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Disintegration process of yttria-stabilized zirconia ceramics using hydrothermal conditions

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Abstract Capability of the recycling of high strength and high fracture toughness yttria-stabilized tetragonal zirconia polycrystalline (Y-TZP) sintered body utilizing ''low-temperature annealing degradation'' phenomenon was investigated. Hydrothermal treatment was employed to induce the phase transformation from tetragonal to monoclinic zirconia and to disintegrate the Y-TZP sintered body. 3 mol% Y_2O_3–ZrO_2 specimens sintered at 1,550 °C and more were disintegrated without leaving the original appearances when the treatment temperature was between 200 °C and 400 °C. The size of the disintegrated fragments of Y-TZP sintered body was much affected by hydrothermal treatment conditions. Only with hydrothermal treatment and simple ball milling, the sintered body was pulverized into the primary particle level. This technique is expected to apply to a sustainable recycling system for the zirconia ceramics, which restrains an energy consumption compared to crushing zirconia using mechanical procedures.

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Introduction

These days, depletion of natural resources and landfill sites is becoming a serious problem and the development of the recycle technique increases its importance more and more. However, recycle of ceramic materials seems to be relatively difficult because of the intrinsic excellent chemical stability, thermal stability and mechanical properties. As for recycling ceramics materials, much more energy and cost are expected to be required than that for recycling metal and polymer materials. Thus, recycle of ceramics may work out only on specific materials, which contains rare metals or consumes a lot of energy for manufacturing from mineral ore. On the other hand, the reuse of ceramic sintered body products itself seems to be difficult because of the lack of reliability, which arise from its intrinsic low fracture toughness. Thus, authors reported [1–5] some particle reclaiming system from ceramic sintered body using hydrothermal conditions for the ''reuse'' of the each primary particles of the sintered body. If the primary particles of the sintered body were reclaimed by low energy process, the consumption of metal resources and energy would be depressed. Even if the reclaimed primary particle cannot be reused directly, material recycle from the reclaimed particles must become much easier than that from bulk sintered body. From the view points of mentioned above, we tried in this study to establish a procedure to reclaim zirconia particles from Y_2O_3-stabilized tetragonal zirconia sintered body.

Y_2O_3-stabilized tetragonal zirconia polycrystalline (Y-TZP) ceramic is well known as one of the high strength and high fracture toughness materials and it is widely used in the field of engineering ceramics [6–13]. The origin of the relatively high fracture toughness of TZP ceramics is explained by the stress induced transformation of tetragonal

zirconia (t-ZrO_2) to monoclinic zirconia (m-ZrO_2) around the cracks which propagate in the sintered body [14–19]. However, this transformation property of Y-TZP sometimes induces the degradation of mechanical properties of sintered body by ''low-temperature annealing degradation'' phenomenon. Kobayashi et al. [7] reported the unusual degradation of the sintered bodies of 4.5–6 mol% Y_2O_3–ZrO_2 solid solution by annealing at relatively low-temperature range between 150 °C and 400 °C. Sato et al. investigated the degradation of the mechanical properties of Y-TZP ceramics by low-temperature annealing and reported that Y-TZP ceramics sintered at 1,600 °C and above are easily transform to monoclinic phase and the mechanical properties were much degraded [20–22]. They also reported that these phenomena were observed notably when chemical species with lone electron-pair such as H_2O existed in the system. Many researchers discussed about the mechanism of low-temperature annealing degradation in detail [7, 20–33] and it was proved that the existence of water much contributed to the degradation mechanism. Therefore, the hydrothermal condition is the worst condition to maintain the mechanical properties of TZP ceramics because it has the suitable conditions for low-temperature annealing degradation and high-pressure water. Recently, Boukis et al. reported that Y-TZP ceramics sintered body fully disintegrated when the sintered bodies were exposed in super critical water oxidation (SCWO) condition [34, 35]. They examined the corrosion behavior of various ceramics materials in super critical water containing hydrogen peroxide and hydrochloric acid, which were added to the system in order to adjust the composition of the supercritical fluid as typical SCWO conditions after decomposition of the organic materials. They investigated the corrosion behavior of Y-TZP, magnesia partially stabilized zirconia (Mg-PSZ), ceria stabilized tetragonal zirconia polycrystals (Ce-TZP) and magnesia and yttria partially stabilized zirconia [(Mg,Y)-PSZ] and proved that the sintered body of the Y-TZP was disintegrated at 465 °C and 25 MPa. They also showed that acidic condition affected the corrosion behavior of zirconia ceramics and reported that yttria and magnesia stabilized zirconia sintered bodies were disintegrated, however, the details about disintegration process of the zirconia sintered body were not reported.

