The Grain Growth Kinetics in the System ZrO₂-Y₂O₃

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Synopsis

The grain growth kinetics of fully- and partially-stabilized zirconia is discussed in this paper. The grain boundary mobilities calculated from experimental data on single-phase zirconia were several order of magnitude smaller than the intrinsic grain boundary mobility. Some drag forces such as solute-drag may retard the migration of grain boundaries in single-phase zirconia. The mixed structure composed of cubic grains and tetragonal grains with nearly equilibrium yttria contents was formed during annealing in the cubic/tetragonal two-phase region, which was termed the dual-phase structure. The grain growth of dual-phase alloys took place much slowly than that of single-phase zirconia. The growth kinetics was examined with a special interest in the dual-phase structure. The grain growth rate of these alloys was satisfactorily described by the rate equation which was derived by assuming the growth of individual grains under the equilibrium partitioning limited by grain boundary diffusion of yttrium ions.

1. Introduction

For the fabrication of ceramic materials, particularly of structural ceramics, it is essential to produce fully-dense sintered bodies with fine and uniform grain size. In general, the inhibition of grain growth during sintering is very important to attain the required properties of ceramics. A lot of technological experiences has been established for the densification and grain size control in commercial ceramics.

In toughened zirconia, powder preparation and sintering techniques have highly been improved in recent years so that the fracture strength of more than 1 GPa and the fracture toughness of around 10 MPa $m^{1/2}$ have been obtained at room temperature in commercial partially-stabilized zirconia (PSZ) or tetragonal zirconia polycrystals (TZP).^{1,2} However, the quantitative data on grain growth kinetics of PSZ or TZP is very limited. In this paper, the kinetics of grain growth in ZrO₂-Y₂O₃ alloys is discussed on the basis of recent experimental results obtained by several workers.³⁻⁵

2. Grain Growth in Single-Phase Region

The rate equation for the normal grain growth of single-phase ceramics is usually described by 6,7)

$$\bar{d}^2 - \bar{d}_0^2 = 2M\gamma V_m t \tag{1}$$

where d and d_0 are the average grain size at a time t and 0, respectively, M is the grain boundary mobility, τ is the grain boundary energy and V_m is the molar volume. In the ideal situation, M is represented by the intrinsic grain boundary mobility M^i , which is given by⁶

$$M^{i} = \frac{D^{ab}}{RT\delta}$$
(2)

where D^{gb} is the grain boundary diffusion coefficient of constituent ions, δ is the grain boundary width and RT is the usual meaning. The intrinsic mobility M^i is related to the ionic diffusivity in the grain boundary.

Fig. 1 is a plot of square of average grain size in cubic zirconia as a function of annealing time at three temperatures.⁵⁾ By assuming the linear relationship between d^2 and t, one can estimate the values of M from Eq.(1) by the slope of straight lines such as Fig. 1. The mobilities thus obtained are shown in Fig. 2, where γ is tentatively assumed to be 0.5 J/m² and V_m is 2 x 10^{-5} m³/mol. The values of M are slightly different by authors even for alloys with the same yttria content. The data for tetragonal phase $(t-ZrO_2)$ is somewhat smaller than that for cubic phase (c- ZrO_2). The intrinsic mobility in Fig. 2 was evaluated from Eq.(2) by using the grain boundary diffusivity data⁸⁾ and by taking δ as 1 nm. The grain boundary mobilities obtained both in $c-ZrO_2$ and $t-ZrO_2$ are much smaller than the intrinsic mobility. The disagreement between experimental mobilities and intrinsic mobility is too large to be responsible for the ambiguity of assumed values quantities used of the for the calculation. This is not only the characteristics of zirconia alloys but also of various ceramic materials. According the to numerous experimental data obtained so far, the grain growth of single-phase ceramics is likely to take place at a rate much slower than that expected from the intrinsic mobility.9,10) The grain growth actually must not proceed in the ideal situation described by the intrinsic mobility. Some drag forces for grain boundary migration must be operated.

