Evaluation of densification and grain-growth behavior during isothermal sintering of zirconia

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The densification behavior during the isothermal sintering of 7.8 mol % Y2O3-stabilized zirconia was examined in the intermediate and final stages of sintering. In the intermediate stage, it is shown that the relationship between the grain size and the relative density is not invariant, but is temperature dependent. The relationship is combined with the measured densification rate to evaluate the grain size exponent, the activation energy and an unspecified function of density. The evaluation of the characteristic parameters indicates that the densification and the grain growth are related to a mechanism of grain-boundary diffusion and sliding. The densification rate predicted with the evaluated parameters shows a good consistency to the measured rate. In the final stage, the densification rate is inversely proportional to the grain size, and the kinetics is well explained by using the diffusive model modified with a gas pressure in closed pores.

Key-words : Densification, Kinetics, Grain growth, Sintering, Activation energy

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1. Introduction

Sintering is a process of densification or pore shrinkage in powder compacts. The process has been divided into three stages: initial, intermediate and final stages, and the representative phenomenon of densification can be characterized by the growth of neck between particles, the shrinkage of open pores and closed pores, respectively. Various mechanisms such as diffusion, grain-boundary sliding, plastic and viscous flows were considered for the densification, and various rate equations were proposed depending on the mechanism.1) The typical rate equation of densification in the intermediate and final stages can be represented as

\[ D = A \exp\left(-\frac{Q_D}{RT}\right) \frac{f(D)}{G^n} \]  \hspace{1cm} (1)

where \(D\) is the densification rate, \(R\) is the gas constant, \(T\) is the absolute temperature, \(Q_D\) is the activation energy of densification, \(n\) is an exponent of the grain size \(G\), and \(f(D)\) is an unspecified function of the relative density \(D\). For the evaluation of the densification mechanism, the activation energy \(Q_D\) and the grain size exponent \(n\) are usually estimated from a slope between \(\ln(TD)\) and 1/T and a slope between \(\log(D)\) and \(\log(G)\) at a given density, respectively. Conventionally, experimental data are collected at a given density in order to avoid the complication of the unknown \(f(D)\).

In the conventional method, \(Q_D\) is usually evaluated under an assumption of the invariant \(G-D\) relationship where the grain size is solely related to the relative density and independent of the history of heating. During sintering of powder, the invariant \(G-D\) trajectory was experimentally reported by several studies,2) so that almost all researches including the master-sintering curve method3)6) adopted the invariant \(G-D\) relationship. Bernard-Granger and Guizard6) analyzed the relationship between densification and grain growth for the shrinkage of the pores located at grain corners, and proposed various theoretical \(G-D\) relationships depending on the mechanism. Though their theoretical relationships should be limited to the final stage of sintering, the concept of a common \(G-D\) relationship may be applicable to the intermediate stage, providing an invariant mechanism of densification and grain growth. The mechanism of grain growth, however, is variable depending on the relative density, grain size and temperature. Since the dominant mechanism of grain growth (diffusion, pore drag, evaporation-condensation, grain rotation etc.) or the contribution of the mechanisms to grain growth may be dependent on the temperature, the \(G-D\) relationship would more or less be dependent on the temperature. The different activation energy between grain growth and densification, which is an important idea in the two-step sintering method,7) would also result in the \(G-D\) relationship to be temperature-dependent, as will be shown later. In the earlier studies reporting the invariant relationship,2)–5) the slight variation of the grain size at different temperatures might not be distinguished with a sufficient accuracy, due to an experimental limit for nano-sized grains in highly porous bodies. In this study, it is shown for the first time that the \(G-D\) relationship is dependent on the temperature and how the densification rate is affected by the \(G-D\) relationship.

Accepting the invariant \(G-D\) relationship makes the experimental evaluation of \(n\) difficult. Under the invariant relationship, only single grain size is allowed at a given density, which is unable to obtain a slope between \(\log(D)\) and \(\log(G)\) for the evaluation of \(n\) in Eq. (1). In order to avoid the problem, Wang and Raj17) used a powder of different initial particle sizes, and Chakravarty and Chokshi18) adjusted the density forcibly by using an external pressure at different grain sizes during sintering. The different powder and the pressure-assisted densification, however, induce a change in the pore structure and resultantly in \(f(D)\) of

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Eq. (1). The non-fixed \( f(D) \) at a given density by the operation causes an error in the evaluated \( n \)-value.