This low-temperature annealing degradation phenomenon of Y-TZP limits its application as structural ceramics or corrosion resistance materials, however, with changing the viewpoint, this degradation property of Y-TZP is suitable for recovery of zirconia resources from its sintered body [2, 36]. If Y-TZP sintered bodies can be pulverized only by hydrothermal process utilizing intrinsic low-temperature annealing degradation phenomenon, we may develop a novel zirconia recycling system. From above background, corrosion and disintegration process of Y-TZP by hydrothermal treatment in pure water was investigated in detail in this paper and the possibility of the reclaiming of zirconia ceramics is also discussed.

Experimental procedure

Hydrothermal treatment conditions

3 mol% Y_2O_3–ZrO_2 (Tosoh Co., TZ-3Y) powder was used as the starting material. The compacts were uniaxially pressed using 1.5 g of 3 mol%Y_2O_3–ZrO_2 powder and sintered at various temperatures for 2 h. An autoclave (Taiatsu Techno, TSC-0096) which can control the pressure using a backpressure-regulating valve and high-pressure pump was used. For all hydrothermal treatment tests, the amount of water in the autoclave was fixed at 46 mL which correspond to the amount of water to keep the pressure of 30 MPa in the autoclave at 400 °C. Ball-milling of the hydrothermally treated specimens were also conducted for 24 h using plastic bottle and zirconia ball with ethanol as the grinding medium.

Characterization

The crystalline phases were identified by X-Ray diffractometry (XRD ; Rigaku, RINT2500) using CuKα radiation with a monochromator. The volume fraction of monoclinic phase, V_m was examined by XRD diffraction measurement using the following equations proposed by Toraya et al. [37],

$$V_m = \frac{1.318X_m}{1 + 0.318X_m} \quad (1)$$

$$X_m = \frac{I_m(11\bar{1}) + I_m(111)}{I_m(11\bar{1}) + I_m(111) + I_t(111)} \quad (2)$$

where I is the integrated intensity of diffraction peak and the subscripts m and t represent the monoclinic phase and tetragonal phase, respectively. The microstrucure of the samples was observed by scanning electron microscopy (SEM; JEOL, JSM-6330F). Particle size distribution and mean diameter of the disintegrated particle was measured by lazar scattering particle size analyzer (HORIBA, LA-920).

Results and discussion

Figure 1 shows the appearances of the specimens hydrothermally treated at 300 °C for 24 h. The specimens used for this test were sintered at between 1,500 °C and

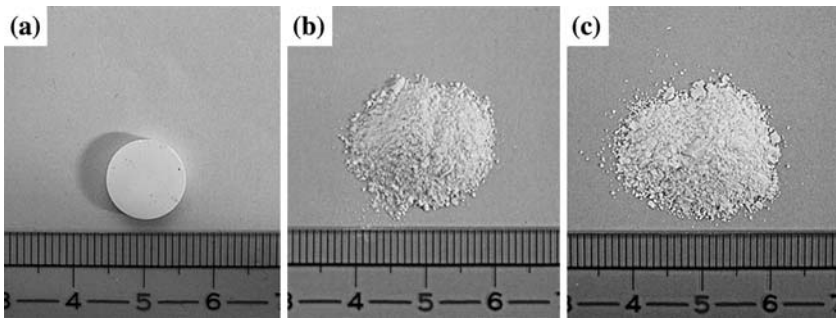

Fig. 1 Appearances of the specimens hydrothermally treated at 300 °C for 24 h. Sintering temperatures of the specimen were (**a**) 1,500 °C, (**b**) 1,550 °C, (**c**) 1,600 °C