First of all, the grain size of sintered products increases from, at least, the second stage of sintering, where pores are still present in grain boundaries and sometimes also in grain interior.11) In this stage, the densification and grain growth simultaneously occur and, therefore, the grain boundary migration may be suppressed by the drag of pores, whose



Fig. 1 A plot of square of average grain size as a function of isothermal annealing time in ZrO_2 -8 mol%Y₂O₃ alloy.⁵)



INVERSE TEMPERATURE / $10^{-4} ext{ k}^{-1}$ Fig. 2 Arrhenius plot of grain boundary mobility of single-phase zirconia. Open and filled circles are the mobilities calculated from experimental data in c-ZrO₂, 3,5) and filled triangles are those in t-ZrO₂.³ Intrinsic grain boundary mobility was calculated from Eq.(2) by using the reported grain boundary diffusion data in c-ZrO₂.⁸

density decreases with a progress of sintering. The grain growth kinetics in this stage may not be expressed by a simple parabolic law.¹⁰) In the period of high-temperature annealing of Fig. 1, the porosity is less than a few percent so that the density change may be neglected. If the majority of grain corners are occupied by pores, and the ratio of pore radius with grain size is kept constant during the sintering period,¹²) then it seems reasonable to consider that the pore-drag limits the overall growth rate. However, microstructural examinations have revealed that pores were located only certain grain corners, and most of corners were pore-free in the stage of Fig. 1.⁵) Furthermore, the grain size was not proportional to pore size.⁵) These facts may suggest that the migration of some grain boundaries was retarded by pores but the pore-drag was not the principal rate-controlling mechanism for grain growth.

Solute-drag may be more important for the suppression of grain growth. It is well-known that the grain growth of ceramics is markedly retarded by a very small amount of solutes or impurities. Solutes are generally segregated into grain boundaries because they are attracted towards the boundary by the force, which is given by the first derivative of the grain boundary-solute interaction energy. This means that each solute exerts a retarding force for grain boundary migration which has an equal magnitude but opposite sign with the attractive force. It is possible to estimate the solute-drag force by adding the retarding force from all solutes concerned. $^{13-16}$ For a stationary boundary, the solute distribution is symmetric with respect to the center of the boundary, and then the net force is zero. However, the drag force arises for a moving boundary because of the unsymmetric solute distribution. This force is critically dependent on the model of grain boundary-solute interaction, the velocity of boundary, the solute content and so on. It is, therefore, not possible to estimate quantitatively the drag-force for grain boundary migration in c-ZrO2. It is only possible to point out the importance of solute-drag effect for explaining the observed mobilities in single-phase zirconia in Fig. 2.

Another interesting fact is the difference of mobilities between t-ZrO₂ and c-ZrO2 in Fig. 2. It has experimentally been found that the grain growth was much faster in c-ZrO₂ than in t-ZrO₂, and the proportional constant $2M_{\gamma}V_m$ in Eq.(1) differed up to 250.³⁾ If the energy of t-ZrO₂ boundary is much smaller than that of c-ZrO₂ boundary due to an enhanced segregation in t-ZrO₂ boundary, then the grain growth rate will be much smaller in t-ZrO₂ than in $c-\bar{Z}rO_2$.³⁾ However, the decrease of the energy up to two order of magnitude is not easily acceptable for the two phases with a similar crystal symmetry. It seems that the difference of grain growth rate cannot solely be caused by the change in grain boundary energy. If the glassy phase is formed in grain boundaries, the mechanism of mass transfer for grain growth will be changed. The glassy phase are often generated by the segregation of various impurities in grain boundaries. Commercial zirconia powders contain HfO_2 , Al_2O_3 , SiO_2 , Fe_2O_3 , Na_2O etc. as impurities, but these impurities exist both in t-ZrO₂ and c-ZrO₂. The presence of glassy phase, therefore, cannot fully explain the difference in grain growth rates. Judging from the recent data in our group, 17) the grain growth rate is surely different between t-ZrO2 and c-ZrO2, but the difference is not so large as reported by Lee and Chen.³⁾ The grain growth occurred considerably faster in ZrO_2 -1.5 mol%Y₂O₃ alloy than in ZrO₂-2.0 mol%Y₂O₃ alloy. The former alloy was fully tetragonal but the latter one included a small amount of second phase. More details on the grain growth in $t-ZrO_2$ will be published elsewhere.

