Densification Kinetics during Isothermal Sintering of 8YSZ

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Abstract

The densification behavior during the isothermal sintering of 8YSZ was examined in the initial and intermediate stages of sintering. In the initial stage, a difficulty in evaluating the densification behavior arises from the transition of the stable pore structure and the limitation of the theoretical two-sphere model. In the intermediate stage, a linear relationship with a slope of $-1/2$ is observed between the densification rate and the time. An empirical equation of the densification kinetics is proposed and found to be valid in a wide density range. At a relative density of 0.6~0.73, the activation energy is 688 kJ/mol. Rapid grain growth is observed at a relative density of 0.73~0.8 and >0.9 for the isothermal sintering at 1200~1300 °C and 1400~1500 °C, respectively. The rapid grain growth reduced significantly the densification rate. The densification mechanism and grain growth behavior are also discussed.

Keywords: Densification; Kinetics; Grain growth; Sintering; Activation energy

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1. Introduction

Sintering is a process of densification or pore shrinkage. 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 close 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 stage can be represented as [2]

$$\dot{D} = A \frac{\exp(-Q/RT)}{T} \frac{f(D)}{G^n} \quad (1)$$

, where $\dot{D}$ is the densification rate, R is the gas constant, T is the absolute temperature, Q is the activation energy, n is an exponent of the grain size G , and $f(D)$ is a function of mainly the relative density D . In order to evaluate the densification mechanism, the activation energy Q and the grain-size exponent n are estimated conventionally from a slope between $\ln(T\dot{D})$ and $1/T$ and a slope between $\log(\dot{D})$ and $\log(G)$ at a fixed density, respectively. For both Q and n , the collection of experimental data at a fixed density is essential to avoid the complication of $f(D)$ in Eq. (1). $f(D)$, which also depends on the pore size and contains a term of the sintering stress, would be the most important parameter determining $\dot{D}$, particularly in the mechanical point of view. Many theoretical equations of $f(D)$ have been proposed, based on the continuum and discrete approaches [3-6]. The experimental $f(D)$, however, was rarely reported. Furthermore, the experimental verification of the theoretical $f(D)$ was not satisfactory [4,7].

Densification is obviously a complicated process, even when the grain growth is negligible. During densification, several phenomena take place simultaneously, i.e. particle rearrangement,

1 local densification, pore growth and shrinkage, size distribution of pores and grains, creep
2 deformation, change in pore shape, etc. Owing to the complication, it is difficult to draw out a
3 theoretical relationship to describe the densification behavior explicitly. For the reason, the
4 experimental determination of $f(D)$ may be an effective way to understand the densification
5 behavior. During isothermal sintering of Al_2O_3 , Coble [8] observed that $\dot{D}$ is inversely proportional
6 to the time t in a wide range of density ($D=0.6\sim 0.95$). The empirical relationship of $\dot{D} \propto t^{-1}$ was also
7 observed during hot pressing of MgO [9], and explained by assuming that G^n in Eq. (1) is
8 proportional to t for constant $f(D)$ [8]. Other empirical relationships of densification kinetics were
9 proposed by Tikkanen and Makipirtti [10] and Pejovnik *et al.* [11]. Although the empirical
10 equations have little physical significance, they can serve a practical function in numerical
11 simulations, and fundamentals for further theoretical analysis.

12 In the present study, the densification kinetics of 7.8 mol% Y_2O_3 -stabilized ZrO_2 (8YSZ) was
13 examined during isothermal sintering at various temperatures. In order to examine the kinetics in a
14 wide range of density, long-time (up to 140 h) sintering was conducted at low temperatures. The
15 observed kinetics is discussed with the existing empirical equations, and a new empirical equation is
16 proposed. The activation energy, grain growth and densification mechanism in the intermediate
17 stage of sintering are also examined and discussed to understand the densification behavior of
18 8YSZ.

