Initial Sintering Mechanism of Fine Zirconia Particles Including a Small Amount of Alumina

Koji MATSUI, Nobukatsu OHMICHI, Michiharu OHGAI, Takanori YAMAKAWA,* Masato UEHARA,* Naoya ENOMOTO¹ and Junichi HOJO¹

Synthetic Chemicals Production, Tosoh Corporation, 4560, Kaisei-cho, Shunan, Yamaguchi 746-8501, Japan
¹Department of Applied Chemistry, Faculty of Engineering, Kyushu University, 6-10-1, Hakozaki, Higashi-ku, Fukuoka 812-8581, Japan

The sinterabilities of fine zirconia powders including 5 mass% Y₂O₃ were investigated with emphasis on the effect of Al₂O₃ addition on densification at the initial stage. The powders were pressed into disks and sintered at 1100–1500°C in air. When a small amount of Al₂O₃ was added, high-density sintered bodies were obtained at a low temperature. The shrinkage of powder compact in the course of heating was measured by a dilatometric method, indicating that the addition of Al₂O₃ increased the densification rate with elevating temperature. The activation energies of sintering were determined by analyzing the densification curves. The activation energy at the initial stage of sintering decreased by Al₂O₃ addition. The analysis of isothermal shrinkage curves exhibited that the diffusion mechanism changed from grain-boundary to volume diffusions by addition of Al₂O₃. It is concluded that the Al₂O₃ addition enhanced the densification because of decreasing the activation energy of sintering.

Key-words: Zirconia, Alumina, Initial sintering, Shrinkage, Diffusion, Activation energy

1. Introduction

Yttria-stabilized tetragonal zirconia polycrystal (Y-TZP) has been known as an important structural ceramics, with excellent mechanical properties such as high strength and fracture toughness, and used for products of the optical fiber connector, grinding media, and precision parts. The appearance of Y-TZP with the higher characteristic and reliability is desired to spread the zirconia product market and to propel a new application development. Hydrolysis is the most common method for synthesizing Y-TZP powder. To develop new Y-TZP powder with high quality, which is excellent in forming and sintering characteristics, by the hydrolysis method, it is important to analyze, in detail, the relationship between the particle structure and the sintering mechanism of Y-TZP powder and to clarify the sintering-control factors. From such a viewpoint, to control closely the particle structure of Y-TZP powder, we have made clear the formation mechanism of monoclinic hydrous-zirconia particles in the hydrolysis of ZrOCl₂ solutions and the mechanism of monoclinic-to-tetragonal phase transformation which occurs with dissolution of a stabilizer at calcination.¹,² We think that the next target of study on Y-TZP powder makes clear the sintering mechanism using the fine zirconia powder, with the particle structure controlled closely, manufactured by the hydrolysis method.

The initial sintering on various ceramics powders has been investigated previously by many researchers and several sintering-rate equations have been reported for the kinetic analysis in the initial stage of sintering.³⁻¹⁰ Young and Cutler have derived the sintering-rate equations which can analyze quantitatively densification in the initial sintering stage under constant rates of heating (CRH) and reported that, as conclusion of the analytical result using derived equation, the initial sintering step for yttria-stabilized zirconia is explained by a grain-boundary diffusion mechanism.⁵ Wang and Raj⁶,⁷ have derived the sintering-rate equation for the quantitative analysis of shrinkage data measured by CRH techniques and, using the derived equation, estimated the activation energies at the intermediate sintering stage of zirconia (with Y₂O₃), and Al₂O₃/zirconia (with Y₂O₃) composite. For research of zirconia sintering mechanism using the kinetic analysis, the effects of various additives on the diffusion mechanism have never been clarified in previous papers. From the industrial standpoint, it is particularly important to clarify the role of Al₂O₃ which is one of the additives.

In the present study, Al₂O₃, which is one of sintering-acceleration agents, was noted, and the effect of added Al₂O₃ on initial sintering of fine zirconia powder manufactured by the hydrolysis method was investigated.

