Synthesis and Compaction Behavior of Monodispersed 3Y-ZrO₂ Spherical Agglomerates

Hong-Goo Choi¹, Seok-Min Yong, and Do Kyung Kim[†]

*Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology (KAIST),
Daejeon 305-701, Republic of Korea*

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ABSTRACT

Monodispersed 3Y-ZrO₂ spherical agglomerates were synthesized by thermal hydrolysis process followed by crystallization processes (hydrothermal treatment and calcination). The crystallization process affected the properties of the final particles, such as the primary particle size, the agglomeration state, and the fraction of ZrO₂ monoclinic phase. The hydrothermal treated spherical particles were porous microstructures (weak agglomerates) composed of small primary particles with a size of 14 nm, but the calcined spherical particles had a dense microstructure due to the hard aggregation between primary particles. While the calcined particles had a low green density due to the hard aggregation, hydrothermal treated ones were soft agglomerates and had a deflection point at 50 MPa due to the rearrangement of secondary spherical particles and the filling of the interstices with the primary particles. Finally, the green density of hydrothermally treated ZrO₂ particles was 58% at 200 MPa.

Key words : 3Y-ZrO₂, Thermal hydrolysis, Hydrothermal, Monodispersed spherical particles, Compaction behavior

1. Introduction

Zirconia is one of the most important ceramic materials and has a wide range of applications, including solid oxide fuel cell electrolytes,¹⁾ high performance toughened structural engineering ceramics,²⁾ catalysts,³⁾ and oxygen sensors.⁴⁾ Zirconia has three different crystalline structures, the cubic, tetragonal, and monoclinic polymorphs. The monoclinic phase, stable at room temperature, is transformed to tetragonal at 1170°C, and then to cubic at 2370°C. These two high temperature phases are unstable in bulk forms at ambient temperature, which is unfortunate because they are more valuable for the technological applications mentioned above than the room temperature monoclinic phase. Consequently, many divalent and trivalent cationic species such as Mg²⁺, Ca²⁺, and Y³⁺ have been incorporated into zirconia to prepare cubic and tetragonal zirconia that is stable at room temperature.⁵⁾ 3Y-TZP ceramics, typically stabilized with 3 mol% Y₂O₃,^{6,7)} have interesting and demanding structural applications due to their high strength and fracture toughness.

The processing conditions for the 3Y-ZrO₂ ceramics, including the powder synthesis, forming, and sintering process, must be well controlled to achieve the desirable properties for desired applications. It is critical to obtain a fine powder

with a narrow size distribution and weakly agglomerated nanometer-sized primary particles. Nano-sized ZrO₂ particles were usually synthesized by the neutral precipitation of Zr salt solution and then crystallization. After neutral precipitation, ZrO₂ amorphous particles have irregular shapes and broad size distribution due to the hard aggregation of each nanoparticle. Several different methods have been investigated for the synthesis of monodispersed zirconia particles, which include thermal hydrolysis,^{8,9)} sol-gel process,¹⁰⁾ homogeneous precipitation,¹¹⁾ and nonhydrolytic sol-gel synthesis.¹²⁾ However, most of these zirconia particles are poorly crystalline or have hard aggregates between the nano-sized primary particles due to calcination.

Hydrothermal synthesis is a simple process to prepare homogeneous, fine and weakly agglomerated powders. Several papers have reported the hydrothermal synthesis of Y₂O₃-doped zirconia powders.¹³⁻¹⁷⁾ However, hydrothermally synthesized nanometer-sized particles are weaker agglomerates than calcined ones, since there is attrition and aggregation between particles and the press mold due to their high surface area. So, conventional forming (uniaxial pressing) is not applied to nanoparticles due to the low green density and non-uniform microstructure caused by wall friction and hard agglomeration.

In this study, monodispersed 3Y-ZrO₂ spherical agglomerates were synthesized by thermal hydrolysis, followed by the crystallization process (calcination and hydrothermal treatment). The influence of the crystallization process on the properties of 3Y-ZrO₂ particles and their compaction behavior was investigated.

[†]Corresponding author : Do Kyung Kim

E-mail : dkkim@kaist.ac.kr

Tel : +82-42-350-4118 Fax : +82-42-350-3310

¹Current address : Samsung Corning Precision Materials, Asan-si 336-725, Republic of Korea

2. Experimental Procedures

Monodispersed spherical ZrO₂ particles with amorphous phase were synthesized following an experimental procedure previously reported by our group.⁹⁾ Zirconium oxychloride (98% ZrCl₄·8H₂O, Aldrich Chemical, USA) was dissolved in distilled water and HPC (Hydroxy propyl cellulose, M_w ~ 100,000, Aldrich Chemical, USA) as a dispersion agent in iso-propanol (Junsei, Japan), and then the two solutions were mixed with stirring. The mixed stock solution was stored in a refrigerator (5°C) to prevent hydrolysis for 24 h. Spherical amorphous ZrO₂ particles were prepared by thermal hydrolysis with microwave heating (kitchen oven 2.53 GHz). These particles were washed with distilled water 5 times to remove the remnant ions such as NH₄⁺ and Cl⁻. To dope the phase stabilizer, Y(NO₃)₃·6H₂O was dissolved in the solution which included the spherical amorphous ZrO₂ particles and then 1% NH₄OH aqueous solution was added at the rate of 1 mL/min. The Y coated amorphous particles were crystallized by hydrothermal treatment at 220°C for 2 h and calcination at 600°C for 2 h. The obtained particles were characterized with X-ray diffraction (XRD, Rigaku D/max-IIIc, Cu Ka radiation), scanning electron microscopy (SEM, Philips XL30), and transmission electron microscopy (TEM, JEOL, JEM3010). A quantitative determination of the volume fraction in the mixture of both monoclinic and tetragonal phases was made by using the following formula:

