The Effects of a Zirconia Addition on the Compressive Strength of Reticulated Porous Zirconia-Toughened Alumina

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Featured Application: Ceramic Membranes.

Abstract: Porous ceramics have attracted researchers due to their high chemical and thermal stability. Among various types of porous ceramics, reticulated porous ceramics have both high porosity and good permeability. These properties of porous ceramics are difficult to replace with porous metals and polymers. ZTA is used in a variety of applications, and a wealth of experimental data has already been collected. However, research reports on reticulated porous zirconia-toughened alumina (ZTA) are insufficient. Therefore, we prepared reticulated porous ZTA via the replica template method. In this study, various processing conditions (average particle size, zirconia content, solid loading, dispersant, and thickener) were adjusted to improve the compressive strength of the reticulated porous ZTA. As a result, the optimized processing conditions for improving the compressive strength of reticulated porous ZTA could be determined.

Keywords: reticulated porous zirconia-toughened alumina; compressive strength; alumina particle size

1. Introduction

Among the various types of porous materials, porous ceramics offer the intrinsic properties of porous materials (separation/collection and sound-absorbing/hear-shielding), high thermal resistance, and superior chemical stability of ceramics simultaneously. These properties of porous ceramics cannot easily be found in porous metals and polymers.

Methods for preparing porous ceramic include the sacrificial template method [1,2], direct foaming method [3,4], partial sintering method [5], and the replica template method [6,7]. Among them, the replica template method can be used to prepare a porous ceramic with a three-dimensional network structure by impregnating a ceramic slurry into a sacrificial polymer template, and then removing the sacrificial polymer template through a heat-treatment process [8,9]. The reticulated porous ceramic prepared through the replica method has high porosity (generally 90% or more) and good permeability simultaneously. Reticulated porous ceramics have potential applications to molten metal filters, diesel particulate filters (DPF), catalyst carriers, and radar-absorbing materials [10–15].

Zirconia-toughened alumina (ZTA), in which zirconia particles are dispersed on an alumina matrix, is the most representative composite material using the strengthening effect of a zirconia-phase transformation. Over the past several decades, ZTA has been used in research on wear resistance and with cutting tools due to its excellent mechanical properties such as toughness, hardness, high strength, and good wear resistance [16–19]. It is known that the mechanical properties of ZTA depend on the properties of the zirconia, as
determined by the type and content of the stabilizer, and are determined by the interaction between the sintering temperature, alumina content, and the t-phase content [20,21]. In addition, these properties depend on the spatial distribution state of the zirconia particles in the alumina matrix and the size and concentration of the zirconia particles [22]. Among the different types of stabilized zirconia, the most widely used commercially is yttria-stabilized zirconia (YSZ). YSZ containing 3 to 5 mol% of yttria has excellent properties such as good strength and fracture toughness compared to stabilized zirconia containing other oxides. The most thermally stable YSZ is YSZ with 3 mol% yttria added [23,24].

ZTA is used in a variety of applications, and much experimental data has already been collected. However, there are relatively few research reports on reticulated porous zirconia-toughened alumina (ZTA). If the zirconia content is close to 50 wt. %, it is an alumina-zirconia composite, and if the content exceeds 50 wt. %, it is zirconia with alumina additive. The content of zirconia in ZTA in the literature generally varies from 5 to 35 wt. %, but up to 40 wt. % can be referred to as ZTA [25–27]. Therefore, the content of zirconia was set here to range from 0 to 40 wt. %. For sintering temperature, alumina and zirconia at a sintering temperature of 1600 °C exist in two-phase states with little to no solid solubility. Therefore, the sintering temperature was set to 1600 °C. In this study, the reticulated porous ZTA was prepared using the replica template method, and the degree of densification according to the change in the particle size of alumina (coarse and fine) and the zirconia content (0 to 40 wt. %), as well as the microstructure and compressive strength changes, were investigated.