\( f(D) \) is a mixed function of the bulk viscosity and the sintering stress, and is related to the pore structure and the densification mechanism. Usually, it is recognized that \( f(D) \) is solely related to \( D \) and independent of the temperature. Dependent on the densification model, various theoretical expressions have been proposed for \( f(D) \), based on the continuum and discrete approaches.\(^9\) The present authors also proposed an equation of \( f(D) \) for a model of densification by grain-boundary sliding/diffusion and by grain-boundary diffusion in the intermediate\(^10\) and final stage.\(^11\) respectively. Hansen et al.\(^12\) estimated experimentally the variation of \( f(D) \) with densification by applying their sintering model. Despite the efforts, however, the experimental comparison of the theoretical analysis was not sufficient and satisfactory.\(^9\) Almost all researches of the densification mechanism are focused on the evaluation of \( Q_0 \) and \( n \), and the empirical or experimental expression of \( f(D) \) has rarely been conducted. Considering that the sintering of powder is obviously a complicated process, it is not easy to draw out the theoretical \( f(D) \) to describe the densification kinetics explicitly. The experimental determination of \( f(D) \) is rather an effective way to evaluate the densification kinetics, and the experimental \( f(D) \) can be compared with the theoretical \( f(D) \) to evaluate the densification model. In this study, a method is proposed to determine experimentally the entire feature of \( f(D) \). By using the experimental \( f(D) \), the grain size exponent \( n \) and the activation energy \( Q_0 \) are evaluated with one kind of zirconia powder. The densification kinetics and mechanism are examined in a more rigorous manner.

2. Experimental

Commercial \( \text{ZrO}_2 \) powder containing 7.8 mol% \( \text{Y}_2\text{O}_3 \) (TZ-8Y, Tosoh; 8YSZ) with a specific surface area of 13 m\(^2\)/g and a crystallite size of 25 nm was used as a raw material. The as-received powder was pressed uniaxially at \( \leq 1 \) MPa into a compact of 30 mm diameter, and then pressed isostatically at 392 MPa in water. The powder compact has a green density of 3.13 g/cm\(^3\), corresponding to a relative density of 0.53 with an absolute density of 5.90 g/cm\(^3\) for 8YSZ. From the powder compact, rectangular specimens of 4 mm \( \times \) 4 mm \( \times \) 10 mm were cut, and the two surfaces of 4 mm \( \times \) 4 mm were carefully machined to be parallel.

The isothermal shrinkage of the specimen was measured in air using a dilatometer (DIL 402C, Netzsch) equipped with an alumina rod and holder. The alumina rod contacted to the specimen at 0.25 N, corresponding to a stress of \( \sim 10 \) kPa that is sufficiently lower than the intrinsic sintering stress of conventional ceramics.\(^13\) The shrinkage measurement was conducted at constant sintering temperatures between 1100 and 1300°C with an interval of 50°C. The specimen was heated to the temperature at a rate of 10°C/min. The measured shrinkage was corrected with the thermal expansion of the fully densified 8YSZ, which had been measured separately, and then converted to the relative density. The measurement was continued until the densification reached a rate of \( \leq 5 \times 10^{-6}/\)min. At above 1200°C, when the densification rate reached \( 4 \times 10^{-6}/\)min, the relative density was higher than 0.98. At 1150°C, the measurement was stopped when the relative density reached 0.86 after a sintering time of 1.8 \( \times \) 10\(^3\) min (\( \sim 13 \) days).

