirconia, it was pointed out that even for the size of residual pores smaller than 50 nm, the porosity should not exceed 100 ppm for obtaining high transparency [8]. Therefore, hot isostatic pressing (HIP) is conventionally employed to remove the residual pores and to attain highly transparent YSZ [7–9]. Tsukuma et al. [8], for example, succeeded in the fabrication of transparent zirconia polycrystals by hot isostatic pressing at 1650 °C under a pressure of 150 MPa. Peuchert et al. [9] sintered transparent cubic ZrO_2 using hot isostatic pressing at 1750 °C under a pressure of 196 MPa. Owing to the high sintering temperatures in HIP, however, those transparent zirconia samples are characterized by large grain sizes (>20 μm) [7,8]. Since grain coarsening results in the reduction of the mechanical properties, which is also very important for engineering applications, fine-grained materials are preferable to coarse-grained ones.

Spark plasma sintering (SPS) is an alternative and effective method to obtain fully dense and nano-grained transparent ceramics at relatively low temperatures within a short time [10–27]. Recently, some research groups have proved the feasibility of producing transparent polycrystalline YSZ with nano-sized grains using SPS [10–12]: Garay and co-workers [10,11] used a two-step load procedure with a traditional die setup, and Anselmi-Tamburini et al. [12] employed a high pressure SPS with a modified die setup. Although the work of Anselmi-Tamburini et al. [12] demonstrated that the application of high pressure during SPS could remarkably enhance the transparency of YSZ, they did not provide an optimization condition for achieving transparent zirconia. The present study, therefore, was performed for sintering nano-grained and transparent YSZ by optimizing the processing conditions during high-pressure SPS, such as sintering temperature, heating rate and duration. Consequently, the resultant nano-grained cubic YSZ exhibited higher in-line transmittance compared to the existing SPS zirconias.

2. Experimental procedure

Commercially available 8 mol% Y_2O_3–ZrO_2 powders (TZ-8Y, Tosoh Corporation, Tokyo, Japan) were used as a starting material. All sintering experiments were conducted under the fixed pressure of 400 MPa. In order to achieve such high pressure, we employed a modified die composed of an external graphite die and an internal, smaller graphite die. The inner diameter of the internal die was 10 mm. Two

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protective discs of silicon carbide were placed at the end of each silicon carbide plunger. The powders were heated to desired temperatures in vacuum (10^{-3} Torr) using a spark plasma sintering machine (SPS-1050, SPS Syntex Inc., Kawasaki, Japan).

Heating was conducted using a sequence consisting of 12 DC pulses (40.8 ms) with the interval of 6.8 ms. The sintering temperatures were measured by an optical pyrometer focused on the non-through hole (1 mm diameter and 2 mm depth) in the graphite die. Different sintering temperatures (1050–1200 °C), heating rates (5–50 °C/min) and duration (2–180 min) were tested during sintering. For easy release after sintering, a graphite paper with the thickness of 0.2 mm was inserted between the powder and the die/punch. After sintering, we obtained the sample disks with a diameter of 10 mm and a thickness of 1 mm.

The as-prepared sample disks were mirror-polished on both sides using diamond slurry. The in-line transmittance was measured using the spectrophotometer (SolidSpec-3700DUV, JEOL) by inserting a slit (3 mm diameter) in front of the detector in order to allow detection of only the specularly transmitted portion of the incident light beam with a 5 mm diameter. The distance between the sample and the detector is about 55 cm. The in-line transmittance was also measured for the samples annealed at 900 °C for 4 h in air in order to characterize the effect of annealing on the transmission.

The fractured surface of the specimen was observed using a scanning electron microscope (SEM) (JSM-6500, JEOL).

3. Results

The evolution of the in-line transmittance, which increases from 1050 °C to 1100 °C and then decreases at 1200 °C, demonstrates that the sintering temperature plays a critical role in transparency (Fig. 1). The optimum sintering temperature is considered to be 1100 °C, which is quite lower compared to the temperatures in HIP [7–9]. Particularly noteworthy is that annealing can greatly enhance the transmittance. This result highly implies some type of defects is produced in YSZ during the SPS process, and the increase of transmittance may come from the removal of these defects through annealing.