2. Materials and Methods

In this study, the main raw materials had average particle sizes of (1) 0.26 µm (“fine”, AKP-30, Sumitomo Chemical, Tokyo, Japan) and (2) 2–4 µm (“coarse”, AM-210, Sumitomo Chemical, Tokyo, Japan). The average particle size was 0.3–0.6 µm for the zirconia powder (Qingdao Terio Corporation, Qingdao, China) to which 3 mol% of yttria was added. A commercial type of polyurethane foam (SKB Tech, Seoul, Korea) with a pore density of 45 PPI (pores per inch) was used as a sacrificial polymer template at a size of 20 mm × 20 mm × 20 mm. The ZTA slurry consisting of 67 wt. % of alumina, 3 mol% yttria-stabilized zirconia (Qingdao Terio Corporation, Qingdao, China) at 0–40 wt. %, with 1 wt. % Dolapix CE 64 (Zschimmer & Schwarz GmbH Co., Burgstädt, Germany) as a dispersant, 100 mL distilled water, and 10 wt. % polyvinyl alcohol (molecular weight (Mn) approx. 500, Junsei Chemical, Japan) as an organic binder was used to coat the polyurethane foam. An impregnation process was used to coat the mixed ZTA slurry on the polyurethane foam, and the impregnated polyurethane foams were squeezed to remove any excess ZTA slurry. Subsequently, the polyurethane foam coated with the ZTA slurry was dried in an oven, heat-treated at 400 °C for two hours, and sintered at 1600 °C for three hours. The ZTA slurry viscosities were measured using a rotary viscometer (ViscoQC 300, Anton Paar GmbH, Graz, Austria), and the compressive strengths of the reticulated porous ZTA specimens after processing at a size of 20 mm × 20 mm × 20 mm were measured with a tensile tester (RB302 Microload, R&B, Daejeon, Korea). The average particle size distributions were determined by a particle size analyzer (LSTM 13 320 MW, Beckman Coulter, Brea, CA, USA). The microstructures were characterized by means of scanning electron microscope (JSM-6610LV, Jeol, Tokyo, Japan), and the changes in the pore properties were assessed by means of Mercury porosimetry (AutoPore IV Series, Micro meritics, Norcross, GA, USA), using the mercury impregnation method.

3. Results

In this study, reticulated porous ZTA specimens with pore density of polyurethane foam of 45 PPI (pores per inch) were prepared using the replica template method. The pore density is expressed in PPI (pores per inch), and the higher the PPI, the greater the number of pores and the smaller the pore size. Reticulated porous ceramic with a pore density of more than 45 PPI is difficult to prepare. As the pore density of the reticulated
porous ceramic approaches 80 PPI, it is difficult to remove the excessive slurry inside the polyurethane foam and form a thin ceramic coating on the strut walls due to the increase in the pore density. In addition, voids are formed inside the polyurethane foam, and the compressive strength is lowered. Figure 1 shows images of the polyurethane foam (left), and the as-prepared reticulated porous ZTA specimen (right) with a pore density of 45 PPI prepared using the replica method, respectively.

Figure 1. Optical images of polyurethane foam with a pore density of 45 PPI (left) and a reticulated porous ZTA specimen (right).

Figure 2a shows a typical SEM image of a fractured strut wall of a polyurethane foam specimen. The reticulated porous ZTA specimens prepared via the replica template method were formed to coat the surface of the polyurethane foam with ZTA slurry, as shown in Figure 2a. Through a heat treatment and sintering, a polyurethane foam-like skeleton structure was formed, as shown in Figure 2b. A typical SEM image of the fractured strut wall of a reticulated porous ZTA specimen prepared via the replica template method is shown in Figure 2b. The triangular void obtained after the heat treatment and sintering of the polyurethane foam, shown in Figure 2b, affects the overall mechanical properties of reticulated porous ZTA. These inevitable triangular voids lower the compressive strength of reticulated porous ZTA. In order to solve this problem, various methods have been attempted, such as dividing the ceramic coating process on the polyurethane foam into two steps or using a ceramic precursor as a raw material [28,29]. Figure 2b shows a reticulated porous ZTA specimen on which a uniform thickness of the strut wall is formed.