3. Generation of Dual-Phase structure

PSZ or TZP is usually sintered or heat-treated at a temperature in the t-ZrO₂/c-ZrO₂ two-phase region. Two types of microstructures are formed during heating in this two-phase region as in Fig. 3. Fig. 3a is the microstructure containing precipitate particles. The precipitation of t-ZrO₂ particles in c-ZrO₂ matrix has been found in Mg-PSZ, Ca-PSZ and Y-PSZ.¹⁸⁻²⁰) This type of

microstructure is usually developed in coarse grained materials. In finegrained materials, the mixed structure composed of t-ZrO₂ and c-ZrO₂ grains such as in Fig. 3b is sometimes formed during heating. This microstructure formed in metallic materials has been referred to be the dual-phase structure or duplex structure for distinguishing two-phase from the structure containing precipitate particles.²⁰⁾ The generation of the dual-phase structure in PSZ results from the equilibrium partitioning of relevant ions between t-ZrO2 and c-ZrO2 grains.4,5)

Fig. 4 is an example of dualphase structures in ZrO₂-4 mol%Y₂O₃ alloy annealed at 1700°C for 10°h. which has an uniform polycrystalline structure with an average grain size of 2.5 μ m.⁵⁾ The results of STEM-EDX analysis, which are shown by numerical figures in Fig. 4, indicate the presence of two types of grains whose yttria content is around 2.0 mol% and 5.5 mol% respectively. The former grains are generally almost featureless except for bend contours, while the latter ones often have twin-like or lenticular microstructures. The yttria contents of 2.0 mol% and 5.5 mol% are close to the equilibrium contents in t- ZrO_2 and $c-ZrO_2$ at 1700°C. This fact seems to indicate that the equilibrium partitioning of yttria is attained between $t-ZrO_2$ and $c-ZrO_2$ grains and the dual-phase structure is formed during the high-temperature annealing in this alloy. The dual-phase structure may be generated when the average diffusion distance of cations is in the same order of grain size.⁵⁾ The grain growth of dual-phase alloys is much sluggish than of single-phase alloys as shown in Fig. 5. Fig. 5 shows that the generation of dual-phase structure is very effective for grain growth inhibition. This fact is probably related to the promotion of densification in dual-phase alloys during sintering.²²

Fig. 5 Grain growth of single-phase $(ZrO_2-8 \text{ mol}\%Y_2O_3)$ and dual-phase $(ZrO_2-4 \text{ mol}\%Y_2O_3)$ alloys at $1700^{\circ}C.5$) The data on c-ZrO₂ by Lee and Chen is shown by a broken line.³)



Fig. 3 Two-phase structure containing precipitate particles in matrix (a) and the dual-phase structure (b). See text.



Fig. 4 Fine-grained polycrystals of ZrO_2 -4 mol%Y₂O₃ annealed at 1700°C for 10 h. Figures in the micrograph is the yttria content of each grain estimated by STEM-EDX analysis. Note that two types of grains with different yttria contents 2.0 mol% and 5.5 mol% are formed.⁵)



A large grain boundary area per unit volume in dual-phase alloys relative to single-phase alloys may be effective for the diffusion of vacancies from grain boundaries to specimen surfaces. It is known that fully-dense and fine-grained TZP is fairly easily produced by sintering in the two-phase region. The dual-phase structure may also be generated in commercial TZP during sintering or annealing in the two-phase region.

4. Inhibition of Grain Growth due to Second-Phase Particles

In general, the grain growth of various materials is effectively suppressed by second-phase particles. This is because the migration of grain boundaries is retarded by the particles. The estimation of the retarding force has first been made by Zener.²³) By considering the interaction of a planar boundary with a spherical particle with a radius r_p , the maximum retarding force estimated to be $\pi r_p \gamma$. Assuming that this retarding force is balanced to the driving force for grain boundary migration, one can obtain the relationship

$$\frac{R_{\text{net}}}{r_p} = \frac{4}{3f} \tag{3}$$

where f is the volume fraction of second-phase particles. The parameter R_{net} represents the net radius of curvature, which is given by