It is recently found that heating rate during SPS can significantly affect the transmittance for some transparent ceramics, such as $MgAl_2O_4$ [20,21] and Al_2O_3 [25,26]. This phenomenon is very likely related to the defects formed during SPS [20,21,25,26]. Fig. 2 represents the in-line transmittance of YSZ sintered at different heating rate, and the corresponding values after annealing. It can be seen that these zirconias present quite similar transparency, so the heating rate during high-pressure SPS does not affect the in-line transmittance. In the work of Quach et al. [28], they showed under the similar experimental conditions, i.e., high pressure (500 MPa) SPS, heating rate did not affect the final density of cubic zirconia, which agreed well with our results. After annealing, there is still a high degree of resemblance of in-line transmittance although the specimen sintered at a heating rate of 10 °C/min shows somewhat better transparency. Furthermore, we observed that extremely high heating rate (for example, 200 °C/min) would result in intensive internal stresses, which easily cracked samples and resulted in inhomogeneous transmittance [9]. For the present zirconia, a heating rate of 10 °C/min yields the highest transmittance. It should be noted that because heating rate and heating time are coupled, a fast heating rate corresponds to a short heating time. Since the heating time plays an important role in the densification, for better understanding the effect of heating rate, a hold should be added for the high heating rate samples to match the entire heating time. The detailed experiments are planned in our lab, and the results will be represented in the further papers.

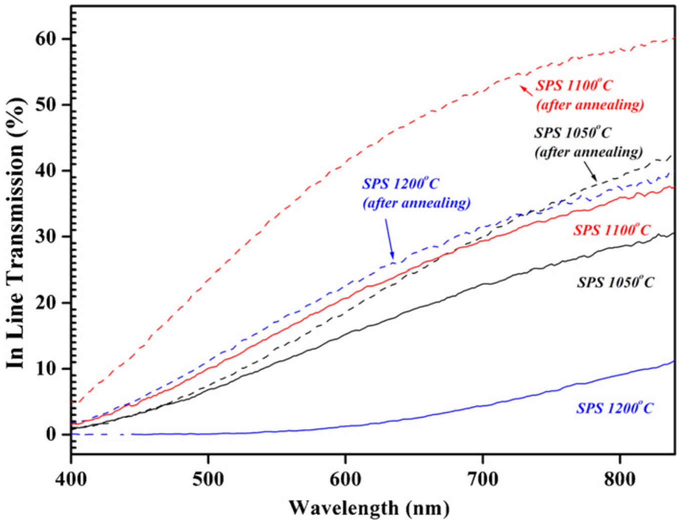

Fig. 1. In-line transmittance dependent on spark-plasma-sintering temperature. During SPS, the holding time at the desired temperatures was 10 min, and the heating rate was 10 °C/min. The in-line transmittance after annealing at 900 °C for 4 h in air was also presented. For comparison, the data were normalized for a thickness of 1 mm. The normalization was conducted using the relation $T_1 = (1-R)[T_2/(1-R)]^{d2/d1}$, where T is the in-line transmittance, R is the reflection loss of two surfaces of the sample, and d is the sample thickness.

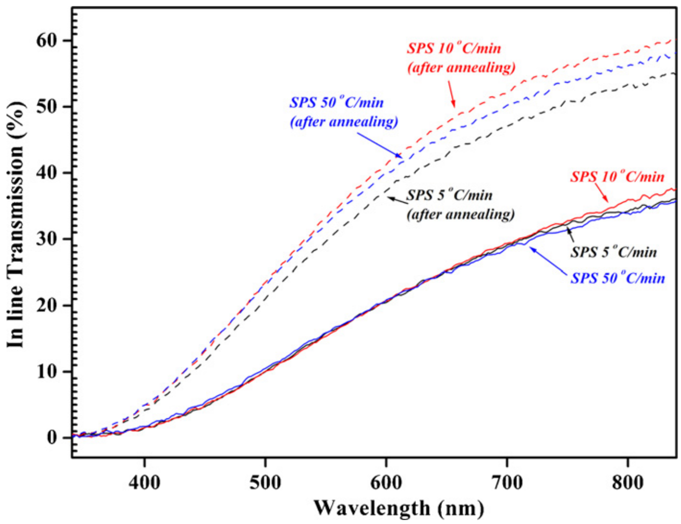

Fig. 2. In-line transmittance of YSZ sintered at different heating rate (solid line) and the corresponding value after annealing (dashed line). The sintering was conducted at 1100 °C for 10 min, and the data were normalized for a thickness of 1 mm.

We also investigated the effect of holding time on the in-line transmittance of YSZ. Fig. 3 is the in-line transmittance spectra of YSZ sintered at 1100 °C for different duration and the corresponding values after annealing. For better clarity, the in-line transmittance evaluated at wavelength of 600 nm is shown in Fig. 4 as a function of holding time. It can be seen from Figs. 3 and 4 that the in-line transmittance shows a decreasing tendency with an increase in the holding time. Nevertheless, after annealing, the increased transmittance is comparable to each other and insensitive to the holding time within the range of 2–20 min. Annealing also can improve the transparency of the sample with prolonged sintering duration (3 h), but the increment is quite limited, as shown in Fig. 4. The in-line transmittance of this zirconia with 3 h holding is much lower than other samples with shorter holding time. So sintering time of 2–20 min is enough to reach dense samples with good optical transparency. Based on above results (Figs. 1–4), under the pressure of 400 MPa, spark plasma sintering at 1100 °C for 2–20 min with the heating rate of 10 °C/min can be regarded as the optimum condition for attaining a transparent YSZ.