Figure 2. Typical SEM images of the fractured strut wall of (a) polyurethane foam, and (b) a reticulated porous ZTA specimen.

The particle size distributions of the alumina and zirconia are shown in Figure 3a. The average particle size of the coarse alumina was 4.241 μm, that of the fine alumina was 0.328 μm, and that of the zirconia was 0.210 μm. Figure 3b,c depict the microstructures of the coarse and fine alumina particles, respectively. The coarse alumina particles do not have enough sintering driving force to be densified fully due to the presence of coarse particles.
The particle size distributions of the alumina and zirconia are shown in Figure 3a. The average particle size of the coarse alumina was 4.241 µm, that of the fine alumina was 0.328 µm, and that of the zirconia was 0.210 µm. Figures 3b and c depict the microstructures of the coarse and fine alumina particles, respectively. The coarse alumina particles do not have enough sintering driving force to be densified fully due to the presence of coarse particles.

Figure 3. (a) Particle size distributions of alumina and zirconia; Typical SEM images of as-received alumina particles are shown: (b) coarse, and (c) fine.

Figure 4 shows part of the preliminary experiment before addition of zirconia; because it is impossible to conduct an experiment at the initial stage of this study, these values for the basis for the setting of the variables. As the amount of solid loading increases, the viscosity, and compressive strength values increase. The compressive strength was highest when the solid loading rate was 67 wt.%. Therefore, the solid loading content was fixed at 67 wt.%. Because slurry prepared from coarse alumina has very low viscosity compared to that with fine alumina, it is not possible to tightly coat the strut walls of polyurethane foam. To coat the strut walls of polyurethane foam tightly, it must have the proper viscosity level. Therefore, alumina particles must be indefinitely added until the coarse alumina approaches the adequate viscosity. However, this approach is not efficient. In addition, if the solid loading value is set based on the coarse alumina when the fine alumina also uses the same composition, the fine alumina cannot be uniformly coated to the inside of the strut walls of the polyurethane foam because the viscosity is too high, meaning that the compressive strength is decreased. Therefore, a preliminary experiment was performed with fine alumina.
Figure 4. Viscosity at a shear rate of 0.01 s$^{-1}$ of the alumina slurries, and the compressive strengths with 58–67 wt. % solid loading.

Figure 5a shows a plot of the viscosity vs. the shear rate of the ZTA slurries used to prepare the reticulated porous ZTA. As the content of zirconia increases, the viscosity increases. The viscosities are higher for the fine alumina particles as a matrix than for the coarse alumina particles as a matrix. This occurs because the average particle size decreases, the larger specific surface area increases, and the area where the polyvinyl alcohol (PVA) adheres to the particle increases. The compressive strength values according to the zirconia content are shown in Figure 5b. As the zirconia content increases, the compressive strength increases. When the matrix used is fine alumina, 40 wt. % of added zirconia, the maximum compressive strength is 0.705 MPa. When the matrix is fine alumina, with 40 wt. % of zirconia added, the maximum compressive strength is 3.171 MPa. Figure 5c shows the densities and linear shrinkage rates according to the zirconia content. Overall, the densities show a trend similar to that of the compressive strength. In addition, the shrinkage rate of fine alumina is higher than that of coarse alumina; it can be observed that the strut walls are not fully densified due to their coarse particle size. In addition, as the zirconia content increases, more zirconia particles exist between the alumina particles, meaning that the densification improves, and the shrinkage rate increases. This confirms that the particle size of the raw material affects the densification outcome. Densification also affects the compressive strength as shown in Figure 5b. The X-ray diffraction patterns of the phases of ZTA with different zirconia contents are shown in Figure 5d. The zirconia consisted of a small amount of monoclinic zirconia and tetragonal zirconia. As the content of zirconia increases, the peak intensity of the tetragonal and monoclinic zirconia increases. The alumina peak intensity also decreases.
Figure 5. (a) Viscosities at a shear rate of 0.01 s$^{-1}$ of the ZTA slurries, (b) compressive strengths of reticulated porous ZTA (c) densities and linear shrinkage rates, and (d) X-ray diffraction patterns of reticulated porous ZTA with different amounts of zirconia added.