After the densification, the density of the specimen was measured by three different methods: the Archimedes method, a change in the specimen length and the dilatometer. For all samples, the three densities are within an error of 1%, which confirms the validity of the shrinkage data. The polished surface of the sample after prescribed densification was observed using a scanning electron microscope (SEM, SU-8000, Hitachi). Before SEM observation, the polished surface was etched in air for 1 h at the temperature lower than the sintering temperature by 150°C, and was coated with Pt. For one sample, 3–7 photographs were taken, each of which includes more than 400 grains. From each photograph, the number and the area of largest grains covering 20–21% of the total area were measured using a software of Photoshop. The grain size in this study was defined as an average size of the largest grains. The number of the largest grains for each photograph is 25–50, and the present grain size is about 2.1–2.4 times the size measured by the conventional mean-intercept method for selected samples. Though the present grain size is different from the conventionally defined size, the two grain sizes would be linearly proportional each other, if normal grain growth occurs. For the isothermal sintering at 1150 and 1250°C, the grain size was examined in the full densification range with an interval of \( \Delta D = 0.02 \) or 0.03.

3. Results and discussion

3.1 Densification

The densification behavior of 8YSZ with respect to the sintering time \( t \) is shown in Fig. 1. In the \( D \)-log\( (D) \) plot, a linearity with identical slope is observed partially at each temperature. The linear relationship, often called a semilogarithmic law in sintering, was derived theoretically by Coble.\(^14\) In the Coble’s model, \( f(D) \) of Eq. (1) is constant, and the grain growth behavior is usually represented as \( G = G_0 \exp(-E/G_t) \), where \( m \) is the grain growth exponent. When \( m \) is equal to the grain size exponent \( n \), Eq. (1) becomes \( D = D_0/t \), and then a linear relationship between \( D \) and log\( (t) \) is obtained. In Fig. 1, however, the linearity is observed in a limited density range of 0.75–0.95. In a range of \( D < 0.75 \) and of \( D > 0.95 \), the densification behavior deviates from the semilogarithmic behavior. The inconsistency arises from both the constant \( f(D) \) in the Coble’s model\(^15\) and the condition of \( n = m \). \( f(D) \) must be a function of \( D \), and the \( m \)- and \( n \)-values may not be identical, as will be shown later. The \( m \)- and \( n \)-values may also be different in the intermediate and final stages. Hence, the semilogarithmic law is insufficient to explain the present densification of 8YSZ in a wide density range.

The entire densification behavior can be understood more intuitively from the dependence of the densification rate \( D \) on the relative density \( D \). As represented in Fig. 2, \( D \) decreases with densification and a linearity between log\( (D) \) and log\( (t) \) is observed in a wide density range. At low densities (0.60 \( \leq D \leq 0.85 \)), \( D \) can be represented approximately as

![Fig. 1. Densification behavior during isothermal sintering. The dotted lines have an identical slope.](image-url)
where the value of \( p \) decreases gradually with increasing temperature; \( p = 8.9 \) at 1150°C and \( p = 7.8 \) at 1250°C. In our previous study using a graphite rod and holder in Ar atmosphere,\(^{15}\) a similar relationship was observed at 0.6 ≤ \( D \) ≤ 0.7, but was interrupted at \( D > 0.73 \) by rapid grain growth. In this study under an air condition, however, the rapid grain growth and the unstable drop of \( D \) did not happen in such density range. The densification proceeded stably in a range of 0.60 ≤ \( D \) ≤ 0.85.

At high densities (\( D \geq 0.85 \)), \( D \) deviates from the linearity, and decreases rapidly. From the density dependence of \( D \), the densification behavior can be divided into two regions with a boundary at \( D = 0.85 \). The low- and high-density regions show different densification behavior, and seem to correspond to the intermediate and final sintering stages, respectively. The microstructural evolution during densification is shown in Fig. 3.

Here, it should be noted that the slope between log(\( D \)) and log(\( D \)) in a range of 0.60 ≤ \( D \) ≤ 0.85 varies slightly depending on the temperature. Why do the curves have a different slope? According to Eq. (1), two possibilities are considered; temperature-dependent \( f(D) \) and temperature-dependent \( G-D \) relationship. \( f(D) \) is widely recognized to be independent of the temperature, when the densification mechanism is fixed. In the next section, the temperature-dependent \( G-D \) relationship is examined, and the theoretical background is discussed.

