FULL PAPER

Microstructural and spectroscopic analysis in non-uniform $\text{Y}_2\text{O}_3$ ceramics fabricated by spark plasma sintering

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In $\text{Y}_2\text{O}_3$ ceramics densified at 1000 °C by spark plasma sintering (SPS), non-uniform sintering behavior of grains and pores occurred for a heating rate of 20 °C/min. The sintered $\text{Y}_2\text{O}_3$ was translucent at the periphery but white and opaque at the center. According to microstructural analysis, the non-uniform sintering was caused by rapid grain growth and pore coarsening at the center. Under complicated electric and magnetic fields during SPS, an assumption of the movement of defects toward the center enables to explain the microstructural non-uniformity. For the non-uniform sintering behavior, spectroscopic analysis was used to investigate the introduced impurities (C, H, O) and by-products (carbonates). In the spectroscopic analysis, the peaks located at 2555, 2950, and 3560 cm$^{-1}$ (O–H stretching band of H$_2$O) were weakly detected for low heating rates but clearly detected for high heating rates. This is because H$_2$O adsorbed to the initial $\text{Y}_2\text{O}_3$ powder was not sufficiently removed and was trapped during rapid densification at high heating rates. Due to the carbon-rich environment during SPS, carbonate was formed by the reaction of carbon with –OH. Most carbons were detected as a C–O peak, indicating that a reaction of carbon with –OH occurred.

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1. Introduction

Among the ceramic materials that can be applied to laser applications, single-crystalline $\text{Y}_2\text{O}_3$ has been researched worldwide.$^{1-4}$ It has suitable properties for laser applications (high thermal conductivity, chemical stability, and low phonon energy) and has the advantage of being easily doped with rare-earth ions. However, polycrystalline ceramic laser technology is emerging that may overcome the technology and cost problems caused by single crystal.$^{5-8}$ Compared with single-crystal ceramics, the merit of polycrystalline transparent ceramics is that they can be fabricated in larger volumes to obtain high-power lasers, and even a complicated shape can be applied to various types of gain media.

The fabrication of polycrystalline transparent ceramics with high oscillation efficiency requires ceramic processes that include appropriately synthesized powder and sintering technologies with advanced sinterability. Recently, vacuum sintering, hot isostatic pressing, spark plasma sintering (SPS), and flash sintering (FS) have been developed to remove residual pores effectively.$^{9-12}$ As compared with conventional sintering, the SPS technology that combines uniaxial pressure with heating by an electrical current has a great potential for fabricating functional laser ceramics.$^1$ Due to the direct heating of the mold and powder by electric current, full densification at low temperatures and fine microstructures can be obtained.$^{13-20}$ Rapid densification and fine microstructures, which are advantages of SPS, improve the mechanical and optical properties in transparent ceramics.

However, in attempting to maximize the advantages of SPS, some problems in the SPS process have been observed when sintering at lower temperatures and higher heating rates. This problem has been reported by various groups investigating transparent ceramics with SPS, and the appearance of a non-uniformly sintered body has been observed. For example, in the Al$_2$O$_3$ and $\text{Y}_2\text{O}_3$ fabricated by SPS, non-uniform sintering behavior was reported at various temperatures (1000–1200 °C).$^{18-20}$ However, as for the phenomena causing the appearance of the sintered body to be different, the reasons and processes claimed by each group are different. For the first time, Grasso et al.$^{18}$ reported that the opaque portion of the center caused by the residual pores affected the formation of non-uniform sintering behavior. They proposed that the main factor for the residual pores is the temperature gradient caused by the low thermal conductivity of the starting powder (alumina) and the high heating rate of the SPS process. Next, Ratzker et al.$^{19,20}$ proposed that because a stress gradient exists in powder compacts due to a significantly high loaded pres-

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sure (500 MPa), the difference in grain growth between the center and the periphery was a major factor in the non-uniform sintering behavior. According to our previous work, when \( \text{Y}_2\text{O}_3 \) was sintered at a high heating rate of 1000 °C, a white and opaque portion formed at the center, and a change in appearance was observed. Scanning electron microscopy (SEM) observation revealed that the white and opaque portion in the center area had noticeably increased grain sizes and intergranular pores. It was confirmed that non-uniform sintering is related to differences in microstructures.