Figure 6a,b show typical BSE images when using coarse alumina as a matrix with zirconia added at rates of 10 wt. % and 40 wt. %, respectively. The lighter-colored particles are zirconia. The coarse alumina particles do not have enough sintering driving force to be fully densified due to the presence of coarse particles. As the content of zirconia increases, the particle size of alumina decreases, and the particle size of zirconia increases. This occurs because zirconia has some drag force at the alumina matrix grain boundary, thereby inhibiting the grain growth of alumina. In addition, as the amount of zirconia increases, the grain growth of zirconia also increases readily with these combinations. Typical BSE images of reticulated porous ZTA specimens using fine alumina as a matrix with zirconia added at rates of 10 wt. % and 40 wt. % are, respectively, shown in Figure 6c,d. It can be seen that when a smaller particle size of alumina is used as a matrix, the outcome is fewer pores and more densification of the microstructure. It was confirmed that the added zirconia particles were present between the alumina particles in the matrix and thus had the effect of inhibiting mutual particle growth between the alumina and zirconia during the sintering process.

The thickener used with coarse alumina as a matrix has relatively low viscosity compared to that used with fine alumina as a matrix. This is done to improve the compressive strength (addition of zirconia: 40 wt. %). The thickener prevents separation between materials by increasing the thickening properties and serves to hold water necessary for hydration, thereby enhancing the mechanical strength of the material. In addition, the thickener acts to increase the uniformity when mixed with water [30]. The thickener imparts adhesive force by hydrogen bonding. However, when the thickener is added, the fluidity is reduced, meaning that the resin does not permeate and diffuse into the micropores on the surface of the adherent, thereby decreasing the physical adhesion. However, if the viscosity is optimized, good hydrogen bonds are formed, which increases the adhesion [31]. Figure 7a shows the compressive strengths and densities at 45, 60, and 80 PPI when the thickener was added. Overall, the densities show a trend similar to that of the compressive strength. At 45 PPI, the compressive strength increased from 0.705 MPa to 1.620 MPa. The value of the compressive strength at 45 PPI is about 1.62 MPa; at 60 PPI it is approximately 2.26 MPa and at 80 PPI it is about 2.32 MPa. Hence, it could be confirmed that the addition of a thickener effectively improved the compressive strength of the reticulated porous ZTA. Figure 7b shows the compressive strengths and densities at 45, 60, and 80 PPI. In the case of fine alumina, because it has sufficiently high viscosity, if a thickener is added, the slurry cannot be uniformly coated onto the strut walls of the polyurethane foam due to the excessively high viscosity, thereby reducing the compressive strength. Therefore,
the fine alumina was used in an attempt to improve compressive strength by increasing the PPI of the polyurethane foam. However, for the polyurethane foams at 60 and 80 PPI despite the fact that the thickener was not added, the ZTA slurry was not uniformly coated deep inside the polyurethane foam due to the high viscosity of the ZTA slurry, causing the compressive strength to be decreased. Overall, the densities show a trend similar to that of the compressive strength. The slurry prepared with coarse alumina has relatively low viscosity compared to that prepared from fine alumina, leading to an increase in the compressive strength when the density of the polyurethane foam strut walls increases. In contrast, fine alumina negatively affects the compressive strength due to the non-uniform coating on the strut walls if the density of the polyurethane foam strut walls is increased due to the high viscosity of the slurry.