2. Experimental

2.1 Specimen preparation

The fine zirconia powder including 5.2 mass% Y₂O₃ with 15 m²/g specific surface area (TZ-3Y grade, Tosoh, Japan) and fine Al₂O₃ powder (Aerosil, Japan) with ~100 m²/g specific surface area were used as starting powders. The fine zirconia powder with 0.23 mass% Al₂O₃ addition (3YAl₂O₃) was prepared by wet-milling the fine zirconia and Al₂O₃ powders with a vibration mill. To compare with the sintering behavior of the 3YA powder, the fine zirconia powder without Al₂O₃ addition (3Y) also was prepared by wet-milling only the fine zirconia powder under the same process. These powders were pressed uniaxially into a disk under 70 MPa and afterwards isostatically at 200 MPa. The resulting green compacts were sintered at 1100–1500°C for 2 h in air (heating rate 100°C/h).

2.2 Density and grain size measurements

The density of sintered bodies was measured by the Archimedes method. In the case of the sintered bodies with relative densities of <80%, the density was calculated from the weight and the size. Scanning electron microscopy (SEM; Model S-5200, Hitachi, Japan) was used to measure the average grain sizes of the sintered bodies. SEM specimens were polished with 3 µm diamond paste and then thermally etched for 1 h at a temperature lower by 50°C below each sintering temperature in air. The average grain size was measured by the Planimetric method.¹¹

2.3 Analysis of sintering behavior

For the green compacts made under the same pressing condition as above, the shrinkage of the green compacts with sintering was measured using a dilatometer (Model DL9700, ULVAC, Japan). The specimen size was 6 mm³ x 15 mm.
The reproducibility of shrinkage data mentioned later has close connection with the densities of the green compacts used for CRH measurements. The range of the relative densities of the prepared green compacts was 48.0–48.6%. The shrinkage measurements by CRH techniques were performed in the range from room temperature to 1500°C at heating rates of 5, 10, 15, and 20°C/min in air. The dilatometer was calibrated using sapphire as a standard specimen. Using the thermal expansion coefficient of Y–TZP, \( \alpha \), the thermal expansions of the specimens were corrected from the observed shrinkages. Assuming isotropic shrinkage of green compact, the density \( \rho(T) \) at a given temperature \( T \) is given by Eq. (1),

\[
\rho(T) = \left( \frac{L_T}{L(T)} \right)^3 \rho_f
\]

where \( L_T \) and \( L(T) \) are the final length and the length at \( T \) for the specimen, respectively. \( \rho_f \) indicates the final density measured by the Archimedes method. The \( \rho(T) \) value at a given temperature was calculated using Eq. (1). The isothermal shrinkage measurements were performed as follows. The temperature of the specimens was firstly raised at a constant rate of 10°C/min to 600°C, held at that temperature for 10 min, and subsequently raised rapidly at about 50°C/min rate to 1025°C. The shrinkage was measured as a function of time at the constant temperature of 1025°C for 3 h. In the same manner as above, the calibration of dilatometer and the thermal expansion correction of the specimens were carried out for the observed shrinkage.

The decrease in specific surface area of the green compacts with sintering was measured for those sintered in a low temperature region in which the shrinkage was little observed. Using the same green compacts as above, they were sintered at 600–800°C for 3 h in air (heating rate 10°C/min). The specific surface areas of the sintered specimens were measured by a BET method using nitrogen as adsorption gas (Model ASAP2000, Shimazu, Japan). Before measurement, the sintered specimens were broken softly to be put in a glass vessel for measurement and then pretreated at 120°C in vacuum.

3. Results and discussion

3.1 Densification and grain growth

Figure 1 shows the change in relative densities of specimens 3Y and 3YA with sintering temperature. The relative density of 3YA including 0.23 mass% \( \text{Al}_2\text{O}_3 \) was higher than that of 3Y at lower temperatures and attained 99% of theoretical density at 1300°C. Figure 2 shows SEM micrographs of polished and etched surface of 3Y and 3YA sintered at 1100, 1300 and 1500°C. The grain sizes of both 3Y and 3YA increased as the sintering temperature increased. To examine quantitatively the grain-growth behavior with the increase in sintering temperature, the average grain sizes of 3Y and 3YA were determined by the Planimetric method. As shown in Fig. 1, the relationships between the grain size and the sintering temperature were plotted onto the same curve for 3Y and 3YA. These experimental results revealed that, on adding a small amount of \( \text{Al}_2\text{O}_3 \) to the fine zirconia powder, the sintering rate increased remarkably, whereas the grain growth process was little affected.