$$X_m = \frac{I(\bar{1}11)_m + I(111)_m}{I(\bar{1}11)_m + I(111)_m + I(111)_t} \quad (1)$$

where the subscripts *m* and *t* refer to the monoclinic and tetragonal phases and *I* refers to the intensity of the corresponding XRD peaks.

To investigate the compaction behavior of prepared 3Y-ZrO₂ particles, a 10 mm diameter mild steel mold was filled with 1 g 3Y-ZrO₂ powders. The powder was uniaxially compacted stepwise to 10, 20, 30, 50, 70, 100, 150, 200 MPa with a universal testing machine (INSTRON #4064, Canton, MA). The fracture surface of the green body which was made by uniaxial pressing was observed with SEM.

3. Results and Discussion

SEM micrographs of the amorphous ZrO₂ particles which were prepared by thermal hydrolysis with microwave heating are shown in Fig. 1. The synthesis solution contained distilled water and iso-propanol, and the RH ratio (iso-propanol/water), HPC content, and concentration of Zr⁴⁺ were 5, 1.5 g/L, and 0.1 M, respectively. Fig. 1 shows that the prepared particles were monodispersed and spherical shaped (size = 194 nm ± 24 nm). The particle morphology can be understood by considering the parameters determining the colloidal stability.¹⁸⁾ According to DLVO theory, the energy barrier between two particles which inhibits agglomeration

Fig. 1. SEM micrographs of amorphous ZrO₂ particles (a) before Y-coating and (b) after Y-coating.

can be expressed as

$$V_b = -\frac{A\kappa a}{12} + 2\pi\epsilon a\psi^2 \quad (2)$$

where *A* is the effective Hamaker constant, κ the Debye-Hückel parameters, *a* the particle diameter, ϵ the dielectric constant of the liquid medium, and ψ the surface potential. The effective Hamaker constant depends on the dispersion medium. The kind and composition of the solvent mixture may not greatly influence the effective Hamaker constant because the Hamaker constants of water and several aliphatic alcohols in free space have similar values, on the order of 10⁻²⁰ J. The colloidal interaction potential depends on the electrolyte concentration, which determines the Debye-Hückel parameters. In this work, other electrolytes did not exist in the solutions. Under these conditions, the magnitude of the energy barrier between the particles is determined mainly by the surface potential and the dielectric constant. Based on this, our previous work demonstrated that the iso-propanol has the appropriate surface potential and dielectric constant to obtain spherical ZrO₂ particles with narrow size distribution.⁹⁾ In addition, HPC also influences the morphology of the prepared particles.

Fig. 2. XRD patterns of (a) the Y-coated amorphous ZrO_2 particles, ZrO_2 particles crystallized by calcination at 600°C for 2 h ((b) non-doped ZrO_2 and (c) Y-doped ZrO_2), and hydrothermal treatment at 200°C for 2 h ((d) non-doped ZrO_2 and (e) Y-doped ZrO_2).

Jean and Ring suggested that a polymeric stabilizer, HPC, could be used to control the colloidal interaction potential.^{19,20)} They reported the advantages of the HPC dispersant: (1) HPC provides thermodynamic stability, not kinetic stability as in electrostatic stabilization; (2) HPC physically adsorbed onto the particles prevents agglomeration during growth; (3) HPC molecules do not act as heterogeneous nucleation sites. To dope the phase stabilizer, Y source ($\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$) was coated on the surface of amorphous ZrO_2 particles by heterogeneous neutral precipitation. 1 vol% NH_4OH was added to the solution at the rate of 1 mL/min. The shape and size of particles were slightly changed after the Y coating (Fig. 1(b)). Small particles which might be homogeneously precipitated could not be found at the surface of the spherical particles. But as the concentration of NH_4OH solution was increased (above 2 vol%), a lot of small particles could be observed. It was

Fig. 3. TEM micrographs of crystallized Y-doped ZrO_2 particles synthesized by (a) calcination and (b) hydrothermal treatment.

also confirmed that the Y source was uniformly coated on the spherical ZrO_2 amorphous particles, by EDS analysis.

