Sinterability of Low-Cost 3Y-ZrO₂ Powder and Mechanical Properties of the Sintered Body

Min-Sung Kim^{***}, Shin-Il Go^{*}, Jin-Myung Kim^{*}, Young-Jo Park^{*†}, Ha-Neul Kim^{*},
Jae-Woong Ko^{*}, Seung-Hwa Jung^{***}, Jae-Yuk Kim^{***}, and Jon-Do Yun^{**}

^{*}*Powder and Ceramics Division, Korea Institute of Materials Science, Changwon 51508, Korea*

^{**}*Advanced Engineering Division, Kyungnam University, Changwon 51767, Korea*

^{***}*Research Institute, Cenotec Co. Ltd., Haman 52013, Korea*

(Received April 25, 2017; Revised June 19, June 20, 2017; Accepted June 20, 2017)

ABSTRACT

This study investigated the effects of grain size and phase constitution on the mechanical properties of 3Y-ZrO₂ by varying the sintering conditions. The raw powder prepared by a low-cost wet milling using the coarse solid oxide powders was sintered by both pressureless sintering and hot-pressing, respectively. As increasing holding time at 1450°C for pressureless sintering, it promoted the microstructural coarsening of matrix grains and the phase transformation to tetragonal phase, whereas the bimodal microstructure embedded with abnormal cubic-ZrO₂ grains was observed regardless of sintering time. On the other hand, the specimens hot-pressed at 1300°C for 2 h reached ~97% of relative density with homogeneous fine microstructure and mixed phase constitution. It was found that the proportion of untransformed monoclinic zirconia had the most adverse effect on the biaxial strength compared to the impacts of grain size and density. The pressureless sintering of the low-cost powder for prolonged sintering time to 8 h led to a decent combination of mechanical properties ($H_V = 13.2$ GPa, $K_{IC} = 8.16$ MPa·m^{1/2}, $\sigma = 981$ MPa).

Key words : Zirconia, Pressureless sintering, Hot Pressing, Biaxial strength

1. Introduction

Zirconia is a high strength and high toughness ceramic material and has been reported to exhibit outstanding properties such as low thermal conductivity, low coefficient of thermal expansion, and high chemical stability.¹⁾ Zirconia is applied to various products including electrical products such as automobile catalysts, electronic circuit boards, and gas sensors along with cutting, bio, and engine products. Especially, oxides MgO, CaO, Y₂O₃, and CeO₂ are added as stabilizers to produce metastable zirconia (Tetragonal Zirconia Polycrystal, TZP) stabilized to a tetragonal system at room temperature; TZP is very widely used. TZP attains excellent strength by suppressing phase transformation to a monoclinic phase by maintaining tetragonal and cubic phase stability at room temperature.^{2,3)} Not only that, when external stress is applied, the metastable tetragonal system absorbs fracture energy during the phase transformation to a stable monoclinic system and the 3~5% volume expansion during the phase transformation prevents crack propagation by inducing compressive stress. This is called stress induced phase transformation^{4,5)} and it is the main mechanism that improves the fracture toughness of TZP. In order to maximize the toughness enhancing effect, the content

fraction of the tetragonal phase needs to be high and the conditions of grain size, grain shape, and high density have to be satisfied.^{4,6)}

The coprecipitation method⁷⁾ is widely known as a fabrication method for uniform dispersion of the stabilizer yttria. Other methods include spray pyrolysis,⁸⁾ the hydrothermal synthesis method, and the sol-gel method. In the case of the coprecipitation method, particulate powder of uniform particle size and high purity can be obtained, but the method becomes relatively costly due to the complexity of the process. On the other hand, the solid state breakdown method gives mechanical energy to solid particles, decreasing the sizes of the particles, increasing the surface area, and making particulate fabrication easier. This method reduces the number of process parameters in comparison to the coprecipitation method, making the method more advantageous in terms of productivity and economic feasibility. In this study, the sintering behavior and mechanical properties of the sintered body were analyzed using low-cost 3Y-ZrO₂ powder as the starting material, which was fabricated by mixing solid state, monoclinic zirconia and yttria through wet milling. Generally, zirconia ceramics are known to be fabricated through pressureless sintering, in which the grain growth according to the sintering temperature and time variation affects the mechanical properties of the zirconia.⁹⁾ In certain conditions, abnormal grain growth occurs and control of the microstructure becomes difficult. In contrast, the hot press method

[†]Corresponding author : Young-Jo Park

E-mail : yjpark87@kims.re.kr

Tel : +82-55-280-3356 Fax : +82-55-280-3392

applies high pressure to accelerate densification, allowing for sintering at temperatures lower than those used with pressureless sintering and suppressing abnormal particle growth. As a result, a sintered body with small grain size and uniform microstructure can be fabricated. In this study, in order to investigate their relationships, the microstructure was observed and the phase fraction and biaxial strength were measured for the densified sintered body based on the sintering temperatures and times of the pressureless sintering and hot press methods.

