Microstructure and Crystal Phase Development of Y₃O₃-Stabilized ZrO₂ Polycrystal Fabricated by the Solid Phase Mixing and Sintering Method

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The microstructure and crystal phase in 2.8 mol% yttria-stabilized zirconia polycrystals were investigated. Starting powders were prepared by wet dispersing and mixing using an agitator mill or by the liquid phase precipitation method. The composites powders were sintered at 1275–1600°C and then analyzed. Solid phase method (SPM) powders showed higher sinterability than those of the liquid phase precipitation method (LPM) powders, and high density samples consisting of fine grains could be obtained at lower sintering temperatures than from LPM powders. Unlike the LPM sample, the cubic and tetragonal phase was formed in the SPM sample at low sintering temperature, because there was the region of high and low Y³⁺ ion concentration in the material. As the sintering temperature increased, the cubic phase decreased and tetragonal phase increased by the progress of the diffusion of Y³⁺ ions. And then, Y³⁺ ions segregated at grain boundaries, and tetragonal grains containing cubic phase at grain boundary regions were formed. The thermal expansion curve for the SPM sample samples sintered at 1275°C exhibited a monoclinic to tetragonal transformation during the heating stage; however, the expansion was linear during the cooling stage, as was the case for both SPM samples sintered at higher temperatures and the LPM samples. The thermal expansion behavior of the SPM sample suggested that the monoclinic phase was essentially not present within the sample, although the transformed monoclinic phase in a surface layer by grinding stresses was exist.

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1. Introduction

Yttria-stabilized tetragonal zirconia polycrystal (Y–TZP) is a very attractive material for use in structural materials, such as mill parts, ferrules for fiber optics and so on. Y–TZP has high strength and fracture toughness, due to a stress-induced tetragonal to monoclinic phase transformation. Therefore, it is very important whether or not the metastable tetragonal phase can be stabilized at room temperature. When the Y₂O₃ distribution is inhomogeneous in ZrO₂ grains, the grain size distribution becomes inhomogeneous, and large cubic grains containing large amounts of Y₂O₃ and/or unstable tetragonal grains containing less Y₂O₃ are formed. It has been stated that tetragonal grains with a small amount of Y₂O₃ causes a tetragonal to monoclinic transformation during the cooling stage of the sintering process, and the metastable tetragonal phase can not be stabilized at room temperature. Therefore, Y–TZP powder is produced by liquid phase precipitation methods, such as the mixing of ZrO₂ powder with yttrium solution, the co-precipitation method, hydrolysis method, alkoide method, and so on, in order to homogenize yttrium distribution. Although many researchers have investigated the mechanical properties of Y–TZP, most of the samples have been prepared by liquid phase precipitation methods (LPM). In addition, the mechanical properties of ZrO₂ produced by the solid phase method have not been thoroughly investigated.

However, in industry terms, the cost of ZrO₂ powder prepared by LPM is high, which becomes an obstacle to expanding the practical application of this material.

Recently, an agitator mill with high efficiency for grinding and dispersing has stimulated progress in this area of processing. Using this type of mill, it is possible to easily and efficiently grind and disperse fine powders to make a homogeneous mixture. For this reason, the solid phase method (SPM) milling process is often applied for the powder processing of electrical materials, such as ceramic condensers, piezo ceramics, etc., which require the homogeneous mixing of many types of raw powders.

We have therefore considered that ZrO₂ powders that have been processed using the agitator mill would be likely to have better characteristics than powders prepared by LPM. If this process is applicable, it is expected that the cost of ZrO₂ powders could be reduced and this could have many advantages in the industrial field.

ZrO₂ powder prepared by LPM is stabilized by the addition of Y₂O₃ in the powder process, while that prepared by SPM is not stabilized. Consequently, the difference in the powder preparation methods will influence the sintering mechanism. In the case of ZrO₂ powder prepared by LPM, the sintering mechanism depends mainly on diffusion reactions. On the other hand, that for ZrO₂ powder prepared by SPM would depend not only on diffusion, but also on the simultaneous reaction between Y₂O₃ and ZrO₂, and the resultant stabilization behavior. Accordingly, the microstructure of the SPM powder is estimated to be different from that of the LPM powder.

For these reasons, this paper investigates the sinterability and microstructure of ZrO₂ prepared by SPM in comparison with that of Y–TZP ceramics prepared by LPM.