19 2. Experimental procedure

20 Commercial ZrO_2 powder containing 7.8 mol% Y_2O_3 (TZ-8Y, Tosoh) with a specific surface
21 area of $13 \text{ m}^2/\text{g}$ was used as a raw material. The as-received powder was pressed uniaxially at <1

1 MPa into a compact of 30 mm diameter, and then pressed isostatically at 392 MPa in water. The
2 powder compacts have a green density of 3.13 g/cm^3 , corresponding to a relative density of 0.53
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7 (D_0) with an absolute density of 5.90 g/cm^3 for 8YSZ. From the powder compacts, small specimens
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9 of 5 mm x 5 mm x 10 mm were cut and pressed once again isostatically at 392 MPa for uniform
10 compaction. The two surfaces of 5 mm x 5 mm of the specimen were carefully machined to be
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12 parallel.
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17 The isothermal shrinkage of the specimen was measured in Ar atmosphere using a dilatometer
18 (DIL 402C, Netzsch) equipped with a graphite rod and holder. The graphite rod contacted to the
19 specimen at 0.25 N, corresponding to a stress of 10 kPa that is sufficiently lower than the sintering
20 stress of conventional ceramics [12]. The shrinkage measurement was conducted at constant
21 sintering temperatures between 1000 and 1500 °C with an interval of 50 °C. For the measurement at
22 1000~1300 °C, the temperature was increased at a heating rate of 10 °C/min, and for higher
23 temperatures at 20 °C/min. The measured shrinkage was corrected with the thermal expansion of the
24 fully densified 8YSZ, which was measured separately, and then converted to the relative density.
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39 After the shrinkage, the density of the specimen was measured by three different methods: the
40 Archimedes method, the change in the specimen length and the dilatometer. For the isothermal
41 sintering at 1000~1400 °C, the three densities are within an error of 1%, which confirms the validity
42 of the shrinkage data. For 1450~1500 °C, however, a damage was observed at the tip of the graphite
43 rod after the long-time measurement, and the error range was expanded a little (2%). The fractured
44 and polished surfaces of the specimen after the shrinkage were observed using a scanning electron
45 microscope (SEM, SU-8000, Hitachi). Before SEM observations, the polished surfaces were etched
46 in air for 1 h at the temperature lower than the sintering temperature by 200 °C. For each specimen,
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5-7 photographs were taken including more than 200 grains. From each photograph, 5 largest grains were chosen, and an average of their sizes was defined as the grain size in the present study. The grain size determined from 5 largest grains was about 1.5-2 times the size of the most popular grains. Though the present grain size is different from the conventional average one, the two grain sizes would be linearly proportional each other, if normal grain growth occurs. It is considered, therefore, that the present grain size would reveal a characteristic of grain growth during densification.

3. Results and Discussion

3.1 Initial sintering stage

In the initial stage of sintering, rapid growth of interparticle neck occurs. The neck growth was analyzed in several works using the two-sphere model [13,14], and was found to dominate the initial shrinkage of 3-5%. The densification kinetics in the initial stage is represented as

$$\Delta L/L_0 = B^m(t - t_0)^m \quad (2)$$

, where ΔL is the change in a length of the specimen, L_0 is the initial length of the specimen, B is a constant, t_0 is the time when the neck growth starts, and m is the value depending on the densification mechanism: 1/2 for lattice diffusion and 1/3 for grain-boundary diffusion. The two-sphere model of Eq. (2) has widely been applied to evaluate the densification mechanism in the initial sintering stage.

The shrinkage during the isothermal sintering of 8YSZ is shown in Fig. 1. The relationship between $\log(-\Delta L/L_0)$ and $\log(t)$ reveals a linearity in the beginning, and the slope m changes gradually with the increasing time at a shrinkage $(-\Delta L/L_0)$ of <10%. When $-\Delta L/L_0$ exceeds 10%, the rate of shrinkage decreases rapidly. The details are examined in Subsection 3.3. For the initial