2. Experimental Procedure

Zirconia (CZ3YB, Cenotec, Korea) containing 3 mol% of yttria was used as the starting material. Calcination was performed for 1 h at 600°C to remove the organic and binder materials in the obtained powder. After weighing 1.2 g of the calcinated powder and uniaxial pressing it using 15 mm circular mold, a green body of approximately 13 mm diameter and 2.6 mm height was fabricated through cold isostatic pressing, which process maintains a pressure of 200 MPa for 5 minutes. The shaped body was placed in an alumina crucible and then inserted into a Kanthal heat treatment furnace. Then, pressureless sintering was carried out at atmospheric pressure for 2, 4, and 8 h at 1450°C. The apparent density of the sintered body was measured using the Archimedes' principle and the relative density was calculated using the theoretical density (6.1 g/cm^3)¹⁰ of the 3 mol% Y_2O_3 containing tetragonal zirconia. For the hot press method, 2 g of the calcinated powder was weighed into the 15 mm circular mold, and uniaxial pressing and subsequent cold isostatic pressing at 20 MPa for 5 minutes were conducted to make green bodies with approximately 14.9 mm diameter and 4.3 mm height which fit into the hot press mold. The sintering temperature of the hot press furnace was 1300°C and experimentation was carried out while maintaining the pressure at 40 MPa for 2 h. In order to analyze the specimen phase according to the raw material powder and sintering method, X-ray diffraction (XRD) analysis (D/MAX 2500, Rigaku, Japan) was performed with

conditions of 20~70°(2 θ) scan range and 4°/min scan rate. The biaxial bending strength of the pressureless sintering specimen was measured according to ISO 6872. Also, to measure the Vickers hardness, a load of 1 kgf was applied (FM-700A, Future Tech, Japan) and a load of 20 kgf was applied to measure the fracture toughness (HV-112, Akashi, Japan). In order to assess the strength of the sintered body according to the pressureless sintering and hot press method conditions, the specimens were grinded to a thickness of 1.2 mm and both sides of the specimens were polished using 1 μm diamond slurry. Observation of the sintered microstructure and EDS composition analysis were conducted using field emission scanning electron microscopy (FE-SEM, JSM-6700F, JEOL, Japan) after thermal etching at 50°C lower than the sintering temperature. The average grain size of the sintered body was calculated by multiplying the average line intercept length by 1.56 using the line intercept method (ASTM E-122-88). Transmission electron microscopy analysis (HR-TEM, JEM-2100F, Jeol, Japan) of the sintered body was performed at an accelerating voltage of 200 kV and the SAED (Selected Area Electron Diffraction) pattern was taken for phase analysis.

3. Results and Discussion

Figure 1 shows the microstructure of the 3Y-ZrO₂ powder, which was dried after wet milling of 10 μm coarse, monoclinic zirconia and 2 μm yttria for 5 h at 12 m/sec using a super mill. The powder morphology is shown in Fig. 1(a); magnified observation of Fig. 1(b) revealed particle sizes of approximately 200 nm in the agglomerated form. Fig. 2 shows the average particle size measured using a particle size analyzer; due to the agglomeration of the starting materials of zirconia and yttria, the average particle size was $D_{50} = 8.8 \mu\text{m}$. Fig. 3 shows the XRD phase analysis results of the mixed raw powder (a) and sintered body (b-e). No peak corresponding to the minimally-added yttria was observed, as can be seen in Fig. 3(a), while it was observed that the zirconia was monoclinic.

Fig. 1. SEM image of 3Y-ZrO₂ raw powder (a) low and (b) high magnification.

Fig. 2. Particle size distribution of 3Y-ZrO₂ raw powder.

Fig. 3. X-ray diffraction patterns of the 3Y-ZrO₂ raw powder and the sintered bodies, (a) 3Y-ZrO₂ Raw powder and Pressureless sintering at 1450°C (b) 2 h, (c) 4 h, (d) 8 h, (e) Hot Pressing at 1350°C for 2 h under 40 MPa.