2. Experimental procedure

2.1 Sample preparation

ZrO₂ powders, prepared by two different methods, were used as the starting raw materials. The first method (SPM) was used to prepare powders by mixing ZrO₂ powder (>99.9%, surface area: 10 m²/g), which was manufactured by the
hydrolysis method, with Y2O3 (> 99.9%, surface area: 12 m²/g) and Al2O3 (> 99.9%, surface area: 7 m²/g) powder. The powders were mixed to adjust 2.8 mol% Y2O3 stabilized ZrO2, and 0.25 mass% Al2O3 for this 2.8 mol% Y2O3-stabilized ZrO2 using a batch type agitator mill, with 1 mm diameter Y-TZP grinding media at 50% concentration and 0.3 mass% polyacrylad (PAA) for powder weight. The surface area of zirconia after mixing was 12 m²/g. The other method (LPM) used the hydrolysis method to prepare powders containing 2.8 mol% Y2O3 and 0.25 mass% Al2O3. The surface area of the LPM powder was measured as 7 m²/g. The chemical composition of each powder is shown in Table 1.

These powders were uniaxially pressed at 20 MPa, and then cold isostatically pressed (CIP) at 100 MPa. The compact green bodies were then sintered at 1275–1600°C for 2 h in an air atmosphere.

2.2 Density and crystalline phase analysis

The density of sintered samples was measured using the Archimedes method with distilled water. Prior to the phase composition analysis using X-ray diffraction (XRD), 0.5 mm of the as-sintered sample surface was ground using a 140-grid polishing wheel and the surface were sequentially polished with 6, 3 and 1 µm diamond paste. XRD profiles were measured with a powder diffractometer system (Model RINT2200, Rigaku Corporation, Osaka) using Cu Kα radiation at 40 kV and 40 mA. Scans of 2θ were conducted between 27–33° and 72–75.5°. Monoclinic, tetragonal and cubic phase fractions within ZrO2 were calculated using the equation reported by Garvie et al.9)

2.3 Microstructure observation

The average grain size was calculated from scanning electron microscope (SEM; Model S–800, Hitachi, Ltd., Tokyo) images using the intercept method.10) SEM observations were made using polished and thermally etched surfaces. Thermal etching was carried out in air at temperatures 50°C below each sintering temperature.

High resolution electron microscopy (HREM) observations were conducted to examine the grain boundary structure using transmission electron microscopy (TEM; Model 002BF, Topcon, Tokyo). The segregation of Y2+ ions at the grain boundaries were examined by energy dispersive X-ray spectroscopy (EDS) with a probe size of 0.5 nm, and the Y2+ ion distribution within grains was examined using scanning transmission electron microscopy (STEM) and EDS.

2.4 Thermal expansion

Thermal expansion behavior was measured using a dilatometer (Thermo Plus 2 TMA8310, Rigaku Corporation, Osaka) at a constant heating and cooling rate of 2°C/min up to 1200°C, with 99.5% Al2O3 used as a reference material.

Table 1. Chemical Composition of Prepared Samples by SPM and LPM

<table>
<thead>
<tr>
<th>Component</th>
<th>SPM (mass%)</th>
<th>LPM (mass%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZrO2+HfO2</td>
<td>94.75</td>
<td>94.81</td>
</tr>
<tr>
<td>Y2O3(mol%)</td>
<td>4.97(2.78)</td>
<td>4.97(2.75)</td>
</tr>
<tr>
<td>Al2O3</td>
<td>0.250</td>
<td>0.254</td>
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<tr>
<td>SiO2</td>
<td>0.015</td>
<td>0.012</td>
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<td>CaO</td>
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<td>0.003</td>
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<tr>
<td>MgO</td>
<td>0.002</td>
<td>0.001</td>
</tr>
<tr>
<td>Na2O</td>
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<td>0.004</td>
</tr>
<tr>
<td>K2O</td>
<td>0.001</td>
<td>0.003</td>
</tr>
<tr>
<td>TiO2</td>
<td>0.002</td>
<td>0.006</td>
</tr>
<tr>
<td>Fe2O3</td>
<td>0.005</td>
<td>0.001</td>
</tr>
</tbody>
</table>

Fig. 1. Relationship between density and sintering temperature for SPM and LPM. The data given by Matsui et al.31) (×) was calculated from the reported relative density multiplied by the theoretical value of 6.1 g/cm³.