1 shrinkage of <3%, the slope m shows a value of 0.14~0.21 at 1000~1200 °C. The measured
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4 m -values are considerably lower than 1/2 or 1/3, indicating that the densification mechanism in the
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7 initial stage is neither lattice diffusion nor grain-boundary diffusion. The measured m -values are
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10 rather close to the theoretical value (2/7) for surface diffusion [1], though the surface diffusion is
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12 known as a nondensifying mechanism.
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15 The inconsistency of m may be caused by the limitation of the two-sphere model where
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17 shrinkage occurs in one dimension. Actual powder compacts have a microstructure of complicated
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20 particle arrangements in three dimensions. In the compacts, the number of neighboring particles and
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23 the instant size of interparticle neck would be distributed in a wide range. Since the whole
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25 densification of the powder compacts is a summation of those all contributions, a superposition of
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28 Eq. (2) at different starting time t_0 will result in a deviation from the original m -value of the
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31 two-sphere model. To describe more explicitly the densification kinetics in the initial stage, a
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34 many-particle model is preferred [15].
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36 Another difficulty in evaluating the densification kinetics in the initial stage may arise from the
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38 unstable pore structure. Usually the measurement of shrinkage is conducted for the powder
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41 compacted by mechanical loading. It is expected that the pore structure formed by the mechanical
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44 loading at room temperature is different from that at high temperatures. The mechanically stable
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47 pore structure would be different from the thermally stable structure during densification.
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50 Accordingly, when the powder compacts are heated to high temperatures, a transition will take place
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53 from the mechanically stable to the thermally stable structure. Though the shrinkage range is very
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56 short in the initial sintering stage, the transition of the pore structure will be counted during the
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59 isothermal measurements, which makes the evaluation difficult. The discussion is continued in
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Subsection 3.4.

3.2 Intermediate sintering stage I ($0.6 < D < 0.73$)

The densification rate $\dot{D}$ during the isothermal sintering at 1000~1300 °C is represented in Fig. 2. $\dot{D}$ increases with the temperature, and at a fixed temperature, decreases gradually with the densification. For the isothermal sintering at 1000~1200 °C, a relatively rapid drop of $\dot{D}$ appears at $D < 0.6$, whereas it occurred during heating to the sintering temperature for 1250~1300 °C. In the density range of 0.6~0.73, a relatively linear relationship is observed between $\log(\dot{D})$ and $\log(D)$, and the interval in $\log(\dot{D})$ between the neighboring densification curves is similar. In the present study, therefore, the density range of 0.6~0.73 is called Stage I. At $D > 0.73$, a rapid drop of $\dot{D}$ is observed again.

The activation energy can be obtained from a slope between $\ln(T\dot{D})$ and $1/T$ in Eq. (1). Owing to low densities and low temperatures, the insignificant grain growth at $D < 0.73$ is ignored, which will be shown later. Figure 3 represents the Arrhenius plot of the densification rate at various fixed densities, where a good linearity is observed. The activation energy Q obtained from Fig. 3 is shown in Fig. 4. The activation energy entirely reveals a decreasing tendency with densification. In particular, the decrease at $D < 0.6$ is remarkable, where Q decreases from 824 kJ/mol at $D=0.55$ to 702 kJ/mol at $D=0.60$. The densification at $D < 0.6$ may be in a transition state from the initial to the intermediate stage of sintering. If the initial stage comes to an end at around $D=0.56$ ($D_0=0.53$), the densification behavior would transition to the next intermediate stage. This consideration is supported by the measured activation energy. The present activation energy (702~824 kJ/mol) at $D < 0.6$ is similar to the Q -value of 757 and 731 kJ/mol obtained in the initial sintering stage of 8YSZ

1 by Matsui *et al.* [16] and Suarez *et al.* [17], respectively. Matsui *et al.* [15] attributed the
2 densification mechanism to the grain-boundary diffusion.
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6 The activation energy, however, is fairly constant at $0.6 < D < 0.73$, as shown in Fig. 4. In Stage I,
7 an average value of Q is 688 kJ/mol. The fairly constant Q -value may indicate a single mechanism
8 prevailing the densification. The densification mechanism in the intermediate stage can be
9 evaluated by obtaining the value of n in Eq. (1). In order to prepare the specimens of identical
10 density and different grain size, the isothermal sintering at 1100 and 1250 °C was stopped when the
11 relative density reached 0.67. The grain sizes, however, were similar and the difference was less
12 than 20%. Whereas the grain size could successfully be controlled at a fixed density during
13 pressure-assisted sintering [18], sufficiently different grain sizes were not obtained in the present
14 pressureless sintering. Conversely, this fact indicates the insignificant grain growth in Stage I.
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33 3.3 Rapid grain growth ($0.73 < D < 0.80$) 34