### 3.2 Grain growth

The grain size defined in this study is focused on large grains, and is different from the conventional intercept size for all grains. For nano-sized grains at low densities, the boundary between pores and grains is unclear, so that it is difficult to distinguish the grains on the polished surface from those on the pore surface. Furthermore, the agglomeration of nano-sized grains makes the intercept size difficult to be measured. This is the reason why we focused on large grains. Large grains are easily distinguished from others. It is shown later [in Fig. (6)] that the present grain size also characterizes effectively the microstructural feature of the porous body during densification, even when the size distribution is bimodal.\(^{15}\)

The grain growth behavior during the isothermal sintering is shown in Fig. 4. At 1250°C in Fig. 4(a), the grain growth kinetics during densification is not constant, and is changed from \( G^{3.2} = G^{2.4} \) at around \( D = 0.85 \). The \( m \)-value of 4.2 at low densities (\( D \leq 0.85 \)) is close to 4, which corresponds to a mechanism of grain rotation accompanied by grain-boundary diffusion.\(^{16,17}\) Grain rotation may be a dominant mechanism of grain growth at low densities, particularly for nano-sized grains.\(^{16}\) Usually, grain rotation is driven by the reduction in the grain-boundary energy, and the rate is controlled by the energy-dissipation due to diffusion and viscous grain-boundary sliding.\(^{17}\) At low densities, many grains have free surfaces and are partially joined to the neighboring grains. Since the driving force for grain rotation is a summation of the change in the grain-boundary energy for all surrounding grain boundaries, the net energy reduction would be larger for the grains with less neighboring grains. In addition, for the grains with free surfaces and less grain-boundary area, the energy dissipated by diffusion for the accommodation of incoherent grain boundaries during rotation would be smaller. The rate of grain rotation accompanied by grain-boundary diffusion is proportional to \( G^{4.6} \) at 1150°C, which is slightly different from that (\( G^{4} \)) at 1250°C, which can also be explained by the grain rotation basically.

From the growth kinetics at low densities (\( D \leq 0.85 \)), the activation energy \( Q_G \) of grain growth was estimated by using an equation of

\[
G^{4.4} - G_0^{4.4} = e \exp(-Q_G/RT)t
\]

where \( t \) is the time, \( e \) is a constant, and \( G_0 \) is the grain size at \( t = 0 \). Here, the grain growth exponent \( m \) of 4.4 is an average value for 1150 and 1250°C. The estimated \( Q_G \) at low densities (\( D \leq 0.85 \)) is 620 kJ/mol, which value is much larger than that (331 kJ/mol) of 8YSZ films at high densities (\( D > 0.82 \))\(^{19}\) and than that (289 kJ/mol) of fully densified 8YSZ polycrystal (\( D > 0.98 \)).\(^{20}\) The considerably large \( Q_G \) can be explained by a difference in the growth mechanism at between low and high densities. The grain growth by grain rotation at low densities accompanies grain-boundary sliding as well as diffusion. The grain-boundary sliding occurs in a viscous manner, so that the rates of both grain rotation and grain growth are dependent on the viscosity of grain boundaries.\(^{17}\) Therefore, the larger \( Q_G \) at low densities can be attributed to the viscous sliding of grain boundaries during grain rotation.

At high densities (\( D \geq 0.85 \)), the number of contacting grains increases, and the rate of grain rotation decreases. Then, the grain
growth is controlled mainly by the diffusional process of boundary migration and pore drag. At high densities, the interaction between boundaries and pores is important for the grain growth. In the final stage of sintering, it is considered that the mechanism of grain growth is a mixture of the boundary-control (m = 2) and the pore-control (m = 2–4). In Fig. 4(a), the grain growth exponent of 2.6 at high densities (D ≥ 0.85) for 1250°C would be a mixture of the two controlling mechanisms. On the other hand, Matsui et al. reported a similar value of m (≈ 3) during sintering of 3 mol% Y₂O₃-stabilized tetragonal ZrO₂ polycrystal at high densities (D > 0.93), which was attributed to a solute drag.