In the various ceramic materials produced by SPS, a significant difference in the appearance of the sintered body according to the heating rates and loaded pressure has been reported. In a previous work, the non-uniform sintering behavior of SPSed \( \text{Y}_2\text{O}_3 \) was induced by non-uniform coarsening between the center and the periphery caused by the movement of defects and increased grain boundary mobility. However, the reasons claimed by the various groups were inappropriate to explain the non-uniform sintering behavior in the present work. First, it was considered that the temperature gradient that occurred within a 10 mm diameter would be insufficient to induce the significant difference in grain size between the center and the periphery obtained in the present work. Therefore, the main mechanism (Grasso et al.\(^{18}\)) was excluded because it was inappropriate for interpreting the non-uniform sintering behavior in the present work. Since the non-uniform sintering behavior occurred even though a conventional loaded pressure (80 MPa) was applied, the proposed interpretation (Ratzker et al.\(^{19,20}\)) that the stress gradient resulting from significantly high loaded pressure (500 MPa) was the main factor is inappropriate. In a previous work, demonstration of the assumption was also insufficient. Therefore, through additional microstructural and spectroscopy analysis, the present work aimed to interpret and demonstrate of the non-uniform sintering behavior in detail.

2. Experimental procedure

2.1 SPS

The starting powder was commercial \( \text{Y}_2\text{O}_3 \) powder (99.99 %, UU-type; Shin-Etsu Rare Earth, Japan) with a manufacturer-determined average particle size of 0.1–0.3 µm. The as-received \( \text{Y}_2\text{O}_3 \) powder was densified with an SPS machine to obtain dense and translucent \( \text{Y}_2\text{O}_3 \) under a vacuum atmosphere of 10 Pa. The powder (0.6 g per sintered \( \text{Y}_2\text{O}_3 \)) was directly sintered in a vacuum without any pretreatment, using a graphite mold with an inner diameter of 10 mm. The sintering temperature (1000 °C) and pressure (80 MPa) were fixed, and the heating rates and holding times were varied. Up to 600 °C, the mold was heated at a rate of 50 °C/min, and then at 5 and 20 °C/min. After reaching the sintering temperature (1000 °C), the sintered \( \text{Y}_2\text{O}_3 \) was cooled after holding for 2, 5, 20, and 60 min. In the previous work, the optical appearance of the sintered \( \text{Y}_2\text{O}_3 \) varied with the heating rate and holding time, so it was set as a variable. Heating was conducted using direct current (DC) pulses without zero current, and the temperature was measured using a thermocouple in the non-through hole of the mold. The mold was covered with carbon felt to reduce heat dissipation. For transmission electron microscopy (TEM) analysis of each region in the non-uniformly sintered \( \text{Y}_2\text{O}_3 \), a thicker sintered \( \text{Y}_2\text{O}_3 \) was fabricated in addition. \( \text{Y}_2\text{O}_3 \) powder (1.5 g) was sintered at 1000 °C with a heating rate of 5 °C/min under 80 MPa, and then cooled after holding for 20 min.

2.2 Characterization

Both sides of the sintered \( \text{Y}_2\text{O}_3 \) were mirror polished, and Fourier-transform infrared (FT-IR) spectra were measured in a range of 1000–4000 cm\(^{-1}\) using an FT-IR spectrometer (Nicolet 6700 FT-IR Spectrometer, Thermo Fisher Scientific, USA). In order to analyze the cross section, the sintered \( \text{Y}_2\text{O}_3 \) was cut into two pieces at intervals of 2 mm. The two pieces were mirror polished, and one of the pieces was thermally etched at 850 °C for 2 h in the air for SEM analysis. The polished surfaces were observed via SEM (SU-8000, Hitachi, Japan). The porosity and pore distribution were evaluated from area fractions of pores on SEM photographs. In order to analyze the carbon and undefined materials, Raman spectra were collected by a laser Raman spectrometer (NRS-4100, JASCO, Japan). For a cross-sectional TEM observation, thin foil specimens of the sintered \( \text{Y}_2\text{O}_3 \) were prepared using a focused ion beam milling method. The cross-sectional observation was performed using TEM equipment (TITAN TM X-FEG, Thermo Fisher Scientific, USA) operated at an acceleration voltage of 300 kV.