$$\frac{1}{R_{\rm net}} = \frac{1}{\rho_1} + \frac{1}{\rho_2}$$
(4)

where ρ_1 and ρ_2 are the radii of curvature of two grains in contact with the relevant grain boundary. An approximate equation obtained by equating $R_{\rm net}$ to the average grain size \bar{d} ,

$$\frac{\bar{d}}{r_p} = \frac{4}{3f} \,. \tag{5}$$

This is the well-known equation which is often referred to be the Zener's relation. Eq.(5) may be an overestimation of the total retarding force because of its assumption that the maximum retarding force is exerted from every particles in contact with the boundary. Modified equations have later been obtained by several workers. Among them, the following one agrees most satisfactorily with various experimental data, 24

$$\bar{d} = \frac{8r_p}{9\phi f} \tag{6}$$

where ϕ is the quantity including the two factors; one is the angle between grain boundary and particle surface, and another is the factor depending on the radius of curvature of the grain boundary and the particle radius. In the following section, the grain growth kinetics of dual-phase ZrO_2 -Y₂O₃ is discussed on the basis of Eq.(6).

5. Grain Growth in Dual-Phase Structure

The dual-phase structure can be regarded as the microstructure in which the minor phase is located on the grain boundaries of major phase. The situation satisfying Eq.(6) is such that the grain growth of major phase is controlled by the growth of minor phase grains or particles, whose volume fraction is kept constant. The situation of grain growth is schematically drawn in Fig. 6. It may be reasonable that the growth of the minor phase takes place by a mechanism of Ostwald ripening. There are two paths of mass transfer for the growth of minor phase, grain interior and grain boundaries of major phase. The rate equations for minor growth controlled by the diffusion along each one of the paths are written by

$$\bar{r}_{p}^{3} - \bar{r}_{p_{0}}^{3} = \frac{8\gamma V_{m}^{\beta} D_{B}^{*} x_{B}^{\alpha}}{9RT (x_{B}^{\beta} - x_{B}^{\alpha})^{2}} t$$
(7)

for volume-diffusion controlled case, 25-28) and

$$\bar{r}_{p}^{4} - \bar{r}_{p_{0}}^{4} = \left(\frac{3}{4}\right)^{3} \frac{2\gamma V_{m}^{\beta} \delta D_{B}^{\mu b} x_{B}^{\beta}}{RT \left(x_{B}^{\beta} - x_{B}^{\alpha}\right)^{2}} t$$
(8)

for grain boundary diffusion controlled case.²⁹⁻³¹) Here, the α - and β -phases are regarded as the major and minor phases in binary A-B alloy, and both phases are assumed to be spherical. In these equations, D_B^{α} is the volume diffusion coefficient of B in α , D_B^{ab} is the grain boundary diffusion coefficient of B, x_B^{α} and x_B^{β} are the solubilities of B in α and β , and r_{p0} is the particle radius at a time 0. The originallyderived rate equations do not contain the concentration factor $(x_B^{\beta} - x_B^{\alpha})^2$ in Eqs.(7) and (8).²⁵⁻²⁷) These original equations are those for the growth of the α -phase consisting of pure component B in the β -phase with negligibly small solid solubility so that the concentration factor is taken to be unity. However, such an approximation can not be applied in present alloys. Substituting Eqs.(7) and (8) into Eq.(6), one obtains

$$\bar{d}^{3} - \bar{d}_{0}^{3} = \left(\frac{8}{9\phi f}\right)^{3} \frac{8\gamma V_{m}^{\beta} D_{B}^{\alpha} x_{B}^{\alpha}}{9RT (x_{B}^{\beta} - x_{B}^{\alpha})^{2}} t$$
⁽⁹⁾

for volume diffusion controlled case, and



Fig. 6 Schematic drawing of grain growth of dual-phase structure.