As-prepared amorphous ZrO_2 particles and Y-coated amorphous ZrO_2 particles were crystallized by hydrothermal treatment and calcination. Fig. 2 shows the XRD results of the ZrO_2 particles crystallized by calcination at 600°C for 2 h and hydrothermal treatment at 220°C for 2 h. The final crystalline phase, a monoclinic phase and/or tetragonal phase, strongly depended on the crystallization method and Y-coating. In the case of calcinations without Y-coating, there was only a monoclinic phase, but a monoclinic and tetragonal phase with Y-coating. As shown in Table 1, increasing the calcination temperature from 600 to 900°C decreased the fraction of monoclinic phase from 24.7% to 14.6%. Finally, only tetragonal phase existed after sintering at 1400°C for 2 h. From these results, it was determined that a calcination temperature above 900°C was needed for homogeneous distribution of the Y source, but higher temperature caused hard aggregation between primary particles and increased the primary particle size. Therefore, calcination was an unsuitable method to synthesize the weakly agglomerated nanoparticles in our work.

In contrast, the hydrothermal treatment with Y-coating formed only tetragonal phase, and mixed monoclinic/tetragonal phase without Y-coating. Several researchers have reported that the tetragonal phase was more stable than the monoclinic phase due to the lower surface energy in nanometer-sized particles.²¹⁾

Table 1. Volume Fraction and Average Primary Particle Size of Each Zirconia Phase with Different Crystallization Condition

Crystallization method	Yttrium doping	Crystallization temperature ($^\circ\text{C}$)	Fraction of monoclinic phase (v/o)	Particle Size, tetragonal (nm)	Particle Size, monoclinic (nm)
Calcination	x	600	100	n/a	21.3
	x	900	100	n/a	42.2
	o	600	24.7	25.6	20.5
	o	900	14.6	32.5	27.3
	o	1400*	0	-	n/a
Hydrothermal	x	200	22.4	14.3	17.0
	x	220	37.5	16.7	19.3
	o	200	0	10.0	n/a
	o	220	0	13.9	n/a

Fig. 4. Compaction behaviors of 3Y-ZrO₂ particles with different crystallization process.

Figure 3 shows the cross-sectional TEM micrographs of crystallized Y-doped ZrO₂ particles synthesized by calcination and hydrothermal treatment. The spherical shape of the amorphous particle was maintained after both crystallization processes. It was observed that the calcined particles had a smooth surface, shrunken size (~ 161 nm), and dense microstructure due to hard aggregation between primary particles (Fig. 3(a)). On the other hand, after hydrothermal treatment, the particle surface was rough and the average particle size was similar to that of Y-coated amorphous ones (Fig. 3(b)). In particular, the hydrothermal treated particles were porous microstructures (weak agglomerates) composed of small primary particles with a size of 14 nm, as calculated by Scherrer's equation (Table 1).²²⁾ When Y(NO₃)₃·6H₂O aqueous solution was used as the Y source in hydrothermal treatment, the initial spherical shape was not retained and separated into individual nanoparticles. In the hydrothermal treatment, the spherical shape was kept in a neutral pH region, but separated at acid and basic pH regions.

To confirm the forming property of the prepared particles, compaction behavior was characterized by relative density as a function of compaction pressure, which is shown in Fig. 4. The curve of pressure vs. green density represents the compaction behavior of the particles. Most commercialized particles for sintering are spray dried particles in order to achieve a high green density.²³⁾ When the spray dried particles were broken into primary particles, the slope of the curve increased due to the rearrangement of secondary spherical particles and the filling of the interstices with the primary particles. However, the calcined particles had a linear relationship between their green density and compaction pressure. On the other hand, the hydrothermally crystallized ones had the same compaction behavior as spray dried particles. The deflection point was 50 MPa (the spherical particles begin to break down) and final green density was 58% relative density at 200 MPa. To compare

Fig. 5. SEM micrographs of the fracture surface of green body made by uniaxial pressing of the Y-doped ZrO₂ powders, which were crystallized by the calcinations (a, c, and e) and hydrothermal treatment (b, d, and f). Applied pressures are 50 MPa (a and b), 100 MPa (c and d), and 150 MPa (e and f).

the degree of agglomeration between calcined particles and hydrothermal treated ones, we observed the fracture surface of the green body which was prepared by universal test machine with 1mm/min cross head speed (Fig. 5). While calcined particles maintained their spherical shape until 150 MPa, the hydrothermal treated ones were broken down at 50 MPa. Usually conventional forming (uniaxial pressing) is not applied to nanoparticles due to low green density and the non-uniform microstructures caused by wall friction and hard agglomeration. These results show that particles which were prepared by thermal hydrolysis followed by hydrothermal crystallization have advantages for green body forming and good sinterability.

4. Conclusions

It was shown that monodispersed spherical 3Y-ZrO₂ agglomerates could be synthesized by thermal hydrolysis, followed by crystallization processes (calcination at 600°C for 2 h and hydrothermal treatment at 220°C for 2 h). While calcined particles had a strong aggregation between primary particles, hydrothermal treated ones had a soft agglomerate of primary particles with a size of 14 nm. The hydrothermal treated ZrO₂ particles showed better compaction behavior than the calcined ones, which is attributed to the rearrangement of secondary spherical particles and the filling of the interstices with the primary particles.

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