35 At $D > 0.73$ in Fig. 2, the considerable decrease in $\dot{D}$ was caused by rapid grain growth. The
36 decreasing $\dot{D}$ due to the grain growth and the increasing $\dot{D}$ with an increase in the sintering
37 temperature made the densification curves tangled each other, as shown in Fig. 2. At $D > 0.75$, the
38 relationship between $\ln(T\dot{D})$ and $1/T$ was seriously non-linear, so that the activation energy could
39 not be obtained. For the evaluation of the activation energy, the behavior of grain growth should also
40 be examined carefully at each sintering temperature.
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52 The behavior of grain growth was examined at 1250 °C only, and is shown in Fig. 5 along with
53 the variation of D and $\dot{D}$. The grain growth roughly corresponds to the decrease in $\dot{D}$. The initial
54 grain size 0.16 μm in the beginning of the isothermal sintering grew to 2.1 μm after 24 h. The grains
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grew more than 10 times for the initial 24 h at 1250 °C. Particularly, rapid grain growth occurred at around $t=100$ min, which corresponds to a rapid decrease in $\ln(\dot{D})$, as shown in Fig. 5. After 24 h, the growth rate decreased and no remarkable grain growth occurred. It is noticeable that whereas the grain growth was accompanied by the corresponding densification up to $t=30$ min, the rapid grain growth after $t=60$ min took place without significant densification: from $G=0.61$ μm at $D=0.76$ to $G=2.07$ μm at $D=0.79$. The rapid grain growth without significant densification is one of the key points for discussing the mechanism.

The microstructures after the isothermal sintering are shown in Fig. 6. The initial grain size (0.16 μm) at 1250 °C is similar to that after 48 h at 1150 °C (Fig. 6a). At 1250 °C, the microstructure is quite uniform during the initial 30 min, as shown in Fig. 6b. After $t=30$ min, however, grains apparently larger than the surrounding ones began to appear (Fig. 6c), and the microstructure after 24 h reveals a bimodal feature in the size distribution of grains (Fig. 6d). In the present study, the bimodal feature was commonly observed at $D\sim 0.8$ after the rapid grain growth, and disappeared when further grain growth and densification had proceeded.

A temperature of 1250 °C is quite low for sintering of 8YSZ. For full densification, temperatures higher than 1400 °C are usually required [16]. The rapid grain growth at such low temperature may be attributed to the graphite holder used in the present study, because it was not observed for the alumina holder [16,17]. Moreover, the rapid grain growth occurred at densities lower than 0.8. Generally, it is recognized that grain growth is suppressed at low densities ($D<0.9$) and is accelerated in the final stage of sintering ($D>0.9$). Several studies have reported the G - D relationship where the grain size increases rapidly at $D>0.9$ [19,20]. The present results are in disagreement with the general understandings.

1 For the grain growth in Y_2O_3 -stabilized zirconia, the distribution of Y^{3+} ions plays a significant
2 role. Whereas the segregation of Y^{3+} ions on grain boundaries for 2~3 mol% Y_2O_3 -stabilized
3 zirconia suppresses the grain growth by a mechanism of solute drag, the relatively uniform
4 distribution of Y^{3+} ions for 8YSZ has a weak effect of solute drag resulting in higher grain growth
5 rate [21,22]. The present unusual rapid grain growth in certain density range, however, cannot be
6 explained by the distribution of Y^{3+} ions. For 8YSZ, it is rational to consider that the Y^{3+} ions are
7 distributed uniformly during the entire density range. The partial fluctuation of the segregation at
8 different densities can be excluded, which may lead to unusual grain growth.