A change in the grain growth kinetics indicates a transition of the mechanism. The growth mechanism of grain rotation at low densities is transitioned to that of the diffusional process at high densities. The transition with densification is explicitly shown in Fig. 4(b). For 1250°C, the G–D relationship can be represented as $G \sim D^{2.8}$ at $D \leq 0.85$ and $G \sim D^{1.4}$ at $D \geq 0.85$. Since the grain growth significantly affects the densification rate of Eq. (1), the change in the G–D relationship indicates that the densification behavior is also changed at around $D = 0.85$, as shown in Fig. 2. That is, for the present 8YSZ, the density of 0.85 is a boundary distinguishing the sintering stage. The upper limit of the intermediate stage can be defined to be $D = 0.85$.

An interesting point in Fig. 4(b) is that the $G$–$D$ relationship is dependent on the temperature, which have not been reported ever. In the intermediate stage, the $G$–$D$ relationship at 1150°C can be represented as $G \sim D^{2.8}$, which is slightly different from that ($G \sim D^{3.4}$) at 1250°C. During densification, the grain size is not only determined by the density, but also affected by the temperature. The temperature-dependent $G$–$D$ relationship may be understood by considering the contribution of various mechanisms. Although the grain rotation is a dominant mechanism of grain growth in the intermediate stage, several minor mechanisms also contribute to the grain growth, such as the pore control (surface diffusion, lattice diffusion, vapor transport) and the boundary control (boundary energy, solute drag). A change in the contribution of the minor mechanisms at different temperatures would yield a change in the grain-growth kinetics. Particularly, the surface diffusion, which is a non-densifying mechanism, may play an important role. The surface diffusion for a long time at low temperatures may contribute to the grain growth without significant densification, resulting in the temperature-dependent $G$–$D$ relationship.

The effect of the minor mechanisms on the $G$–$D$ relationship, however, might be insignificant in such small temperature range ($\Delta T = 100^\circ$C). The temperature-dependence can be explained theoretically by considering the activation energy. At a given density and grain size, the rate of densification and grain growth can be represented as $D \sim \exp(-Q_D/RT)/T$ and $G \sim \exp(-Q_G/RT)$, respectively. Then, $\Delta G/\Delta D$ is proportional to $T \exp[(Q_D - Q_G)/RT]$. For the present 8YSZ, the activation energy of grain growth ($Q_D$) and densification ($Q_D$) is 620 and 698 kJ/mol, respectively. The value of $Q_D$ is obtained in the next section. Using the two activation energies, the calculated value of $T \exp[(Q_D - Q_D)/RT]$ decreases from $10.4 \times 10^5$ K at 1150°C to $7.2 \times 10^5$ K at 1250°C with increasing temperature. That is, $\Delta G/\Delta D$ decreases with an increase in the temperature, which is qualitatively consistent to the temperature-dependent $G$–$D$ relationship in Fig. 4(b); $\Delta G/\Delta D$ at 1150°C is smaller than at 1250°C. Owing to the larger activation energy of densification in the intermediate stage, $\Delta G/\Delta D$ in Fig. 4(b) is at 1250°C than at 1150°C. The value of $\Delta G/\Delta D$ calculated from the experimental $D$ in Fig. 2 and the grain growth kinetics in Fig. 4(a) is also smaller at 1250°C than at 1150°C. Thus, the temperature-dependence of the $G$–$D$ relationship of the present 8YSZ can be attributed to the difference in the activation energy between densification and grain growth. Only for $Q_D \approx Q_D$, the $G$–$D$ relationship would nearly be independent of the temperature.

### 3.3 Densification kinetics in intermediate stage

The density dependence of the grain size is deeply related to the $p$-value or $D$ in Fig. 2. From Eq. (1) and the $G$–$D$ relationship in Fig. 4(b), the densification rate is represented as $D \sim f(D)D^{-2.86}$ and $D \sim f(D)D^{-2.48}$ at 1150°C and 1250°C, respectively. The larger density dependence of $D$ at 1150°C is responsible for the larger $p$ (8.9) compared to that (7.8) at 1250°C. It is obvious, therefore, that the varying slope between log($D$) and log($D$) in Fig. 2 is determined by the temperature-dependent $G$–$D$ relationship.