The relative density of the sintered body was calculated using the density 6.1 g/cm³ of the tetragonal zirconia, assuming that the zirconia with 3 mol% yttria added was stabilized to a tetragonal phase after sintering. However, Fig. 3(b)~(e) for the sintered body phase analysis results shows that, due to the nonuniform mixture of yttria in the powder used in this study, the 3 phases of monoclinic, tetragonal, and cubic all existed after sintering. Thus, the relative density calculated using the assumption that the entirety of the mixture was tetragonal slightly underestimates the actual value. The relative density of the shaped body before sintering was 56~57%; the relative density of the 1450°C pressureless sintering specimen was measured and is plotted in Fig. 4. Sintering for 2 h at 1450°C resulted in densification of over 98%; extension of the sintering time slightly increased the density, which was measured and found to be about 99%. Due to its relatively nonuniform mixture, the low-cost powder used in this study was found

Fig. 4. Relative density and average grain size of the pressureless sintered body with different sintering time.

to have poor phase stability compared to that of the coprecipitation method powder; however, there were no problems in terms of the densification or the related sinterability.

After thermal etching of the polished surface of the pressureless sintered body, the microstructure was observed using FE-SEM (Fig. 5); the average particle size of the sintered body is plotted in Fig. 4. The densified microstructure, with almost no voids, matched the high density shown in Fig. 4. The phase analysis results of the pressureless sintering specimens are shown in Fig. 3(b-d), where it can be seen that the initial monoclinic zirconia partially remained where most underwent phase transformation to tetragonal and cubic due to the presence of yttria. In relation, the tetragonal phase was used as the basis for the theoretical density when calculating the relative density of the sintered body, but because phase analysis revealed that the monoclinic phase with lower density remained, the relative density somewhat underestimated the actual value. This result was in agreement with the intricate microstructure observed with almost no voids as mentioned for Fig. 5.

An interesting finding for the zirconia sintered body microstructure was that the bimodal distribution microstructure, shown in Fig. 5, was composed of matrix particles smaller than or equal to 1 μm, and also of anomalous coarse grains with diameters greater than or equal to 1 μm for all sintering times. As can be observed in the high magnification SEM imagery in Fig. 5(d-e) and the average grain size in Fig. 4, the matrix particles were found to experience grain growth as the sintering time increased. However, in the low magnification imagery in Fig. 5(a-c), it can be seen that the coarse grains existed in similar fractions regardless of the sintering time; it can also be observed that the fractions did not increase as the sintering time increased. Through the above observation, it was determined that the coarse grains of 1 μm or greater were cubic zirconia produced from the nonuniform mixture of yttria particles. However, since the tetragonal and cubic XRD peaks were obtained in close proximity and overlapped each other, as can be seen in the XRD phase analysis results in Fig. 3,¹¹⁾

Fig. 5. SEM images of pressureless sintered bodies with different sintering time (a), (d) 2 h, (b), (e) 4 h, (c), (f) 8 h.

the quantitative distribution between the two phases required Rietveld refinement. In this study, SEM EDS and TEM analyses were carried out for more direct and visual distinction.

Figure 6 shows the SEM observation image (a) and the corresponding EDS analysis results (b-d). In Fig. 6(c), the yttrium concentration was measured and found to be higher than that of the matrix particles in the anomalous

Fig. 6. (a) SE image of the 3Y-ZrO₂ ceramic by pressureless sintering. EDS maps of (b) Zr, (c) Y, (d) Layered image combining all maps.

Table 1. EDS Analysis of Matrix and Coarse Grain

Location	Zr (at%)	Y (at%)	O (at%)	Y/(Y+Zr) (at%)	Y ₂ O ₃ (mol%)
Matrix	31.5	1.5	67.0	0.045	2.3
Coarse grain	29.0	4.6	66.4	0.136	7.3

coarse grains. Table 1 shows the EDS quantitative analysis results for the yttria concentrations of the matrix particles and of the anomalous coarse grains, which had values of 2.3 and 7.3 mol%, respectively. The matrix particles were a mixture of the starting material, monoclinic zirconia, and 3 mol% yttria-containing tetragonal zirconia; the yttria concentration of the matrix particles was measured and found to be 2.3 mol%. On the other hand, due to the nature of the EDS analysis, the yttria concentration of the coarse grains was measured and found to be 7.3 mol%, which reflected the matrix particles on the periphery (monoclinic phase of 0 mol% yttria and tetragonal phase of the 3 mol% yttria), although general cubic zirconia is stabilized by 8 mol% yttria.^{1,2)} Meanwhile, the determination that the coarse grains were cubic zirconia was also supported by the TEM

SAED pattern analysis (Fig. 7). In this way, the formation of all 3 crystal phases of the zirconia in the sintered body was due to the nonuniform mixture of the solid phase starting material powders. Thus, in order to obtain tetragonal zirconia sintered bodies, although 3 mol% yttria was added in relation to the total mixture powder, the parts lacking in yttria maintained the starting material of monoclinic zirconia and the parts with excessive yttria formed cubic zirconia.