3.2 Densification behavior in the initial stage

To probe the effect of added \( \text{Al}_2\text{O}_3 \) on the sintering rate, the shrinkage behavior of green compacts of 3Y and 3YA in the course of heating was analyzed by a dilatometric method. Figure 3 shows the change of the shrinkage in the course of heating at 10°C/min. As seen in Fig. 3(A), the starting temperature of shrinkage was \( \sim 930°C \) and nearly equal for 3Y and 3YA. The shrinkage of 3YA was greater than that of 3Y at temperatures above \( \sim 1090°C \) and beyond this temperature, the shrinkage of 3YA increased rapidly.

To compare the behavior of the initial shrinkage between 3Y and 3YA, the shrinkage curves were enlarged in the initial stage (Fig. 3(B)). Up to the temperature of \( \sim 1090°C \), the shrinkage of 3Y was greater than that of 3YA, whereas beyond this temperature, the shrinkage of 3YA increased rather than that of 3Y. The results obtained at heating rates of 5, 15, 20°C/min also showed the similar tendency as above. To clarify the influence of added \( \text{Al}_2\text{O}_3 \) on the initial shrinkage region, the decreasing behavior of the specific surface area with the in-
increase in temperature was examined in the range from 600 to 800°C in which the shrinkage was little observed (Fig. 4). The specific surface areas of both 3Y and 3YA decreased as the temperature increased. At each temperature, the specific surface area of 3Y was smaller than that of 3YA. This result revealed that added Al₂O₃ interfered with the decrease in specific surface area in the low temperature region. The decrease in specific surface area corresponds to formation and growth of neck parts between particles. The present results mean that added Al₂O₃ interfered with the neck formation and growth in the low temperature region until the shrinkage started.

3.3 CRH shrinkage analysis

Using the shrinkage curves in Fig. 3, the temperature dependences of the relative density (ρ) and the densification rate (dp/dT) were determined by Eq. (1) (Fig. 5). The relative density of 3YA was higher than that of 3Y at temperatures above ~1100°C. The densification rate of 3YA increased more rapidly than that of 3Y when the temperature exceeded ~1050°C, and the temperature at peak maximum of the densification-rate curve of 3YA shifted to the lower temperature than that of 3Y. Figure 6 shows the temperature dependences of the densification rates of 3Y and 3YA measured at 5-20°C/min heating rates. The densification-rate curves of both 3Y and 3YA shifted to higher temperature as the heating rate increased. The shift of the densification-rate curve of 3YA with the increase in heating rate was greater than that of 3Y. The present results indicate that the densification rate of the fine zirconia powder increased remarkably by adding Al₂O₃ in the low temperature range below 1300°C.

To analyze quantitatively the effect of added Al₂O₃ on the densification rate, the activation energy at the initial stage of sintering was determined by applying the sintering-rate equation to the above results. The sintering-rate equation at initial stage in the CRH process is given by Eqs. (2) and (3).⁴

\[ \ln \left[ T \frac{dT}{dt} \left( \frac{dp}{dT} \right) \right] = \frac{Q}{RT} + \alpha \]  \hspace{1cm} (2)

\[ \alpha = \ln \left[ f(\rho) \right] + \ln \left[ \frac{C_1^{1/2}}{R} \right] - m \ln d \]  \hspace{1cm} (3)

Here, \( T \) = absolute temperature, \( t = \text{time} \), \( \rho = \text{density} \), \( Q = \text{activation energy} \), \( R = \text{gas constant} \), \( f(\rho) = \text{function of density only} \), \( C = \text{constant} \), \( V = \text{molar volume} \), \( d = \text{grain size} \), and \( m = \text{grain size power law} (m = 3; \text{lattice diffusion}) \). Eqs. (2) and (3) can be applied in the following way. For different \( dT/dt \)-values of 5, 10, 15, and 20°C/min, the \( T \) and \( dp/dT \)-values at the same relative density were determined, and these values were plotted in the Arrhenius-type between \( T(dT/dt) \) \( (dp/dT) \) and 1/\( T \). The activation energy at each relative density was determined from the slope of the straight line in the Arrhenius-type plot (Fig. 7). The value of \( \alpha \) term was also determined from the intercept of the straight line in the plot. Here, the present analysis was performed in the shrinkage range below ~4% (namely, corresponding to the relative density range below 54%), which satisfy the initial sintering condition without grain growth. Figure 8 shows the activation energy and \( \alpha \) at 49.5-54% relative densities. Up to the relative density of 50%, the activation energies of 3Y and 3YA revealed similar values, whereas beyond this relative density, the activation energies of 3YA were lower than those of 3Y. Averaging severally the activation energies of 3Y and 3YA revealed similar values, whereas beyond this relative density, the activation energies of 3YA were lower than those of 3Y. According to Eq. (3), the low \( \alpha \)-value of 3YA suggests that the surface
energy of zirconia particles was reduced by Al₂O₃ addition.