9 As a possible mechanism of the rapid grain growth at low densities and temperatures, surface
10 diffusion is a first candidate. Several researchers suggested the surface diffusion as a mechanism of
11 grain growth in porous structures. Greskovich and Lay [23] observed the grain growth at a relative
12 density of 0.31~0.40, and attributed it to the surface diffusion. Shi *et al.* [24] observed directly the
13 densification of TiO_2 powder using a transmission electron microscope, and found the surface
14 diffusion to be responsible for the grain growth. During sintering at low densities, grain-boundary
15 and lattice diffusions accompany a densification, whereas surface diffusion is a nondensifying
16 mechanism. The rapid grain growth at specific low densities ($0.76 < D < 0.8$) with relatively small
17 densification may support the surface diffusion as a possible mechanism.

18 It is considered that the surface diffusion was accelerated due to the present reducing
19 environment. The graphite rod and holder in Ar in this study would make the oxygen vacancies be
20 formed easily on particle surfaces, and then accelerate the surface diffusion and the grain growth. A
21 graphite is commonly being used as a mold material in spark plasma sintering and hot pressing. For
22 both techniques, 8YSZ has also been sintered in the reducing environment using the graphite mold

[25]. However, the rapid grain growth at low densities and temperatures was not observed. For the reason, the influence of the reducing environment was not considered prior to the study. The rapid grain growth under the present testing condition was not expected. Consequently, we have found that the rapid grain growth occurs due to the surface diffusion in the reducing environment at low densities of 0.73~0.8. In the conventional pressure-assisted sintering, the density region of 0.73~0.8 is quickly passed at low temperatures, so that the rapid grain growth due to the surface diffusion can sufficiently be suppressed even in a similar reducing environment.

3.4 Empirical kinetics of densification

As shown in Fig. 2, a relatively linear relationship is observed between $\log(\dot{D})$ and $\log(D)$ in the density range of 0.6~0.73. A linearity is also found in Fig. 5 between $\log(\dot{D})$ and $\log(t)$ at $t > 900$ min ($D > 0.79$) for the isothermal sintering at 1250 °C, and the slope is about -1/2. In the density ranges where the linearity appears, the rate of grain growth is slow and its effect on $\dot{D}$ is insignificant. The relationship between $\log(\dot{D})$ and $\log(t)$ at other temperatures is shown in Fig. 7.

For the isothermal sintering at 1000 °C, the linear relationship with a slope of -1/2 is found after 400 min. At $t < 400$ min, $\dot{D}$ represents a transition-like behavior which was probably caused by the transition of the pore structure, as discussed in Subsection 3.1. In the beginning of the isothermal sintering, the mechanically stable pore structure may first transition to the thermally stable one. This is supported by the reduced transition time at higher temperatures. For 1100 °C, the transition behavior almost disappeared and the entire relation between $\log(\dot{D})$ and $\log(t)$ represents a linearity with a slope of -1/2, as shown in Fig. 7. For 1000 °C, the relative density D at $t = 400$ min is 0.54, which means that the densification of 1% took place during the transition. Assuming that the

densification required for the transition is 1%, it would take place during the heating process at higher sintering temperatures. For 1100 °C, the relative density at $t=0$ min is 0.54, which means no transition behavior during subsequent isothermal sintering.

For the isothermal sintering at 1200 °C, the linear relationship is observed in the beginning, and deviates significantly from the linearity due to the rapid grain growth at $D>0.73$, as in the case of at 1250 °C in Fig. 5. The slight deviation at $t<10$ min is due to the non-uniform temperature distribution within the specimen. Just when the sintering temperature is reached at a heating rate of 10 °C/min, the temperature distribution would be non-uniform within the specimen and approach the uniform distribution during the subsequent isothermal sintering. For 1300 °C, the linear relationship disappeared in the beginning, and appeared after the rapid grain growth. At $t>200$ min, the linear relationship with a slope of $-1/2$ was not influenced significantly by the possible grain growth, as in the case of at 1250 °C (Fig. 5).