The mechanical properties of the pressureless sintered specimens were measured and are plotted in Fig. 8. Figure 8(a) shows the measured biaxial strength of the disc shaped specimen, in which the biaxial strength for the 4 h specimen (965 MPa) was greater than that for the 2 h specimen (881 MPa), while the 8 h specimen (981 MPa) had a value of biaxial strength that slightly increased compared to that for the 4 h specimen. As the sintering time increased, overall grain growth occurred and, despite the anomalous coarsening of the cubic phase, which has less strength than that of the tetragonal phase, a tendency of slight strength increase was observed. This tendency was determined to be related to the decrease in the starting phase monoclinic

Fig. 7. TEM images of 3Y-ZrO₂ pressureless sintered at 1450°C for 2 h, (a) TEM image, (b) SAED diffraction pattern of the C region.

Fig. 8. The mechanical properties of pressureless sintered body with different sintering time, (a) Biaxial strength, (b) Hardness and Toughness.

Fig. 9. SEM images of 3Y-ZrO₂ hot pressing at 1350°C for 2 h under 40 MPa, (a) × 10 K, (b) × 30 K.

residual amount. This relationship is discussed further in the hot press experiment results section. On the other hand, the measured values of the hardness (approximately 13 GPa) and toughness ($6.5\sim 8 \text{ MPa}\cdot\text{m}^{1/2}$) were in agreement with the general value range widely reported for 3Y-ZrO₂; also, when the sintering time increased, the hardness remained almost constant, while the toughness increased slightly (Fig. 8(b)). The industrial significance of the mechanical properties, shown in Fig. 8, was highly evaluated. Thus, considering that, for price competitiveness, the powder was produced using a low-cost process, sufficient material properties are expected to be obtainable when the target is an application requiring mid-tier performance and not maximum performance.

To investigate the relative impact of the sintered body microstructure and phase distribution on the strength, hot pressing was performed because hot press sintering allows for low temperature sintering compared to pressureless sintering; it also allows a strength comparison, with decreased anomalous size difference, between the matrix particles and the cubic grains. Hot press sintering with conditions of '1300°C-2 h-40 MPa' revealed a sintered body relative density of 97% which was slightly lower than pressureless sintered bodies. Fig. 9(a) shows the low magnification microstructure, which reveals that anomalous coarse grains of 1 μm or greater, which existed in the pressureless sintered specimen, decreased significantly. Suppression of grain growth was observed in the high magnification microstructure shown in Fig. 9(b). The average grain size of the sintered body was measured and found to be $0.230 \pm 0.015 \text{ μm}$, which was a grain size less than half that of the pressureless sintered body. Since a uniform microstructure with suppression of both normal and anomalous grain growth was obtained, the biaxial strength of the hot press sintered specimen was predicted to improve, but the biaxial strength was measured at 416 MPa, which represents a decrease to less than 50% of the value of pressureless sintered specimen. The first cause behind this result was the residual porosity due to the relatively low density, which acted as a

fracture source; the second cause, observed in the phase analysis results in Fig. 3(e), was the incomplete phase transformation due to low temperature sintering. As a result, due to the following two causes, the most important factor affecting the strength in this study was found to be the degree of phase transformation difference of the starting material, monoclinic zirconia. First, the relative density difference of about 1 - 2% between the process of hot press and pressureless sintering was thought in reality to signify similar degrees of densification when considering that the residual amount of the low density monoclinic particles in the hot press sintering specimen was high. In other words, the effect of the residual porosity due to the density difference on the strength was determined to be minimal. Second, as shown in the phase analysis results in Fig. 3(e), a significant amount of monoclinic particles remained in the 1300°C low temperature hot press sintering specimen, causing residual stress within the sintered body due to the thermal expansion coefficient difference between these monoclinic particles and the tetragonal particles that compose the matrix; this difference ultimately leads to strength degradation. The strength variation according to the sintering time for the pressureless sintered specimen in Fig. 8(a), as discussed earlier, can be explained through the same mechanism explained above. Thus, as the sintering time increased, the residual monoclinic volume decreased, as can be seen in Fig. 3(b-d), increasing the strength. The ratios (B/A) of the monoclinic main peak A to the tetragonal and cubic mean peak B for each of Fig. 3(b), (c), and (d) corresponding to the sintering times of 2, 4, and 8 h were 7.6, 20.6, and 20.3, respectively. The strengths of the 4 and 8 h sintered bodies of high phase transformation showed significant improvement compared to the 2 h sintered body with low phase transformation. In conclusion, the strength of the zirconia sintered body investigated in this study was determined according to the crystal grain size, anomalous grain growth, and phase transformation of the monoclinic phase compared to the porosity.