A typical zirconia sample obtained under the optimum condition is shown in Fig. 5. This specimen exhibits a yellowish brown appearance. Compared to the existing SPS plus annealing YSZ [10–12], the current zirconia shows higher transparency: the in-line transmittance reaches 42% at the wavelength of 600 nm, which

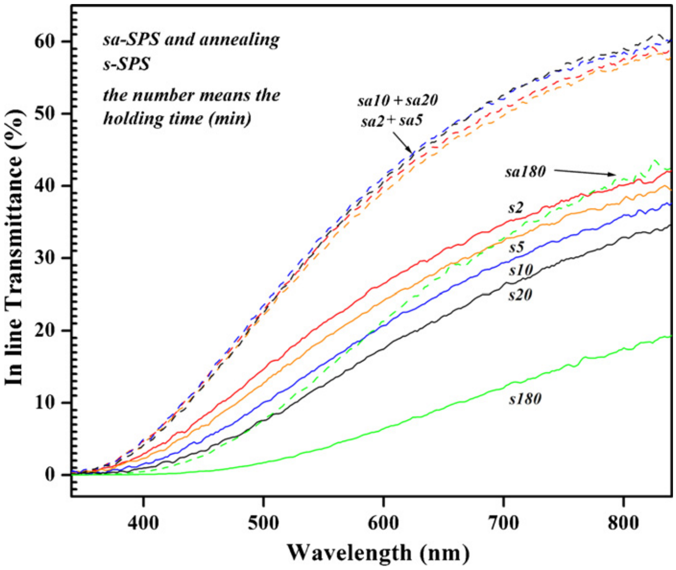

Fig. 3. In-line transmittance spectra of YSZ sintered at 1100 °C for different holding time (solid line) and the corresponding values after annealing (dashed line). The samples were heated at 10 °C/min and the data were normalized for a thickness of 1 mm.

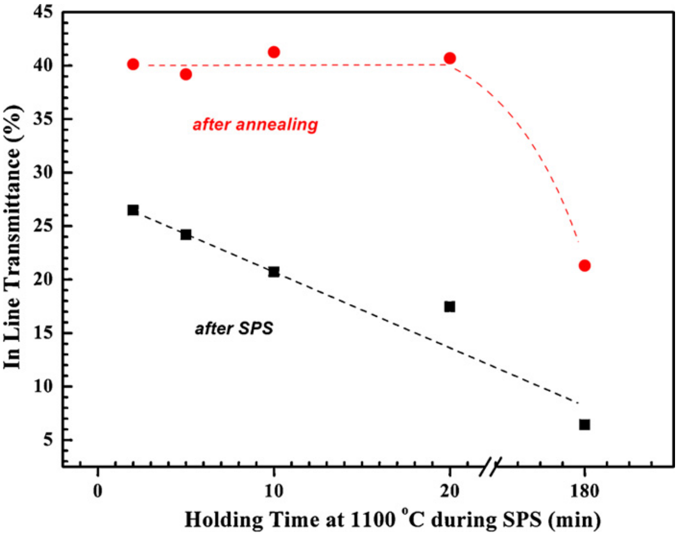

Fig. 4. In-line transmittance measured at wavelength of 600 nm and plotted as a function of holding time at 1100 °C.

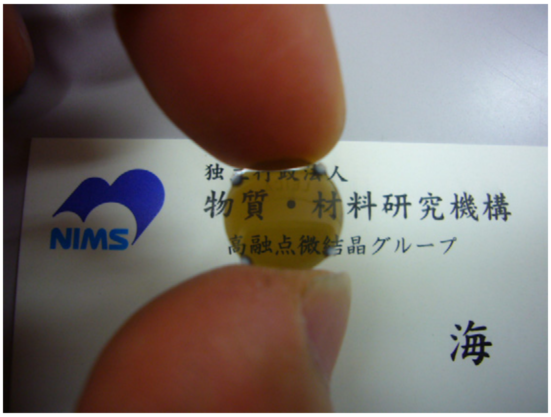

Fig. 5. Photograph of yttria stabilized zirconia disk produced by SPS at 1100 °C for 10 min under the pressure of 400 MPa. The sample was placed 30 mm above the text. The thickness of the sample is about 1 mm.