With the above experimental relationships, $f(D)$ and $n$ in Eq. (1) can be evaluated. From Eqs. (1) and (2) and the experimental $G$–$D$ relationship, $f(D)$ can be represented as

$$f(D) = cDG^n = D^{-8.9}D^{2.86}$$

at 1150°C  

(4a)

and

$$f(D) = cDG^n = D^{-7.8}D^{2.48}$$

at 1250°C  

(4b)

Since $f(D)$ is independent of the temperature, from the two equations, we obtain $n = 2.75$ and $f(D)D^{-1.31}$. The experimental $f(D)D^{-1.31}$ is useful for evaluating the theoretical models. The theoretical $f(D)$ can be represented as $f(D) = DP/K$, where $P$ and $K$ are the density term of the sintering stress and the bulk viscosity, respectively. Many theoretical equations have been
proposed as a function of $D$ for both $K$ and $P$, and the combination gives more than 50 theoretical equations of $f(D)$. Among them, some selected equations are compared with the experimental $f(D)$ in the intermediate stage. Here, the sintering stress $P = D^2$ is applied, which was proposed by Skorohod. For the bulk viscosity $K$, four equations of $D/(1 - D), D/\left[3 - 2D - (3D - 2D^2)^{1/2}\right], \ln(1 - D + 0.5D(D + 2))/D$ and $D/(1 - D)$ are selected, which were proposed by Skorohod, Scherer, Venkatachari and Raj, and Mackenzie and Shuttleworth, respectively. All these equations are clear without any adjustable parameters. The theoretical equations of $f(D) = DP/K$ are compared with the experimental $f(D)$ in Fig. 5, where only the empirical equation of Venkatachari and Raj shows a consistency to the experimental $f(D)$ in a density range of 0.76–0.85. Although all theoretical models are not examined, the comparison indicates that most existing densification models are insufficient for describing the actual densification behavior of the present 8YSZ powder in the intermediate stage. More elaborated densification model is required.

The $n$-value of 2.75 obtained from Eqs. (4a) and (4b) is close to 3, which corresponds to a mechanism of grain-boundary diffusion. Kim et al. analyzed the shrinkage of spherical pores during densification by the deformation of dense matrix surrounding the pores. In their model, the densification occurs by both grain-boundary diffusion and sliding, and the $n$-value is between 1 and 3 in the intermediate stage. Owing to the viscous sliding of grain boundaries, $n$ is less than 3, and the deviation from 3 increases with increasing boundary viscosity. The present $n$ of 2.75 is within the prediction of the model, and is also similar to the value (2.6) obtained for the identical powder under the reducing atmosphere, as reported in our previous study.

By using the experimentally determined $f(D)$, $n$ and $G$, the densification rate $[-d(D)/G^n]$ predicted from Eq. (1) is compared with the measured one in Fig. 6. In the intermediate stage $(0.60 \leq D \leq 0.85)$, the two $D$s are linearly proportional to each other, indicating that the determined $f(D)$ and $n$ are valid to predict the actual densification rate. Figure 6 also shows the data obtained using a graphite holder in Ar. In the reducing atmosphere, rapid grain growth occurred in a range of $0.73 < D < 0.80$. The grain size increased rapidly from 0.3 $\mu$m at $D = 0.74$ to 1.9 $\mu$m at $D = 0.79$, and the size distribution was remarkably bimodal. Owing to the rapid grain growth, the densification rate decreased rapidly by an order of 2. Despite the unnormal behavior of grain growth and densification, $D$ predicted using the present $f(D)$ and $n$ surprisingly reveals the identical linearity, as shown in Fig. 6. This means that the present $f(D)$ and $n$ determined in air is valid for the reducing condition, and also that the present grain size focused on large grains is useful in charactering the densification behavior of porous body with a bimodal size distribution.

With the determined $n$, the activation energy $Q_0$ of densification at different relative densities. $Q_0$ for the temperature-dependent $G-D$ relationship was obtained by taking the grain size into account.