3.4 Isothermal shrinkage analysis

It is thought that the decrease in activation energy with the addition of Al₂O₃ occurs by the change in diffusion mechanism. The isothermal shrinkage behavior of 3Y and 3YA was examined to clarify the diffusion mechanism. Figure 9(A) shows the change of the shrinkage with heating time at a constant temperature of 1025°C. When the heating time increased, the shrinkage of 3YA was greater than that of 3Y. The sintering-rate equation of isothermal shrinkage in the initial step of sintering is given by Eq. (4).
\[
\left( \frac{\Delta L}{L_0} \right) = \left( \frac{K \eta D}{kT a^p} \right)^n t^n
\]

Taking logarithms, it becomes
\[
\log \left( \frac{\Delta L}{L_0} \right) = n \log t + n \log \left( \frac{K \eta D}{kT a^p} \right)
\]

where, \( \Delta L \) = change in length of the specimen, \( L_0 \) = initial length of the specimen, \( K \) = numerical constant, \( \eta \) = atomic volume, \( k \) = Boltzmann's constant, and \( a \) = particle radius, \( D \) = diffusion coefficient, \( p \) = constant, \( n \) = order depending on the diffusion mechanism. Eq. (4) is applicable to the shrinkage range below \( \sim 4\% \) which satisfy the initial sintering condition.

To apply Eq. (5) to the above results, the isothermal shrinkage curves were converted to the log-log plots (Fig. 9 (B)), and the \( n \)-values of 3Y and 3YA were determined from the slopes of the straight lines. The determined \( n \)-values of 3Y and 3YA were \( n = 0.32 \) and \( n = 0.40 \), respectively. According to two-sphere shrinkage models proposed by several researchers, the \( n \)-value ranges of grain-boundary and volume diffusions are of \( n = 0.31 - 0.33 \) and \( n = 0.40 - 0.50 \), respectively.\(^{18}\) Comparing them with the above \( n \)-values determined experimentally, the diffusion mechanisms of 3Y and 3YA are assigned to grain-boundary and volume diffusions, respectively. Young and Cutler\(^{18} \) reported that the initial sintering for yittria-stabilized zirconia was explained by grain-boundary diffusion. The analytical result of 3Y agrees with this report. This result reveals that on adding \( \text{Al}_2\text{O}_3 \), the diffusion mechanism changed from grain-boundary to volume diffusion. Taking into account the results obtained from CRH and isothermal shrinkage analyses, it is clarified that added \( \text{Al}_2\text{O}_3 \) changes the diffusion mechanism from grain-boundary to volume diffusions, and increases remarkably the densification rate because of decreasing the activation energy of volume diffusion.

3.5 Sintering mechanism in the initial stage

Based on the present results, the effect of added \( \text{Al}_2\text{O}_3 \) on the initial sintering stage is considered as follows. In general, at the initial sintering stage, when the green compact is sintered, the necks are first formed and then grow at the contact points among particles to which the diffusion species migrate. When the mass transport proceeds by the surface diffusion mechanism, the shape change of the green compact is not observed because the distances between the centers of particles do not change. In case of the grain-boundary and volume diffusion mechanisms, the green compact shrinks because the center of particle approaches to each other. The change of surface area without shrinkage observed below 800°C (Fig. 4) means that the surface diffusion occurs in the low temperature range. Above \( \sim 930^\circ\text{C} \), the densification occurs by grain-boundary or volume diffusion, but the behavior is complicat-
ed with or without added $\text{Al}_2\text{O}_3$.