From the above results of Figs. 5 and 7, it is concluded that the densification kinetics of 8YSZ is represented as

$$\dot{D} = Ct^{-1/2} \quad (3)$$

, where C is a constant. This empirical equation of densification kinetics is valid in a wide range of density (0.54~0.9), except when the rapid grain growth takes place. The validity at $0.8<D<0.9$ is shown in the next section. The disturbance of the empirical kinetics by the rapid grain growth can be corrected using the grain size. Integrating Eq. (3) with respect to t , we obtain a relationship of $D \propto t^{1/2}$ and hence $\dot{D} \propto 1/D$. Then, $f(D)$ in Eq. (1) is empirically determined to be $1/D$. The relationship between $D\dot{D}$ and G in Eq. (1) is shown in Fig. 8 for the above grain sizes at 1250 °C, where $\log(D\dot{D})$ is linearly proportional to $-\log(G^{2.6})$. This means that Eq. (1) with $f(D)=1/D$ is applicable to

the densification even during the rapid grain growth. Thus, the densification rate of Eq. (1) with the $f(D)$ obtained from the empirical kinetics of Eq. (3) can describe the densification behavior of 8YSZ in a wide density range. In addition, the grain size exponent n of 2.6 is close to a value of 3 for the densification mechanism of grain-boundary diffusion [1,6]. In the density range of 0.73~0.8, it can be concluded that the densification is dominated by the grain-boundary diffusion, whereas the grain growth by the surface diffusion.

Among the other empirical kinetics [10,11], the equation proposed by Tikkanen and Makiirtti [10] was examined for the present shrinkage data, because of the simple expression, $(1-D_o/D)/(1-D_o)=Ct^m$. The empirical equation is represented in Fig. 9. At $t>60$ min, a linear relationship is observed for 1000~1150 °C, but the value of m increases with the increasing temperature: from $m=0.32$ for 1000 °C to $m=0.38$ for 1050 °C and to $m=0.45$ for 1100 °C. m is not a constant and dependent on the temperature. Whereas both empirical equations of Coble [8] and of Tikkanen and Makiirtti [10] were well fitted for the isothermal sintering of UO_2 [11], it is found that they are not valid for the case of 8YSZ. Equation (3) is the only empirical equation of densification kinetics for 8YSZ under the present testing condition.

3.5 Intermediate sintering stage II ($0.8<D<0.9$)

The densification rate during the isothermal sintering at 1350~1500 °C is shown in Fig. 10. In the density range of 0.8~0.9, a relatively linear relationship between $\log(\dot{D})$ and $\log(D)$ is observed for 1400~1500 °C, and the slope is similar to those in Stage I, as shown in Fig. 2. This density range is called Stage II in the present study. However, the interval in $\log(\dot{D})$ between the neighboring densification curves is not constant, indicating a non-linear relation between $\ln(T\dot{D})$ and $1/T$. The