![Fig. 5](image1.png) **Fig. 5.** Comparison of experimental and theoretical $f(D)$ for $P = D^2$ in the intermediate stage. $f(D)$ is normalized with the value at $D = 0.85$.

![Fig. 6](image2.png) **Fig. 6.** Comparison of predicted and measured densification rate at $0.60 \leq D \leq 0.85$.

![Fig. 7](image3.png) **Fig. 7.** Activation energy $Q_0$ of densification at different relative densities. $Q_0$ for the temperature-dependent $G-D$ relationship was obtained by taking the grain size into account.

### 3.4 Densification kinetics in final stage

The densification in the final stage has been characterized by...
the shrinkage of closed pores. According to the examination of open and closed pores during sintering of 8YSZ,\textsuperscript{30} the density range where solely closed pores exist is $D > 0.94$. At $0.87 < D < 0.94$, open and closed pores coexist. When the sintering stage is distinguished by the pore shape, the density range of the pure final stage is $D > 0.94$. However, from the apparent change both in the densification rate of Fig. 2 and in the $G$–$D$ relationship of Fig. 4(b), the upper limit of the intermediate sintering stage was defined to be $D = 0.85$ in this study. In the following, the density range of $D \geq 0.85$ is regarded as the final sintering stage.

In the final stage, the pore structure and/or the densification mechanism are different from those in the intermediate stage, so that the form of $f(D)$ should also be different. The typical densification behavior in the final stage has been described by the shrinkage of spherical pores located at grain corners by a mechanism of grain-boundary diffusion. Wilkinson,\textsuperscript{31} Pan and Cocks,\textsuperscript{32} and Kim et al.\textsuperscript{33} analyzed the shrinkage of the corner pores, and proposed the rate equation of densification as

$$DG^3 = cf(D)$$

$$= c(1 - \rho^{2/3})D^2[3\rho^{2/3} - (1 + \rho^{2/3})\ln \rho - 3]^{-1}$$

(5)

$$DG^3 = cf(D)$$

$$= cD[4.96\rho^{2/3} - 1.92\rho^{5/3} - 1.28 \ln \rho - 3.20]^{-1}$$

(6)

and

$$DG^3 = cf(D)$$

$$= cD^4[4.96\rho^{2/3} - 1.87\rho^{5/3} - 1.10 \ln \rho - 3.14]^{-1}$$

(7)

respectively. Here, $\rho (=1 - D)$ is the porosity, and the equations were reproduced using $P = D^2$ in pressureless sintering.\textsuperscript{52} The corner-pore models employing a mechanism of grain-boundary diffusion yield the $G^{-1}$-dependence ($n = 3$) of $D$, which is a typical feature of Coble creep.\textsuperscript{34} Eqs. (5)-(7) are compared with the experimental $DG^3$ ($= DD^4$) in Fig. 8(a). The experimental $DG^3$ increases with densification in a density range of $0.85 < D < 0.92$ and then decreases, whereas the theoretical $f(D)$ decrease continuously. From the comparison, the inconsistency is obvious, and the corner-pore models cannot explain the densification behavior of the present 8YSZ in the final stage.

Unlike the corner-pore model, Kim et al.\textsuperscript{15} proposed the $G^{-1}$-dependence ($n = 1$) of $D$ from the analysis of the shrinkage of the single spherical pore existing in a dense polycrystal by a mechanism of grain-boundary diffusion. In the diffusive model, the rate equation of densification can be reproduced as

$$DG = cf(D)$$

$$= c\rho^{2/3} D^{5/3}(3\rho^{-1} - 8\rho^{-2/3} + 6\rho^{5/3} - \rho^{-1/3})^{-1}$$

(8)

with the sintering stress of $P = D^2$. Despite the identical densification mechanism of grain-boundary diffusion, $D$ of Eq. (8) represents the $G^{-1}$-dependence ($n = 1$). Actually, in the diffusive model, $D$ shows larger dependence on the pore size than on the grain size.\textsuperscript{55} Equation (8) is also compared with the experimental $DG$ in Fig. 8(b). Equation (8) shows a good consistence to the experimental results in the final stage. Both $f(D)$ and $DG$ decrease with densification, and the slopes at $0.85 < D \leq 0.94$ are almost identical. The theoretical $f(D)$ begins to deviate from the experimental $DG$ at around $D = 0.94$, where all open pores are considered to be closed.\textsuperscript{30}