1,600 °C for 2 h. Table 1 summarizes the mean grain size of Y-TZP sintered body estimated from SEM observation and the volume fraction of the monoclinic phase at the surface of the sintered body. Only tetragonal phase was detected by XRD measurements conducted on the surface of each sintered bodies. When Y-TZP specimens sintered at 1,500 °C and below were hydrothermally treated, no change was identified on the appearance of the sintered body. On the other hand, Y-TZP specimens sintered at 1,550 and 1,600 °C were disintegrated completely and the morphology of the relatively large disintegrated fragments were scale-like thin-plate. Formations of these kinds of plate-like fragments are reported when the surface of the sintered body was depredated [28]. The reason of this abruption of plate-like fragments was explained by the stress concentration at the corner of the sintered body arising from the volume expansion accompanying the transformation of zirconia. Therefore, these plate-like fragments would arise from disintegration of the corner of sintered body at the initial stage of the disintegration process. Figure 2 shows the XRD profiles of the specimens hydrothermally treated at 300 °C for 24 h. The used specimens are the same ones shown in Fig. 1. XRD measurement of the sample sintered at 1,500 °C was conducted on the surface of the sintered body, while those of sintered at 1,550 and 1,600 °C were conducted for the disintegrated powders. After hydrothermal treatment, the transformation from tetragonal to monoclinic phase was observed in all specimens. Table 2 summarizes the mean particle size (mean diameter of volume distribution) and the volume fraction of the monoclinic phase of hydrothermally treated specimens. Particle size measurement was conducted

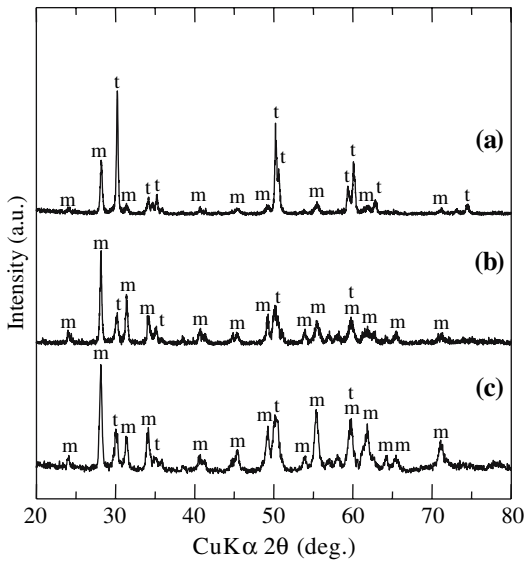

Fig. 2 XRD profiles of specimens hydrothermally treated at various 300 °C for 24 h. Sintering temperatures of the specimen were (**a**) 1,500 °C, (**b**) 1,550 °C, (**c**) 1,600 °C. t: tetragonal zirconia, m: monoclinic zirconia

without ultrasonic irradiation in the sample circulation vessel in order to maintain the size of brittle disintegrated fragments. Volume fraction of the monoclinic phase sintered at 1,500 °C was much lower than that of 1,550 and 1,600 °C. This difference in the volume fraction must result in the difference of the appearance of hydrothermally treated specimens. The grain size of zirconia sintered body slightly increased with increasing sintering temperature (Table 1). Generally, tetragonal phase of zirconia is

Table 1 Mean grain size and volume fraction of monoclinic phase of as-sintered specimens

Sintering temperature (°C)	Mean grain size (μm)	Volume fraction of monoclinic phase (%)
1,500	0.43	0
1,550	0.53	0
1,600	0.60	0

Table 2 Mean particle size and volume fraction of monoclinic phase of the specimen hydrothermally treated at 300 °C for 24 h

Sintering temperature (°C)	Mean particle size (μm)	Volume fraction of monoclinic phase (%)
1,500	Non-disintegration	41
1,550	5.9	83
1,600	7.2	77

unstable at temperature range between 200 °C and 400 °C and it is known to exist as a metastable phase [38]. However, with decreasing the grain size of zirconia, it has a tendency to be more stable even in the temperature region that is favorable for monoclinic phase [39–43]. Therefore, the difference in the grain size affects the degree of disintegration and the transformation behavior.

Figure 3 shows the appearances of the samples hydrothermally treated at various temperatures. When the specimens sintered at 1,550 °C were hydrothermally treated between 200 °C and 400 °C, all specimens were disintegrated. Table 3 summarizes the mean particle size (mean diameter of volume distribution) and volume fraction of the monoclinic phase of hydrothermally treated specimens. The sample treated at 300 °C shows smallest fragments size. Figure 4 shows the particle size distribution of the sample, hydrothermally treated at 300 °C for 24 h. The measured particle size was distributed between 0.4 μm and 45 μm, however, this result did not consist with the results of SEM observation. In this measurement, relatively large fragments may be omitted due to the sedimentation and abnormal behavior in the sample circulation vessel of particle size analyzer results from the too large size and highly anisotropic plate-like morphology of the fragments. Despite the obvious difference in the appearances of each specimen, estimated volume fraction of monoclinic phase was almost same. These results are attributed to the existence of considerable fraction of large fragments with diameters of millimeter order in the disintegrated specimens. XRD profiles conducted on the relatively large fragments may reflect only the diffraction from the surface part and the crystalline structure of the inner part of relatively large fragment may not be reflected. It is reported that the transformation of the tetragonal to monoclinic phase by hydrothermal treatment proceeds from the surface to the inside of the sintered body [28]. Therefore, it seems to be difficult to evaluate the overall volume fraction of the monoclinic phase by XRD measurement of the disintegrated fragments, and the inside of the relatively large fragments has a possibility to maintain the tetragonal phase.