3. Results and discussion

3.1 Appearance and microstructure of each sintered \( \text{Y}_2\text{O}_3 \)

The appearances of sintered \( \text{Y}_2\text{O}_3 \) at various heating rates (5 and 20 °C/min) and holding times (0, 5, 20, and 60 min) are shown in Fig. 1. There are various factors such as heating rates, holding times, mold materials, that affect various ceramic materials sintered with SPS technology. In the case of \( \text{Al}_2\text{O}_3 \) and \( \text{MgAl}_2\text{O}_4 \) sintered by SPS, a significant difference has been reported in the appearance of the sintered body according to the heating rate.\(^{22,23}\) In addition, in SPS of \( \text{La}_2\text{O}_3 \), a discussion on the difference between the loaded pressures and the heating rates has

![Fig. 1. Optical appearances of sintered \( \text{Y}_2\text{O}_3 \) at various heating rates (5 and 20 °C/min) and holding times (0, 5, 20, and 60 min).](image-url)
been reported. In the present work, the heating rates and holding times, which had a great influence, were set as main variables. At a low heating rate (5 °C/min), uniform sintering behavior was observed with every holding time. On the other hand, at a high heating rate (20 °C/min), sintered Y2O3, which was held for more than 5 min at 1000 °C, had a non-uniform appearance and microstructure. In the non-uniformly sintered Y2O3, a white and opaque portion was created at the center, while the periphery of the sintered Y2O3 was translucent. Irrespective of each sintering behavior, the center region sintered at both heating rates was sufficiently densified at the early stage of holding (0 min), as shown in Fig. 1. Non-uniform sintering behavior then occurred with longer holding times in Y2O3 sintered at a high heating rate (20 °C/min). It can be interpreted that the sintering of Y2O3 proceeded sufficiently for both heating rates, although some other factors produce opaque parts during sintering at 20 °C/min.

The main goal of the present work was to analyze the difference in microstructure according to the heating rate. The two specimens sintered for 20 min at different heating rates (5 and 20 °C/min) were suitable as candidates because there were obvious differences. The cross section of the sintered Y2O3 was divided into four-point parts with a distance between each point of 1.5 mm from the center “1” to the periphery “4,” as shown in the schematic diagram of Fig. 2(a). The Y2O3 sintered at a heating rate of 20 °C/min in Fig. 2(c) shows different pore sizes and porosities depending on the region (center or periphery). The periphery (c-4) shows a smaller pore size and lower porosity, while the opposite tendency is observed at the center (c-1). In addition, the pore size was clearly observed to decrease (125 → 47 nm), as well as the porosity decrease (11.3 → 1.4 %) from the center (c-1) to the periphery (c-4). Notably, no difference in pore distribution was observed in uniformly sintered Y2O3 with a heating rate of 5 °C/min in Fig. 2(b). This result sufficiently supports the interpretation of the previous work, which explained that defects moved to the center, and subsequently, mass transfer to the periphery occurred.

For non-uniformly sintered Y2O3, a sintered Y2O3 approximately 1.8 mm thicker than previous specimens (about 0.8 mm) was fabricated in order to analyze the detailed microstructures. The sintered Y2O3 with a thickness of 0.8 mm was so small that it was not possible to prepare specimen pieces for each region. Therefore, Y2O3, which was thickly sintered to a thickness of 1.8 mm, was fabricated to prepare specimen pieces for each region. The additional sintered Y2O3 was consolidated by heating to 1000 °C at 5 °C/min for 20 min. SEM and optical images of the microstructure for each region prior to detailed microstructural analysis (TEM) are summarized in Fig. 3. As shown in Fig. 3(a), a white and opaque portion in the center and translucent portions on the periphery were observed. The microstructures at the center and periphery are shown in Figs. 3(b) and 3(c), respectively. From the above results, in the case of sintered Y2O3 with a thickness of 0.8 mm, uniformly sintered Y2O3 was obtained by sintering at a low heating rate (5 °C/min). However, in the case of thicker sintered Y2O3 (1.8 mm), non-uniform sintering behavior occurred despite the heating rate being the same (5 °C/min). With the same sintering conditions, the sintering behavior varies depending on the thickness of the sintered body or the amount of powder. The SPS proceeds by passing an electric current corresponding to the heating rate. When the heating rate is high or the amount of loaded powder is large, a larger amount of electric current and a higher current density are applied to the SPS process. Since rapid densification is accompanied by high current density during the SPS process, despite the sintering conditions being same, the sintered Y2O3 with a thickness of 1.8 mm was sintered non-uniformly at a low heating rate (5 °C/min). A summary of the microstructural properties is as follows: the average grain size, ; the porosity, ; and the average pore size, were, respectively, d = 432 nm, f = 14.4 %, and p = 104 nm at the center region, while they were d = 163 nm, f = 2.8 %, and p = 29 nm in the periphery region. The difference in porosity between the center (f = 14.4 %) and the periphery (f = 2.8 %) was considered to be driven by the effect of mass.
transfer from the center to the periphery and the diffusion of defects to the center, as mentioned in the previous work.\textsuperscript{21)}