3. Results

3.1 Densification

The relationship between density and sintering temperature is shown for the SPM and LPM derived materials in Fig. 1. The SPM powder could be sintered at lower temperatures than the LPM powder. In the case of the LPM sample, a high density, over 6.0 g/cm³, was only obtained when the sintering temperature was above 1400°C. On the other hand, a density of over 6.0 g/cm³ was achieved for the SPM sample after sintering at 1350°C. The difference in sinterability is attributed to the surface area of the LPM powder (7 m²/g) being lower than that of the SPM powder. The density data given by Matsui et al.31–33) is also shown in Fig. 1, in which the values were calculated from the reported relative density multiplied by the theoretical value of 6.1 g/cm³. Although the sinterability of the SPM sample and Matsui’s samples were almost the same, the surface area of the SPM sample was smaller than that reported by Matsui et al.31–33) This result implies that the SPM powder has higher sinterability than the LPM powder.

3.2 Microstructure

Figure 2 shows typical SEM micrographs for SPM and LPM samples sintered at 1350, 1400 and 1440°C. The average grain sizes for these samples are shown in Fig. 3. The grain growth rate for the SPM sample was faster than that for the LPM sample below 1440°C, while the grain size was almost the same for both SPM and LPM samples sintered at 1440°C. However, the grain growth rate for the LPM sample increased sharply over 1440°C.

Figure 4 shows typical STEM micrographs and YKα mapping images obtained by the STEM-nano probe EDS method for SPM samples sintered at 1350 and 1440°C. At 1350°C, the region with high and low Y2+ ion concentration was observed. When the sintering temperature increased to 1440°C, the segregation of Y2+ ions at grain boundaries progressed much and the Y2+ ion concentration increased at grain boundaries. Matsui et al.31–33) reported that Y2+ ions are homogeneously dispersed in grains of Y-TZP when it is sintered below 1300°C. However, the present investigation revealed different results from those reported by Matsui et al.31–33)

Figure 5 shows typical HREM micrographs of the grain-boundary faces for SPM samples sintered at 1350 and 1440°C.
Fig. 2. SEM micrographs of etched surface for SPM and LPM samples sintered at 1350, 1400 and 1440°C. Etching condition was 1300–1400°C for 10 min in an air atmosphere.

Fig. 3. Relationship between grain size and sintering temperature for SPM and LPM samples.

No amorphous or secondary phases were observed along the grain-boundary faces. This result agrees with the observation by Matsui.11–13 Figure 6 shows typical $Y^{3+}$ ion distribution profiles across the grain boundaries for SPM samples sintered at 1350 and 1440°C. The $Y^{3+}$ ion in the sample sintered at 1350°C (1350°C – I) was broad, but at 1440°C the distribution was narrow, and the segregation of $Y^{3+}$ ion at grain boundaries was clearly apparent. On the other hand, a different $Y^{3+}$ ion distribution profile from that for 1350°C – I was observed for the sample sintered at 1350°C (1350°C – II). The $Y^{3+}$ ion concentration for 1350°C – II was more than twice as large as that for 1350°C – I. Matsui et al.11–13 reported that the $Y^{3+}$ ion distribution was broad in Y–TZP sintered at lower temperature, and that the $Y^{3+}$ ion distribution at grain boundaries became sharp and narrow when the sintering temperature was increased. The distribution characteristics observed in the present investigation agree with these results. In addition, Matsui et al. reported that in some cases, the $Y^{3+}$ ion distribution across the tetragonal-tetragonal grain boundaries in Y–TZP sintered over 1500°C exhibited an asymmetric distribution, regardless of the distribution peak at the grain boundaries. It should be noted that they also reported finding that some tetragonal grains had the same $Y^{3+}$ ion distribution as that of Y–TZP sintered below 1500°C. However, in this experiment, an asymmetric distribution of $Y^{3+}$ ion was observed for a sintering temperature of 1350°C, which was lower than that reported by Matsui et al.11–13
3.3 Crystalline phase and thermal expansion

Figure 7 shows the XRD patterns of SPM samples sintered at 1275–1440°C and LPM samples sintered at 1350–1600°C. When the sintering temperature was low (1275°C), the diffraction pattern for the tetragonal and cubic phases was broad, and as the sintering temperature increased, the peaks of each diffraction pattern became sharp and clear. The cubic pattern for the LPM sample began to appear as that observed by Ohmichi et al. [14] Figure 8 shows the relationship between the tetragonal, monoclinic and cubic phase fraction of ZrO₂ on the polished and ground surfaces for SPM and LPM samples. The monoclinic phase was not observed for the LPM sample; however, the cubic phase fraction increased with increase in the sintering temperature. On the other hand, the tetragonal phase fraction for the SPM sample increased as the sintering temperature increased, especially in the range from 1275 to 1300°C. Increasing the sintering temperature for the SPM sample was accompanied by a decrease in the monoclinic phase fraction; however, it was not decreased to 0 vol%. The cubic phase fraction was the highest among the three phases for the SPM samples sintered at 1275°C, and decreased above 1275°C. The monoclinic phase fraction determined for the ground surface of the SPM sample sintered at 1275°C was almost the same as that for the polished surface, but decreased with increased grain size. In contrast, the monoclinic phase fraction found on the ground surface of the LPM samples increased with an increase in the grain size. This result indicates that the tetragonal phase is easily transformed to the monoclinic phase by grinding stresses. [5]