In order to examine the time dependence of disintegration properties, hydrothermal treatment at 300 °C for 0 h (with no retention time) was also conducted. The specimen sintered at 1,550 °C for 2 h was used in this experiment. The autoclave employed in the present study took about 20 min to raise the temperature from 200 °C to 300 °C and took about 50 min to lower the temperature from 300 °C to 200 °C, respectively. Thus, even when the retention time was 0 h at 300 °C, the specimens were exposed to the solvent in the temperature range between 200 °C and 300 °C for 1 h and more. TZP sintered bodies were disintegrated independently of the hydrothermal-treatment time, and the appearance of the fragments were almost same as that treated for 24 h. This result shows that the disintegration process is very fast. Yoshimura et al. [28] reported that the thickness of the exfoliated fragments from the sintered body by low-temperature annealing increases with decreasing the degradation speed of the sintered body. Thus, relatively small size of the disintegrated fragment at this temperature range must be attributed to the rapid transformation of zirconia.

From above results, the sintering temperature must be set at 1,550 °C and more, in order to obtain 3Y-TZP that could be disintegrate by hydrothermal treatment. However, the reported fracture strength of the specimen sintered at 1,500–1,600 °C is about 10% lower than that sintered at 1,400 °C [8, 9]. Thus, the disintegration of zirconia sintered body by hydrothermal treatment can not be applied to the zirconia ceramics that is sintered in pursuit of superior properties in fracture strength. It is needless to add that resistance for low-temperature annealing degradation is much lower than Y-TZPs with optimized microstructure. The consistent optimization of the microstructure, mechanical properties and disintegrative properties will be a future problem of this study. However, at the present stage, the optimum sintering temperature of specimen must be 1,550 °C and the best hydrothermal treatment temperature is 300 °C, taking account of the mechanical properties and disintegration property. The sintering temperature 1,550 °C seems to be a little higher than that suitable to prepare high strength material, but the decrease in strength

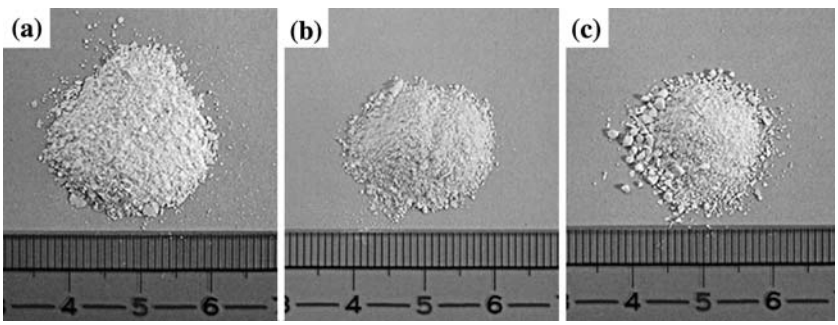

Fig. 3 Appearances of the specimens hydrothermally treated at various temperatures for 24 h. (**a**) 200 °C, (**b**) 300 °C, (**c**) 400 °C (sintered at 1,550 °C for 2 h)

Table 3 Mean particle size and volume fraction of monoclinic phase of hydrothermally treated specimen (specimens sintered at 1,550 °C for 2 h)

Hydrothermal treatment temperature (°C)	Mean particle size (μm)	Volume fraction of monoclinic phase (%)
200	9.2	83
300	5.9	83
400	27.3	84