Figure 10 shows the model of the initial sintering process in the fine zirconia powder with a small amount of $\text{Al}_2\text{O}_3$. The specific surface areas of the starting zirconia and $\text{Al}_2\text{O}_3$ powders were 15 and $\sim 100 \text{ m}^2/\text{g}$, respectively. Using Eq. (6), the average particle sizes of these powders were estimated by assuming spherical particle shape.

$$D = \frac{6}{\rho S}$$

Here, $D$ = average particle size, $\rho$ = density, $S$ = specific surface area. The $\rho$-values of zirconia and $\text{Al}_2\text{O}_3$ were used as 6.05 and 3.99 g/cm$^3$, respectively. The average particle sizes of the zirconia and $\text{Al}_2\text{O}_3$ powders were 66 and $\sim 15$ nm, respectively. Therefore, the 3% zirconia powder in the present experiment was the mixture of zirconia particles with finer $\text{Al}_2\text{O}_3$ particles. In the temperature region where the shrinkage is not observed (that is, below $\sim 1000^\circ\text{C}$), since the decrease in the specific surface area is retarded, added $\text{Al}_2\text{O}_3$ interferes with neck formation and growth by surface diffusion (Fig. 10 (A)). Contrary to this behavior, at above $\sim 1000^\circ\text{C}$, added $\text{Al}_2\text{O}_3$ changes the diffusion mechanism from grain-boundary to volume diffusions and increases remarkably the densification rate because of decreasing the activation energy of volume diffusion (Fig. 10 (C)). Hence, it seems that the existental state of added $\text{Al}_2\text{O}_3$ changes at $\sim 1000^\circ\text{C}$.

$\text{Al}_2\text{O}_3$ and $\text{ZrO}_2$ (without $\text{Y}_2\text{O}_3$) are known to exhibit very limited mutual solubility ($\sim 0.1\%$ at $1300^\circ\text{C}$) and the solubility of $\text{Al}_2\text{O}_3$ in $\text{ZrO}_2$ increases as the temperature increases. Ikuhara et al. have reported that the dynamic behavior with heating (from 900 to 1350°C) of the mixed powder of fine zirconia particles including 2.5 mol% $\text{Y}_2\text{O}_3$ (with 50 nm diameter) and $\text{SiO}_2$ particles (with 10 nm diameter) was observed by in-situ observation technique using a transmission electron microscopy, and most of $\text{SiO}_2$ particles in the mixed state were adsorbed into the zirconia grains at $\sim 1300^\circ\text{C}$. Analogizing from these reports, it is assumed that a part of added $\text{Al}_2\text{O}_3$ particles begin to dissolve in zirconia particles at the temperature of $\sim 1000^\circ\text{C}$ so that the behavior of neck formation and growth reverses (Fig. 10 (B)), and the amount of dissolved $\text{Al}_2\text{O}_3$ increases as the sintering temperature increases (Fig. 10 (C)). The decrease of $\alpha$-value by $\text{Al}_2\text{O}_3$ addition in Fig. 8 means the decrease in surface energy. Therefore, the segregated dissolution of $\text{Al}_2\text{O}_3$ on the particle surface may be considered. Accordingly, it is concluded that as the result of dissolution of added $\text{Al}_2\text{O}_3$, the diffusion mechanism changes to volume diffusion and the densification rate increases remarkably through the decrease in activation energy of volume diffusion.

4. Conclusions

In the present study, the effect of added $\text{Al}_2\text{O}_3$ on initial sintering of fine zirconia powder including 5 mass% $\text{Y}_2\text{O}_3$ manufactured by the hydrolysis method was investigated. The following conclusions were obtained.

(1) When a small amount of $\text{Al}_2\text{O}_3$ particles was added to the fine zirconia powder, the sintering rate increased remarkably whereas the grain growth process was little affected. CRH shrinkage and specific surface area measurements revealed that added $\text{Al}_2\text{O}_3$ interfered with the decrease in the specific surface area in the low temperature region in which the shrinkage was little observed, and beyond the temperature range, increased remarkably the densification rate.

(2) CRH and isothermal shrinkage analyses revealed that added $\text{Al}_2\text{O}_3$ changed the diffusion mechanism from grain-boundary to volume diffusions, and increased remarkably the densification rate because of decreasing the activation energy of volume diffusion. This initial sintering behavior can be explained by taking into account that added $\text{Al}_2\text{O}_3$ particles dissolve in zirconia.

Reference

[in Japanese].