Figure 9 shows the expansion-temperature curve for SPM
samples sintered at 1275 and 1300°C, in addition to the LPM sample sintered at 1400°C. The curve for the LPM sample demonstrated a linear relation during the heating and cooling stage. The curve for the SPM sample sintered at 1275°C showed a monoclinic to tetragonal phase transformation during the heating stage, but a linear relationship was observed during the cooling stage, as that seen for the SPM sample sintered at 1275°C. In addition, the coefficient of thermal expansion (CTE) between 20 and 1200°C was almost the same value as those of other samples (SPM–1300°C and LPM–1400°C) regardless of the higher monoclinic phase concentration (37vol%) in the SPM–1275°C sample (see Fig. 8).

4. Discussion

SPM prepared samples have a higher sinterability than that of the LPM prepared samples, because the SPM samples not only had a larger surface area, but also the sintering mechanism may be different from that of the LPM samples. Because the LPM sample was stabilized by Y2O3 at the stage of powder preparation, sintering may only proceed by the diffusion mechanism. On the contrary, the SPM sample was not stabilized before sintering, so that sintering should progress by not only diffusion, but also by solid phase reaction. The reaction between ZrO2 and Y2O3 would result in stabilization of ZrO2 to the tetragonal or cubic phase, and might contribute to an acceleration of mass transport during sintering. Therefore, the reaction and resultant stabilization, as well as the large surface area, may contribute to the densification (i.e., enhancement of sinterability).

From the relationship between the density and sintering temperature (Fig. 1), and the effect of sintering temperature on the tetragonal and monoclinic fraction (Fig. 8), it could be considered that the stabilization of ZrO2 by Y2O3 to the tetragonal phase progresses sharply at over 1300°C. This can be confirmed by the XRD analysis (Fig. 7) in which diffraction peaks indicative of the tetragonal phase became apparent over sintering temperatures of 1300°C.

As the sintering temperature increased, the tetragonal phase fraction for the LPM sample decreased slightly while the cubic phase fraction increased, because the tetragonal phase separated into the tetragonal and cubic phase as reported by Matsui et al.11–13 SPM sample sintered at 1350°C indicated evidently the difference of the Y³⁺ ion distribution for the results of EDS analysis and Y³⁺ ion distribution pattern for 1350°C–I and II (Figs. 4 and 6), even if the sintering temperature was the same. This difference would be attributed that Y³⁺ ion distribution in ZrO2 grains was inhomogeneous due to SPM compared with LPM. In the case of SPM sample, there were the regions with high and low Y³⁺ ion concentration in the microstructure. Considering that a large amount of cubic phase existed in the SPM sample sintered at 1275°C, it is estimated that the region of high Y³⁺ ion concentration was cubic phase and that of low Y³⁺ ion concentration was tetragonal and only a little monoclinic phase. As an increase in the sintering temperature over 1350°C, the diffusion of Y³⁺ ions progressed more, and the cubic phase fraction decreased and the tetragonal phase fraction increased. When the sintering temperature increased to 1440°C, the segregation of Y³⁺ ion distribution progressed more than that of 1350°C. The cubic phase and/or the increase of more stabilized tetragonal phase were caused by the phase separation, and then, tetragonal grains containing cubic phase at the peripheral regions around the grain boundaries were formed by the segregation of Y³⁺ ions. The microstructure was similar to that of the LPM sample, as reported by Matsui et al. This result is supported that the tetragonal and cubic phase fraction for SPM sample were nearly the same as those for LPM sample.