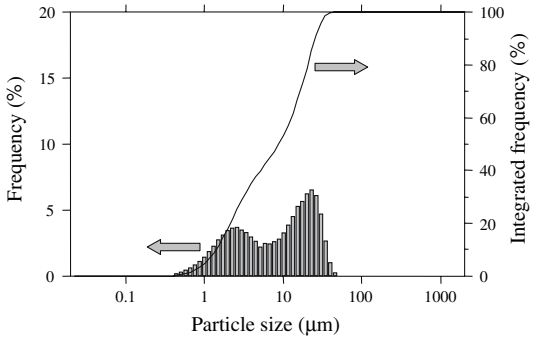

Fig. 4 Particle size distribution of the specimen hydrothermally treated at 300 °C for 24 h (sintered at 1,550 °C for 2 h)

must be smaller than that sintered at 1,600 °C and more. However, the size and the size distribution of recovered zirconia fragments seem to be too large for reuse of the particles and further recycling process. Thus, ball milling of the disintegrated fragments was performed for further pulverizing. Figure 5 shows the SEM photograph of the ball-milled specimen. The sintering condition and the hydrothermal treatment condition of the sample was at 1,550 °C for 2 h and 300 °C for 24 h, respectively. The hydrothermally treated specimen was efficiently pulverized into primary particle revel only by simple ball milling. Figure 6 shows the particle size distribution of ball-milled

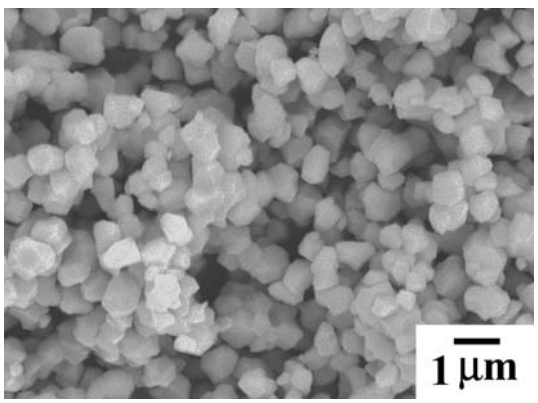

Fig. 5 SEM photograph of the specimen after hydrothermal treatment and ball-milling. (sintered at 1,550 °C for 2 h, hydrothermally treated at 300 °C for 24 h)

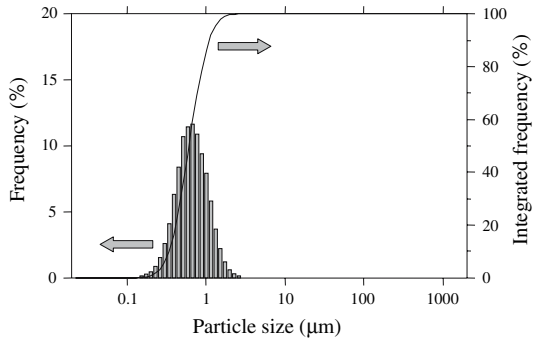

Fig. 6 Particle size distribution of the specimen after hydrothermal treatment and ball-milling. (sintered at 1,550 °C for 2 h, hydrothermally treated at 350 °C for 24 h)

sample. In this measurement, ultrasonic irradiation was employed in the sample circulation vessel for avoiding aggregation of particles. The mean particle size of the sample was 0.6 μm and size distribution range was between 0.2 μm and 3.0 μm. This value almost consists with the results of SEM observation (Fig. 5) and grain size of as sintered body (Table 1). This recovered powder seems to be difficult to use directly for preparation of high strength, zirconia structural ceramics because of low levels of formability, sinterability and grain size. However, recovery of zirconia resources from the reclaimed powder must be easier than that from bulk sintered body. Moreover, the reclaimed powder may be used as the source powders for thermal spray without any additional treatment.

In the present study, it was proved that zirconia sintered body was disintegrated efficiently by hydrothermal treatment even using pure water. These results show the high potential of recycling of zirconia sintered body utilizing the hydrothermal treatment, and this method have a possibility to become a lasting procedure for recovering zirconia powder by further optimization of sintering and treatment conditions.

Conclusions

Y-TZP sintered bodies which sintered at 1,550 °C and 1,600 °C for 2 h were disintegrated into small fragments by hydrothermal treatment around 300 °C without maintaining the original appearance of the sintered body. The degree of disintegration was much dependent on the grain size of the sintered body and the disintegration process was very fast. The size of the disintegrated fragments were micrometer to millimeter order revel and it easily pulverized into primary particle level with average diameter less than 1 μm only by simple ball milling. This procedure has a possibility to be applied for a recycling system of zirconia sintered body.

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