4. Conclusions

Pressureless sintering at 1450°C of a 3Y-ZrO₂ powder obtained through a low-cost process was carried out; the results revealed a trend of slight increases in the strength and toughness, while the hardness was similar between the sintering time cases of 2, 4, and 8 h. The 8 mol% yttria-containing cubic zirconia grains exhibited anomalous coarse growth due to the local and nonuniform mixture between the main material monoclinic zirconia and phase stabilizer yttria, but the effect on the strength degradation was insignificant. The strength, hardness, and toughness of the 8 h pressureless sintered specimen were 981 MPa, 13 GPa, and 8.1 MPa·m^{1/2}. Meanwhile, the specimen hot press sintered at 1300°C, a temperature 150°C lower than the pressureless sintering temperature, had a relatively uniform microstructure, with anomalous grain growth suppressed compared to the pressureless sintering; however, the strength decreased to less than 50% of the value of the pressureless sintered body. Phase analysis showed that the phase transformation of the starting material, monoclinic zirconia, to tetragonal or cubic phase for hot press sintering conducted at low temperature was delayed, generating residual stress within the sintered body and decreasing the strength due to the high residual amount of monoclinic phase. That is, the strength of the zirconia sintered body from the low-cost process nonuniform mixture powder was determined to be dominantly affected by the degree of phase transformation to the tetragonal phase, rather than by the uniformity of the microstructure.

Acknowledgments

This study was carried out as part of the Advanced Manufacturing Technology Research Center Project (ATC) (Project Number 10052448), which is supported by the Ministry of Industry, Trade and Industry.

REFERENCES

1. I.-W. Kim and S.-J. Lee, "Effect of Particle Size on Zirconia Gel-Casting Process," *J. Korean Ceram. Soc.*, **52** [6] 449-54 (2015).
2. D. Owen and A. Chokshi, "The High Temperature Mechanical Characteristics of Superplastic 3 mol% Yttria Stabilized Zirconia," *Acta Mater.*, **46** [2] 667-79 (1998).
3. R. Garvie, "Stabilization of the Tetragonal Structure in Zirconia Microcrystals," *J. Phys. Chem.*, **82** [2] 218-24 (1978).
4. A. Evans and A. Heuer, "Review—Transformation Toughening in Ceramics: Martensitic Transformations in Crack-tip Stress Fields," *J. Am. Ceram. Soc.*, **63** [5-6] 241-48 (1980).
5. D. L. Porter and A. Heuer, "Mechanisms of Toughening Partially Stabilized Zirconia (PSZ)," *J. Am. Ceram. Soc.*, **60** [3-4] 183-84 (1977).
6. F. F. Lange, "Transformation Toughening," *J. Mater. Sci.*, **17** 225-34 (1982).
7. K. S. Mazdizasni, C. T. Lynch, and J. S. Smith, "Cubic Phase Stabilization of Translucent Yttria-Zirconia at Very Low Temperatures," *J. Am. Ceram. Soc.*, **50** [10] 532-37 (1967).
8. H. Ishizawa, O. Sakurai, N. Mizutani, and M. Kato, "Homogeneous Y₂O₃-Stabilized ZrO₂ Powder by Spary Pyrolysis Method," *Am. Ceram. Soc. Bull.*, **65** [10] 1399-404 (1986).
9. R. Singh, C. Gill, S. Lawson, and G. P. Dransfield, "Sintering, Microstructure and Mechanical Properties of Commercial Y-TZPs," *J. Mater. Sci.*, **31** 6055-62 (1996).
10. M. Ghatee, M. Shariat, and J. Irvine, "Investigation of Electrical and Mechanical Properties of 3YSZ/8YSZ Composite Electrolytes," *Solid State Ionics*, **180** [1] 57-62 (2009).
11. R. Srinivasan, R. J. De Angelis, G. Ice, and B. H. Davis, "Identification of Tetragonal and Cubic Structures of Zirconia Using Synchrotron X-radiation Source," *J. Mater. Res.*, **6** [6] 1287-92 (1991).
12. Y. Chen, M. Qi, J. Wu, D. Wang, and D. Yang, "Mechanical Alloying Process of The Zirconia–8 mol% Yttria Ceramic Powder," *Appl. Phys. Lett.*, **65** [3] 303-5 (1994).