In addition to the SEM analysis above, a TEM analysis was performed to investigate the more detailed microstructures of the sintered Y$_2$O$_3$. The microstructure of the center is shown in Figs. 4(a) and 4(b), and that of the periphery is shown in Figs. 4(c) and 4(d); the magnification in Figs. 4(a) and 4(c) is higher than that in Figs. 4(b) and 4(d). The TEM analysis also provided detailed information about porosity, pore size, and pore distribution. In the center region [Figs. 4(a) and 4(b)], all of the pores...
were located at grain boundary junctions (intergranular pores), and the average pore size \( p = 115 \text{ nm} \) and porosity \( f = 11.2\% \) were significantly larger than those at the periphery [Figs. 4(c) and 4(d)]. On the other hand, the pore sizes in the periphery region are 1–30 nm, and these small pores tend to be distributed within the grains. The high-magnification TEM image of the periphery for Figs. 4(c) and 4(d) shows that pores of 1–30 nm are distributed within each grain. With TEM analysis at high magnification, such intragranular pores were not observed in the center region, and intragranular pores were predominant at the periphery. This result suggests that there was noticeable coarsening in the center region but very little in the periphery region: in the center region, the grains and pores increased in size significantly due to the dramatic coarsening.

### 3.2 Interpretation and discussion of non-uniformly sintered \( \text{Y}_2\text{O}_3 \)

The mechanism for the non-uniform sintering behavior proposed in the present work differs from that of the other groups. Grasso et al.\(^{18}\) proposed that the main factor for the residual pores is the temperature gradient caused by low thermal conductivity of the starting powder (alumina) and the high heating rate of the SPS process. It was considered that the temperature gradient occurring within a 10 mm diameter would be insufficient to induce the significant difference in grain size between the center and the periphery obtained in the present work. Compared to the experiments of Ratzker et al.\(^{19,20}\) because the non-uniform sintering behavior occurred even though a conventional loaded pressure (80 MPa) was applied, the proposed interpretation that the stress gradient resulting from significantly high loaded pressure (500 MPa) was the main factor is inappropriate. In order to appropriately interpret the non-uniform sintering behavior in the present work, a modified mechanism was proposed.

Through SEM and TEM analysis, it was possible to sufficiently demonstrate the differences in microstructures related to non-uniform sintering behavior claimed in the previous work.\(^{21}\) As with the TEM image of the periphery region [Fig. 4(d)], lots of residual defects have been proven by the numerous tiny pores [yellow arrows in Fig. 4(d)] in the grain. This is because the residual defects of sintered \( \text{Y}_2\text{O}_3 \) were transformed into numerous tiny pores. When there are a lot of residual defects inside rapidly densified \( \text{Y}_2\text{O}_3 \) due to the high heating rate, more defects diffuse into the center as compared with the periphery, as claimed in the previous work.\(^{21}\) In the SPS process using an electric field, lots of defects are known to lead to an increase in grain boundary mobility. For this reason, the center region, in which the number of defects is higher than in the periphery region, has rapid grain growth and increased grain boundary mobility. Due to rapid grain growth and increased grain boundary mobility, significant coarsening was induced, and grain and pore size were increased in the center region. Finally, during the sintering process, coarsening was more dominant than densification in the center region, and unlike in the periphery region, a dramatically coarsened microstructure was created. Based on the above analysis results, it was possible to discuss the differences in the appearance of the sintered \( \text{Y}_2\text{O}_3 \). Sintering the \( \text{Y}_2\text{O}_3 \) at a high heating rate \( (20\, ^\circ\text{C/ min}) \) led to dramatic coarsening in the center as compared with the periphery. Not only did the grain size increase, but the pore size and porosity also increased significantly. That is why this dramatic coarsening occurred noticeably in the center, resulting in an opaque appearance. Consequently, non-uniform sintering behavior occurred with significant differences in the microstructure and appearance between the center and periphery.

Although the fabrication of transparent \( \text{Y}_2\text{O}_3 \) ceramics with similar SPS conditions has not yet been achieved, the possibility of preventing non-uniform sintering behavior is suggested. The carbon contamination and incidental oxygen vacancies were the major factors in accelerating matter and defect diffusion by strong electric fields in the non-uniformly sintered \( \text{Y}_2\text{O}_3 \). Therefore, the suppression of carbon contamination and incidentally occurring oxygen vacancies may prevent non-uniform sintering behavior.