In addition, when the sample is sintered over 1440°C, the diffusion of Y³⁺ ions proceed further in the cubic phase regions and the cubic phase regions extend to the tetragonal phase regions, and the grains with only cubic phase would be formed. Matsui et al.11–13 reported that the crystalline phase development in Y–TZP, prepared by LPM, proceeded through sintering exhibited by four steps: (a) a network of monophase tetragonal particles, (b) tetragonal grains containing cubic phase grain boundary regions are formed by the segregation of Y³⁺ ions, (c) tetragonal and cubic dual-phase grain structure and (d) the formation of monophase cubic grains. On the contrary to their results, the material prepared by SPM in this study did not show any monophase tetragonal grains, because of the existence of a solid-solution reaction of Y2O3 into ZrO2 during the sintering process. Therefore, the plausible phase and microstructure development for the SPM samples, according to the increase of sintering temperature used in this study is considered as follows: (a) cubic and tetragonal phase are formed by the solid-solution reaction of Y2O3 into ZrO2, and no or only a little monoclinic phase exist, (b) cubic phase decreases and tetragonal phase increases by the progress of the diffusion of Y³⁺ ions, (c) tetragonal grains containing cubic phase at peripheral regions around the grain boundary are formed by the segregation of Y³⁺ ions, (d) tetragonal and cubic bi-phase morphology.

The monoclinic phase observed on the ground surface of the LPM sample was removed by polishing. This is a clear indication that this monoclinic phase is formed by mechanical grinding and a resultant tetragonal to monoclinic transformation effect. In the case of SPM, the monoclinic content of both the ground and polished surfaces decreased with increasing sintering temperature. However, the monoclinic phase that appeared on the ground surface could not be completely removed by polishing.

These results showed that the SPM samples contained the monoclinic phase within the sample or that the transformation zone created by grinding stresses was deep and could not be removed even by polishing. The monoclinic to tetragonal phase transformation was not identified on the expansion-temperature curve during the heating and cooling stage for the SPM sample sintered at 1300°C, and the curve showed a linear relation. In the case of the SPM sample sintered at 1275°C, which contained a large amount of monoclinic phase, the transformation was observed during the heating stage, but was
not present during the cooling stage, where only expansion behavior to the LPM sample was confirmed (see Fig. 9). If the monoclinic phase was included within the sample, a hysteresis curve caused by reversible transformation should be observed during the cooling stage. Therefore, it is concluded that the monoclinic phase was essentially not present in the sintered SPM sample, or if present, it was in too small quantity to affect the thermal expansion behavior. A monoclinic to tetragonal transformation was observed during the heating stage for the SPM sample sintered at 1275°C (Fig. 9). However, this might be due to the formation of a deeper transformation region caused by surface grinding, resulting in a larger amount of stress-induced monoclinic phase compared with other samples sintered at higher temperatures.

Consequently, it was estimated that this behavior is due to the tetragonal phase in the SPM sample sintered at 1275°C, which is easily transformed, because the stabilizing Y$_2$O$_3$ content in tetragonal grains is less than that in the SPM samples sintered above 1275°C. It is suggested that the monoclinic fraction present on the polished and ground surfaces indicated almost the same, because the transformation zone was deep and could not be removed, even by polishing. All of these characteristic would have a strong effect on the mechanical properties of the sintered samples. Detailed investigation of the mechanical properties will be reported elsewhere.

5. Conclusion
Zirconia polycrystals containing 2.8 mol% Y$_2$O$_3$ were fabricated by sintering of two types of powders prepared by the solid phase method (SPM), involving wet dispersing and mixing using an agitator mill, and the liquid phase precipitation method (LPM). The microstructure and phase development of these polycrystals were then investigated. Consequently, we succeeded to fabricate Y$_2$O$_3$-stabilized ZrO$_2$ polycrystals by reactive sintering, using the solid phase method with the agitator milling technique, and concluded the following.

1. ZrO$_2$ powder prepared by the solid phase method (SPM) showed higher sinterability than that of the liquid phase precipitation method (LPM). The sample prepared by SPM showed a higher density than that prepared by LPM, and consisted of fine grains.

2. For the sample by SPM and sintered at lower temperature, a region with higher Y$^{3+}$ ions concentration was formed at the peripheral region in the ZrO$_2$ grains, and the cubic phase was confirmed. As the sintering temperature was increased, the diffusion of Y$^{3+}$ ions progressed, and cubic phase decreased and tetragonal phase increased. And then, tetragonal phase containing cubic phase at peripheral regions around the grain boundary by the phase separation.

3. Sintering of the SPM sample at more than 1300°C resulted in an increase in the tetragonal phase fraction and a sharp decrease in the monoclinic phase fraction. On the other hand, no monoclinic phase was observed for the LPM sample and the cubic phase fraction was slightly increased with increase in the sintering temperature.

4. The thermal expansion-temperature curve for the SPM sample showed a monoclinic to tetragonal phase transformation during the heating stage. However, a tetragonal to monoclinic phase transformation during the cooling stage was not identified. In spite of the detection of a monoclinic phase by XRD, it was assumed that the sample did not essentially contain the monoclinic phase.

References