![Typical BSE images of the reticulated porous ZTA specimens, zirconia amounts when using coarse alumina as a matrix: (a) at 10 wt. %, and (b) at 40 wt. %; zirconia amounts when using fine alumina as a matrix: (c) 10 wt. %, and (d) 40 wt. %.

Figure 6. Typical BSE images of the reticulated porous ZTA specimens, zirconia amounts when using coarse alumina as a matrix: (a) at 10 wt. %, and (b) at 40 wt. %; zirconia amounts when using fine alumina as a matrix: (c) 10 wt. %, and (d) 40 wt. %.

![Compressive strengths and densities with pore densities of 45, 60, and 80 PPI with a thickener (using a coarse particle size for the matrix), and (b) compressive strengths and densities with pore densities of 45, 60, and 80 PPI (using a fine particle size for the matrix).

Figure 7. (a) Compressive strengths and densities with pore densities of 45, 60, and 80 PPI with a thickener (using a coarse particle size for the matrix), and (b) compressive strengths and densities with pore densities of 45, 60, and 80 PPI (using a fine particle size for the matrix).
To confirm the effect of the particle size, using coarse alumina as a matrix, zirconia at 40 wt. % and the ZTA slurry with the thickener added were used to control the particle size. The particle size distribution of ZTA according to the ball-milling time is shown in Figure 8a. The particle size is a process variable used to obtain the optimal composition of the reticulated porous ZTA. As the ball-milling time increases, the particle size distribution decreases to 1.360 µm, 1.218 µm, 1.165 µm, and 1.031 µm, relative to the aforementioned particle sizes. Figure 8a shows the viscosities as a function of the shear rate of the ZTA slurries according to the ball-milling time. As the particle size decreases due to ball-milling, the specific surface area increases, and the area where the PVA becomes attached to the particles increases. Accordingly, the viscosity increases as the ball-milling time increases. The compressive strength outcomes according to the ball-milling time are shown in Figure 8c. The effect of ball-milling was not visible because the raw particle size was coarse, the densification outcome was poor, and the particle size was not effectively reduced through ball-milling. Figure 8d shows the density values. Overall, this figure shows a trend similar to that of the compressive strength.

Controlling the particle size had only limited effects on improving the strength. Therefore, the particle size was fixed with fine alumina, which has higher compressive strength, and the contents of the dispersant and thickener were adjusted to optimize the slurry. A plot of the viscosity vs. the shear rate of ZTA slurries prepared with different amounts of dispersant is shown in Figure 9a. When more dispersant is added, the viscosity of the slurry

![Figure 8.](image-url)

**Figure 8.** (a) Particle size distributions of ZTA for the as-received, coarse, intermediate, and fine cases. (b) A plot of the viscosity vs. the shear rate of ZTA slurries used to prepare the reticulated porous ZTA: as-received, coarse, intermediate, and fine ZTA particles, and (c) compressive strength outcomes of reticulated porous ZTA specimens prepared from the as-received, coarse, intermediate, and fine ZTA particles (d) density levels.
is decreased more. The type and amount of dispersant are important when optimizing the slurry. Dispersants with low molecular weights effectively reduce agglomerates because the rate of diffusion within the suspension is rapid and it can easily penetrate between the cracks of the agglomerate, thus affecting the size of the aggregate. Dispersants with higher molecular weight have longer chains and can be adsorbed into several particles, but not to one, causing agglomeration [32]. In addition, as the amount of dispersant increases, more dispersant is adsorbed on the surfaces of the particles to increase the repulsive force, meaning that the slurry is stabilized even if the powder content increases, whereas excess dispersant is present in the solvent, causing cohesion of the dispersants [33]. In contrast, if the amount of the dispersant decreases, it cannot effectively disperse the slurry because the amount of the dispersant is not sufficient to prevent aggregation between the particles by adsorbing the polymer material on the particle surface. Dolapix CE 64 (~660 g/mol) has a low molecular weight compared to other dispersants, completely dissociates in water, and has an electrostatic stabilization effect immediately after it is added [34]. Figure 9b shows the compressive strength and density according to the amount of thickener used. The content of the dispersant at 1 wt. % has the highest compressive strength. Dolapix CE at 64 1 wt. % was reported to have the highest compressive strength [35]. These results were confirmed experimentally to be consistent. When the content of the dispersant is 1 wt. %, it has the highest compressive strength, but there is a limit to the addition of the thickener because it already has high viscosity. Therefore, the content of the dispersant having the second-highest compressive strength at 2 wt. % was fixed. The density trend is similar to that of the compressive strength.