### 3.3 Spectroscopic analysis

FT-IR spectra of spark plasma sintered \( \text{Y}_2\text{O}_3 \) at different heating rates \( (5 \text{ and } 20\, ^\circ\text{C/ min}) \) for 60 min showed the most obvious difference, so those are shown in Fig. 5. Among all of the spectra, two strong absorption peaks around 1500 cm\(^{-1}\) were most noticeable. Two peaks were observed irrespective of the heating rates and correspond to the C–O bond stretching vibration and bending belonging to the carbonate.\(^{25}\) For the low heating rate \( (5\, ^\circ\text{C/ min}) \), no absorption peaks were observed except for those around 1780 and 1500 cm\(^{-1}\). Both peaks correspond to the C–O bond of the carbonate. The IR transmittance graph of the low heating rate \( (5\, ^\circ\text{C/min}) \) shows the same trend as that of the typical pattern of commercial \( \text{Y}_2\text{O}_3 \).\(^{26}\) However, in the case of the high heating rate \( (20\, ^\circ\text{C/min}) \), a difference was observed as compared to the typical IR transmittance graph of \( \text{Y}_2\text{O}_3 \). The peaks located at 2555 and 2950 cm\(^{-1}\) were

![Fig. 5. FT-IR spectra of sintered \( \text{Y}_2\text{O}_3 \) at 1000 °C for 60 min at 5 °C/min (black profile) and 20 °C/min (red profile).](image)
very weakly detected at the low heating rate but clearly detected at the high heating rate. For the low heating rate, the strong absorption peak located at 3560 cm$^{-1}$ was not observed at all, but the intensity increased significantly and became apparent as the heating rate increased. This peak is the O–H stretching band of H$_2$O. The reason is that H$_2$O adsorbed to the initial Y$_2$O$_3$ powder was not sufficiently removed and was trapped inside in the process of rapid densification due to the high heating rate. Additionally, two C–O bonding peaks corresponding to the carbonate were weakly detected around 1875 and 1780 cm$^{-1}$. The peaks corresponding to the carbonate were strongly detected in the non-uniformly sintered Y$_2$O$_3$ at the high heating rate, while the peaks were indistinct in the uniformly sintered Y$_2$O$_3$ at the low heating rate. Notably, a peak around 2340 cm$^{-1}$ corresponds to CO$_2$ and was strongly detected in the non-uniformly sintered Y$_2$O$_3$. It was concluded that the SPS process, which was performed in a carbon-rich environment, inadvertently introduced carbon, and the carbon reacted with the O–H bands involved in the starting powder and was detected as the carbonate and CO$_2$.

During the SPS process, Raman spectroscopy was performed, as shown in Fig. 6, for a detailed analysis of carbon, because one can predict the introduction of carbon from a graphite punch, die, and carbon paper. A difference in peak position depending on heating rates, a critical factor influencing the evolution of the sintering behavior, was not observed; only a difference in strength was observed. The results for the low heating rate (5 °C/min), in which the intensities of the two broad bands detected in the range of 3000–3500 and 2100–2600 cm$^{-1}$ are noticeably different, are shown in Fig. 6. Among all of the Raman spectra, the same spectrum as that of the Y$_2$O$_3$ powder was detected in the peak at 2450 cm$^{-1}$ and in the range below 1150 cm$^{-1}$. In the Raman spectroscopy, no differences in the positions or existence of the peaks were observed irrespective of the heating rate, but as the holding time increased, the intensity of the wide band corresponding to O–H and C–O strains increased. In general, carbon contamination is known to occur as sintering proceeds in the SPS process. As a result, the amount of carbon contamination increases, and the reaction into the carbonate increases with the holding time.

4. Conclusions

The non-uniform microstructure of spark plasma sintered Y$_2$O$_3$ was investigated by microstructural (SEM, TEM) and spectroscopic (FT-IR, Raman spectroscopy) analysis. In the SPS process with high heating rates, the non-uniform sintering behavior of Y$_2$O$_3$ was observed and accompanied differences in the appearances and microstructures. From the center to the periphery, the pore size, porosity, and grain size significantly decreased, and it was concluded that defects and pores gathered at the center, in contrast to a uniformly sintered Y$_2$O$_3$. Due to the electric and magnetic fields in the SPS process, the defects lead to increased grain boundary mobility and coarsening. The relatively large number of defects in center region accompanied the rapid grain growth and coarsened microstructure. Consequently, during the SPS process, the coarsening was more dominant than the densification in the center and, unlike in the periphery, dramatically coarsened microstructures were induced. The carbon was unintentionally introduced by a carbon-rich environment, and it reacted with the –OH involved in the starting powder and was detected as the carbonate and CO$_2$. As the holding time increased, the intensity of the wide band corresponding to O–H and C–O strains increased. As a result, the amount of carbon contamination increased, and the reaction to the carbonate increased with the holding time.

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