In the density range where solely closed pores exist, a gas pressure in the pores increases with densification, which reduces the effective sintering stress and resultanty the densification rate. The theoretical $f(D)$ of Eq. (8) can be modified by considering the effect of the gas pressure. According to Wilkinson,\textsuperscript{35} the gas pressure within the closed pores is given by $p_a(D - D_0)/\rho$, where $p_a$ is the atmospheric pressure and $D_0$ is the relative density where the gas pressure begins to increase due to the shrinkage of the closed pores. Then, Eq. (8) can be modified by multiplying $[1 - a(D - D_0)/\rho D^2]$, where $a$ is a constant. As shown in Fig. 8(b), $DG$ modified with the gas pressure ($a = 0.25$ and $D_0 = 0.94$) shows an excellent consistence to the experiments. It is obvious, therefore, that the densification behavior in the final stage can theoretically be explained by the $G^{-1}$-dependence of $D$ rather than by the well-known $G^3$-dependence. The $G^{-1}$-dependence of $D$ was also observed during pressure-assisted sintering of MgAl$_2$O$_4$ spinel.\textsuperscript{10,36} Although the experimental $f(D)$ was not determined in the final stage, the theoretical $f(D)$ of Eq. (8) explains well the densification behavior of the present 8YSZ.

Finally, in this study, the role of the viscous sliding of grain boundaries was discussed on both grain growth and densification. Conventionally, the sintering stage has been distinguished according to the pore shape. Kim et al.\textsuperscript{10,11} however, distinguished the sintering stage by a densification mechanism. In the intermediate stage of low densities, there is enough space of pores for particle re-arrangement (or grain-boundary sliding), and the shrinkage deformation caused by the grain-boundary sliding is the primary densification mechanism. In the final stage of high densities, there is no enough space for the shrinkage deformation of grain-boundary sliding, and the densification is dominated by diffusion only. The $G^{-1}$-dependence of $D$ in Eq. (8) is a result of the diffusive model. Hence, it was proposed that the presence or
absence of the viscous grain-boundary sliding is a criterion distinguishing the sintering stage. The present experimental results support the criterion, and the viscous sliding of grain boundaries should be considered more significantly in the intermediate stage of sintering.

4. Summary and conclusions

In the intermediate sintering stage of YSZZ (0.60 ≤ D ≤ 0.85), an experimental relationship was obtained between the densification rate D and the relative density D as D~D^γ. The value of γ is temperature-dependent and decreases gradually with increasing temperature. The variation of the p-value is related with the grain growth, and can be explained by using the G-D relationship. In the intermediate stage, the G-D relationship is not constant, and ∆G/AD decreases with an increase in the temperature, which corresponds to the variation of the p-value. The temperature-dependent G-D relationship can theoretically be explained by a difference in the activation energy between densification (698 kJ/mol) and grain growth (620 kJ/mol). Using the G-D relationship, the unspecifified function f(D) and the grain size exponent n in Eq. (1) were evaluated. The densification rate predicted using the evaluated parameters is consisten well to the measured rate. In the intermediate stage, the grain growth exponent (m) of ~4 indicates a mechanism of grain rotation, and the n-value of 2.75 is within the prediction of the densification model of grain-boundary diffusion/sliding. The role of the viscous grain-boundary sliding on both grain growth and densification was discussed during sintering of YSZZ. In the final sintering stage (D ≥ 0.85), the G-D relationship, the grain-growth kinetics and the densification rate are changed remarkably. DG decreases continuously with densification, and the behavior is well explained by the densification model of grain-boundary diffusion. The diffusive model modified with a gas pressure in closed pores shows an excellent consistence to the measured densification kinetics in a density range of D ≥ 0.85. The present study supports the G^-1-dependence of D in the final stage.

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References