![Figure 9](image-url)

**Figure 9.** (a) Viscosities of the ZTA slurries with the amount of dispersant, and (b) compressive strengths and density levels of ZTA slurries depending on the amount of dispersant used.

Figure 10a shows a plot of the viscosity vs. the shear rate of ZTA slurries prepared with different amounts of a thickener. As the amount of the thickener increases, the viscosity increases. The viscosity of the aqueous solution gradually increases as the amount of the thickener used increases. The compressive strength and density according to the amount of thickener are shown in Figure 10b. When this amount is 1 wt. %, the highest compressive strength of about 4.17 MPa is realized. When the thickener added exceeded 1 wt. %, the compressive strength decreased due to the high viscosity of the ZTA slurry. Overall, the densities show a trend similar to that of the compressive strength. In order to improve the compressive strength of the reticulated porous ZTA, it is most important to optimize the slurry. If the composition of the ZTA slurry is optimized further, an improvement in the compressive strength can be expected. Accordingly, additional experiments are required.
4. Conclusions

In this study, reticulated porous ZTA specimens were prepared via the replica template method. The viscosities of the ZTA slurry were controlled by the average particle size, zirconia content (0–40 wt. %), solid loading level, dispersant, and the thickener used. In addition, optimized processing conditions for improving the compressive strength of reticulated porous ZTA were discussed.

The optimum process conditions for each average particle size of alumina (coarse and fine) were determined. The compressive strength of the reticulated porous ZTA specimen was about 0.71 MPa when prepared using coarse alumina as a matrix with an addition of zirconia at 40 wt. % To enhance the compressive strength of reticulated porous ZTA further, a thickener was introduced. Interestingly, the compressive strength of the reticulated porous ZTA specimen was enhanced further to approximately 1.62 MPa. When the reticulated porous ZTA uses fine alumina as a matrix with an addition of zirconia at 40 wt. % and dispersants at 1 wt. %, the compressive strength outcome is approximately 3.17 MPa. The thickener was added to enhance the compressive strength; the compressive strength of the reticulated porous ZTA specimen was about 4.17 MPa when prepared using fine alumina as a matrix with an addition of zirconia at 40 wt. %, dispersants at 2 wt. %, and thickener at 1 wt. %. The matrix has a finer particle size (fine alumina) and higher compressive strength due to densification between the particles. As a result, in order to improve the compressive strength of reticulated porous ZTA, a finer particle size and the addition of a thickener are effective.

An acceptable compressive strength range for reticulated porous ceramic applications is around 1 MPa. We consequently prepared a reticulated porous ZTA with a compressive strength value of 4.17 MPa. Therefore implying that reticulated porous ZTA can potentially be used for reticulated porous ceramic applications, such as diesel particulate filters (DPF) and radar-absorbing materials.

Author Contributions: J.-H.H. and K.-S.M. conceived of and designed the experiments, C.-Y.L. and S.L. performed the experiments; J.L. and J.-H.H. analyzed the data, I.-H.S. contributed in the areas of the reagents/materials/analysis tools, and C.-Y.L. wrote the paper. All authors have read and agreed to the published version of the manuscript.

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