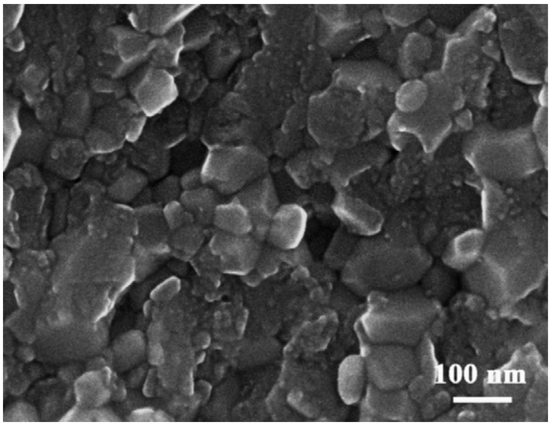

Fig. 6. SEM image of a fracture surface of yttria stabilized zirconia disks densified by SPS at 1100 °C for 10 min under the pressure of 400 MPa.

is 76% of the theoretical limit (Fig. 1). Relatively, the in-line transmittance approached 32% at the wavelength of 600 nm in the work of Anselmi-Tamburini et al. [12], and Garay and co-workers [10,11] reported the total forward transmittance with the value of 42% at the wavelength of 633 nm.

Fig. 6 is a typical SEM image of a fracture surface of YSZ. The resultant sample maintains a nano-grained structure. The grain growth is significantly suppressed due to the low-temperature sintering.

4. Discussion

When a light passes transparent/translucent material, besides transmission, incident light is reflected, scattered and absorbed by a solid. Scattering by residual pores is a primary reason for the low transparency or opacity of most ceramics. Due to the residual pores, the transmittance of the current polycrystalline zirconia is lower than that of single crystal YSZ [8].

However, most phenomena of the current work are related to another factor: absorption by defects. The yellowish brown or blackish appearance (Fig. 4) is a typical phenomenon in oxide ceramics, such as Al_2O_3 [19], spinel [20,29,30] and ZrO_2 [10–12], when they are produced using SPS. The colorizing may be related to the existence of carbon impurities [27,29–31] and/or point defects [11,12,19,32]. The presence of carbon impurities is usually attributed to the contamination of the raw powders and/or graphite dies during the SPS processing [27,29–31]. In our experiments, however, this consideration can be excluded because carbon impurities will induce the formation of pores during annealing in air and then deteriorate the transparency [31], conflicting with our increasing transparency after annealing (Figs. 1–4). Therefore, the yellowish brown appearance very likely originates from the defects produced within the YSZ samples during SPS. It is well known that under a reducing environment, oxygen vacancies are the typical defects formed in YSZ [10–12]. In our experiments, vacuum and the graphite die at high temperatures create a highly reducing environment, which can contribute to the formation of oxygen vacancies [10–12]. Another evidence for the formation of oxygen vacancies comes from the annealing tests: the in-line transmittance can be significantly improved by annealing at the appropriate condition (900 °C for 4 h in air in the present study). So it is very reasonably speculated that this phenomenon is due to the removal of the oxygen vacancies since annealing in air can diffuse oxygen back into the samples. Compared to residual pores, the oxygen defects are very small, so they only contribute to the absorption of the incident light. The decreased transparency of the zirconia samples with the prolonged durations (Figs. 3 and 4) is attributed to the increasing absorption effect with an increase in the oxygen defects.

Although grain boundaries are also a kind of defects, their contribution to the light loss is very weak. From experiments and theory analysis [11,12,20–22], the absorption loss at grain boundaries can be neglected for yttria stabilized zirconia. Also, due to a symmetric cubic crystal structure, yttria stabilized zirconia does not exhibit birefringent scattering at grain boundaries [11,12].

During annealing, the coalescence of the oxygen vacancies will produce pores to decrease the transmittance, particularly for large vacancy concentrations [32]. For the sample with the holding time of 3 h, annealing in air only can remove some defects because too high concentration of oxygen vacancies may have been generated during the SPS process, and the remaining oxygen vacancies eventually develop to form pores. For annealing of the zirconia with high defect concentration, therefore, the decrement of transparency due to pore formation is more significant than the increment of transparency due to defect annihilation. Consequently, the zirconia sintered for 3 h represents low transparency even after annealing, as shown in Figs. 3 and 4. For the similar reason, sintering at too high temperature (1200 °C) is negative to transparency (Fig. 1) because of the generation of more oxygen defects. On the other hand, samples sintered at too low temperature (1050 °C) cannot achieve full densification, and high porosity decreases the transmittance (Fig. 1).

5. Conclusion

A novel optically transparent yttria-stabilized zirconia was produced using a high-pressure spark plasma sintering technique. Under the pressure of 400 MPa, fabrication at 1100 °C for 2–20 min with the heating rate of 10 °C/min could be regarded as the optimum condition. The resultant specimen showed higher in-line transmittance compared to the existing SPS samples, and maintained nanoscale grain size. The decreasing transmittance of the zirconia with holding time and temperature was very likely due to the formation of oxygen vacancies during sintering under a reduced environment. Post-sinter annealing in air could remove these oxygen vacancies, and then improve the transmission.

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