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2 activation energy roughly obtained at $D=0.85$ for 1400~1500 °C is about 354 kJ/mol, which value is
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4 considerably lower than that in Stage I (688 kJ/mol). The lower activation energy at higher densities
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6 was also reported for the tetragonal zirconia doped with 3 mol% Y_2O_3 [26], and attributed to the
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8 easy formation of point defects.
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12 For the isothermal sintering at 1350~1500 °C, the rapid grain growth at $0.73 < D < 0.8$ occurred
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14 during both the heating process and the initial isothermal sintering. For 1400 °C, the grain size at
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16 $D=0.80$ and 0.88 is 2.0 and 5.0 μm , respectively. Unlike the insignificant grain growth in Stage I, the
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18 grain growth is considerable in Stage II, probably due to the higher densities and temperatures. The
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20 rate of grain growth was accelerated at $D > 0.9$ for 1400~1500 °C, and the rapid drop of $\log(\dot{D})$
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22 appeared. The grain size at $D=0.93$ for 1400 °C is 13.1 μm . The accelerated grain growth at $D > 0.9$
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24 limited further densification, and the maximum D achieved was 0.93. The n -value roughly
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26 estimated from the two grain sizes at $D=0.8$ and 0.88 is about 0.3, which is less than 1 for a
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28 mechanism of grain-boundary sliding [1]. Though the estimation is incorrect due to the insufficient
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30 data, the n -value of 0.3 indicates that the densification mechanism is apparently different from that
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32 at $0.73 < D < 0.8$ ($n=2.6$).
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42 Nevertheless, the empirical densification kinetics of Eq. (3) is still valid in Stage II. As shown
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44 in Fig. 11, the relationship between $\log(\dot{D})$ and $\log(t)$ is fitted well by Eq. (3) prior to the rapid grain
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46 growth at $D > 0.9$ for the isothermal sintering at 1400~1500 °C. Despite the large difference in the
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48 grain size and in the rate of grain growth between Stages I and II, the identical slope of $-1/2$ is
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50 obvious. For 1350 °C, the rapid grain growth after Stage I continued up to $D=0.84$, so that the
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52 density range of Stage II was shortened. For 1350 °C, Eq. (3) is valid in a range of $t=100\sim1000$ min,
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54 as shown in Fig. 11. It is interesting that the Coble's empirical relationship of $\dot{D} \propto t^{-1}$ is observed,
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1 after the rapid drop of $\dot{D}$ at $D>0.9$. Thus, it has been verified that the empirical densification
2 kinetics of Eq. (3) is valid in a wide range of density. Although more detailed studies are required for
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4 the densification mechanism in the entire density range, the empirical kinetics would be useful for
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7 predicting the actual sintering behavior and referable to further theoretical modeling.
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11 12 13 14 15 **4. Conclusions**

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17 In the initial stage of sintering, the transition of the pore structure and the limitation of the
18 two-sphere model make the evaluation of the densification mechanism difficult. The effects of the
19 transition on the densification rate were confirmed in the beginning of the shrinkage at low
20 temperatures. In the intermediate stage, a linear relationship with a slope of $-1/2$ was observed
21 between $\log(\dot{D})$ and $\log(t)$, and the empirical densification kinetics of Eq. (3) was proposed. The
22 empirical kinetics is valid in a wide density range ($D=0.54\sim 0.9$), except when the rapid grain growth
23 takes place. During the rapid grain growth, the densification rate of Eq. (1) with the $f(D)$ obtained
24 from the empirical kinetics of Eq. (3) is applicable. The rapid grain growth observed at $D>0.73$ can
25 be attributed to the surface diffusion, whereas the densification is dominated by the grain-boundary
26 diffusion. The activation energy in the intermediate stage I ($0.6<D<0.73$) is 688 kJ/mol.
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Figure captions

Fig. 1. Shrinkage during the isothermal sintering at different temperatures.

Fig. 2. Variation of the densification rate with the density at various temperatures (1000~1300 °C).

1 RGG means the density range of rapid grain growth.

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4 Fig. 3. Arrhenius plot of the densification process at fixed densities.

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7 Fig. 4. Activation energy at different relative densities.

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10 Fig. 5. Variation of the grain size, density and densification rate with the time at 1250 °C.

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12 Fig. 6. Microstructure after the isothermal sintering a) at 1150 °C for 48h ($D=78\%$), b) at 1250 °C
13 for 0.3h ($D=74\%$), c) for 1h ($D=76\%$) and d) for 24h ($D=79\%$).

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17 Fig. 7. Variation of the densification rate with the time at various temperatures (1000~1300 °C).

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20 Fig. 8. Verification of Eq. (1) with $f(D)=1/D$ and $n=2.6$ at 1250 °C

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23 Fig. 9. Empirical relationship proposed by Tikkanen and Makipirtti [10]. The slope increases with
24 an increase in the sintering temperature.

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27 Fig. 10. Variation of the densification rate with the density at various temperatures (1350~1500 °C).

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30 The densification rate at 1300 °C is represented for comparison.

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33 Fig. 11. Variation of the densification rate with the time at various temperatures (1350~1500 °C).

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