Fig. 7 A log-log plot of grain growth data of dual-phase $ZrO_2-4 \mod Y_2O_3$ alloy at $1700^{\circ}C.^{5}$



Fig. 8 Grain growth of dual-phase ZrO_2-4 mol% alloy at (a) 1800°C and (b) 1700°C; Chain and broken lines are the calculated growth rates by Eqs.(9) and (10), respectively.⁵)

$$\bar{d}^{4} - \bar{d}^{4}_{0} = \left(\frac{8}{9\phi f}\right)^{4} \left(\frac{3}{4}\right)^{3} \frac{2\gamma V_{m}^{\theta} \delta D_{B}^{qb} x_{B}^{qb}}{RT (x_{B}^{\theta} - x_{B}^{\eta})^{2}} t$$
(10)

for grain boundary diffusion controlled case. Next, the theoretical growth rates calculated from Eqs.(9) and (10) are compared with the observed growth rates.

Fig. 7 is the log-log plot of grain size and annealing time at 1700° C in ZrO_2-4 mol%Y₂O₃ alloy. The slope of the straight line in Fig. 7 is close to 1/4. This fact may support the grain boundary diffusion controlled mechanism. However, the slope of straight line in the log-log plot is not so accurate enough to identify the rate-controlling mechanism. It is better to compare the theoretical growth rates for the two mechanisms and the experimental data.

Fig. 8 is the comparison of theoretical and experimental growth rates at two temperatures. For the theoretical calculation, the following values were used. The interfacial energy γ was assumed to be 0.5 J/m². On the basis of the reported relationship between grain boundary enrichment ratio of solute and its solid solubility, 3^{2} the yttria content in grain boundary was taken to be twice of solid solubility of yttria in c-ZrO₂. The data of phase equilibrium between t- ZrO_2 and c-ZrO₂ was used to estimate the solid solubility in each phase.³³⁻³⁵) The volume and grain boundary diffusion coefficients were calculated from the reported data on c-ZrO₂. At each temperature, the theoretical growth rate evaluated from Eq.(10) for grain boundary diffusion is considerably higher than that from Eq.(9) for volume diffusion. Yttrium ions must diffuse along both of the two diffusion paths. However, if one of them gives much larger diffusive flux than another, the one will control the overall mass transfer and consequently the grain growth rate. It may, therefore, be expected from the theoretical growth rates in Fig. 8 that the grain boundary diffusion of yttrium ions will be a possible mechanism controlling the grain growth. The observed growth rates of the dual-phase ZrO_2-4 mol%Y₂O₃ alloy agree with the grain boundary diffusion controlled growth within a factor of two at the two temperatures as expected. Taking into account the uncertainty of various quantities used for the calculation, it may reasonable to conclude that the grain growth of this dual-phase alloy is induced by grain boundary diffusion of yttrium ions. Since the equilibrium partitioning of yttria is maintained between t-ZrO2 and c-ZrO2 grains during grain growth of dual-phase alloys, yttrium ions have to move for grain growth. In this case, the grain boundary migration of each phase is mutually pinned by other phase grains. The present result indicates that the mutual pinning effect is reasonably represented by the modified Zener's equation, and the mass transfer for grain growth is determined by the diffusion along grain boundaries.

6. Conclusion

The grain growth during isothermal annealing at high temperatures was examined in ZrO_2 - Y_2O_3 alloys, and the following results were obtained.

- (1) The normal grain growth of $c-ZrO_2$ proceeds at much slower rate than expected from the intrinsic grain boundary mobility. Some retarding forces for grain boundary migration in $c-ZrO_2$ must be rate-controlling.
- (2) The dual-phase structure was developed during annealing in the $t-ZrO_2/c-ZrO_2$ two-phase region for fine-grained alloys with an uniform grain size. This structure was formed by equilibrium partitioning of yttria between $t-ZrO_2$ and $c-ZrO_2$ grains when the average diffusion distance of yttrium ions was in the same order of average grain size.
- (3) The grain growth of dual-phase alloys was much sluggish than that of single-phase alloys, i.e. the generation of dual-phase structure is effective for retarding the grain growth.

7

(4) The grain growth kinetics of dual-phase alloys could satisfactorily be explained by the rate equation of forth-power law, which was derived by combining the Zener's relation and the rate equation for Ostwald ripening limited by grain boundary diffusion of yttrium ions.

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