Transactions of the Materials Research Society of Japan 27 [2] 329-332 (2002)

New Models and Rate Equations for Sintering and Grain Growth

Hidehiko TANAKA
National Institute for Materials Science, Advanced Materials Laboratory
1-1 Namiki, Tsukuba-shi, Ibaraki-ken, 305-0044, Japan
Fax:81-298-51-3613, e-mail: TANAKA.Hidehiko@nims.go.jp

In this study, initial-stages of sintering and grain growth were investigated in connection with the new two-sphere model. The rate equations for sintering and grain growth were formulated based on Inomata-Tanaka's free energy theory for mass transport. In the models two grains join together at boundary without neck growth. Sintering proceeds by expanding grain boundary with constant grain volumes, while grains grow or shrink by mass transportation from the small grain to the large grain. The sintering and grain growth rate equations were formulated by assuming that the total free energy on surface and boundary drove sintering and grain growth. From the equations sintering behavior of two grains was simulated.
Keywords: Sintering, Grain growth, Rate equation, Free energy theory, simulation

1. INTRODUCTION

The traditional theories for sintering that are cited in many textbooks for ceramists[1,2,3], have used a model in which two grains form a contact with a neck. They assume that the difference in chemical potential due to the curvatures of the neck and the grain surfaces drives mass transport, and causes grains to sinter. The neck formation, however, may be a wrong assumption if grains sinter by a solid-state diffusion process and if there is grain boundary energy between two grains. In the grain growth model mass transport is also assumed to be driven by surface curvature[3].

It seems oblique that surface curvature makes chemical potential in the solid body because the surface has only surface energy, but not surface tension. The traditional theories seem to have made some basic misunderstandings. The sintering and grain growth theories need to be reconsidered[4].

During sintering grains loose surface area but gain grain boundary area. The total free energy in grains decreases, that is, grains have excess energy. This excess energy must drive mass transport for sintering. In the same way, during grain growth, excess energy on the grain surface drives mass transport. The rate equations for mass transport by excess energy in the system were formulated by Y.Inomata and H.Tanaka as the following expressions[5,6].

$$\frac{dv}{dt} = D_x\left(\frac{a_x}{\lambda_x}\right)\left\{1 - \exp\left(\frac{-\Delta G}{RT}\right)\right\}$$

and usually $\Delta G \ll RT$,

$$\frac{dv}{dt} = D_x\left(\frac{a_x}{\lambda_x}\right)\left(\frac{\Delta G}{RT}\right)$$

$$\left(\frac{a_x}{\lambda_x}\right)^{-1} = \int_{system}\left(\frac{a_m(x)}{\lambda_x}\right)^{-1} dv \Big/ \int_{system} dv \qquad (1)$$

where D_x is the diffusion coefficient, a_x and λ_x are the effective diffusion area and length, ΔG is the excess free energy in the system, and R and T are the gas constant and temperature, $a_m(x)$ is the mean cross sectional area where material in a small volume, dv, flows from dv to an outlet. The term for diffusion path (a_x/λ_x) is calculated by the harmonic average of mean cross sectional area $a_m(x)$ on hole volume where mass transports.

It is clear that the sintering process and the grain growth process simultaneously take place, and these two processes cannot be separated. So that, in the present study, the models for sintering and grain growth were first proposed, and the new rate equations for sintering and grain growth were formulated. In the model, two spherical grains with different radii were in contact at the boundary. To derive the rate equations, Eq.(1) above was applied to the models. Sintering behavior of two grains was then simulated using the rate equations, assuming that sintering and grain growth proceeded simultaneously. Based on the numerical calculations, the influence of grain boundary energy and grain size ratio on sintering behavior was discussed.

2. MODELS AND THEORY

2.1 Sintering and grain growth models

In order to analogy sintering of fine powder, two-sphere grain models were proposed in Fig.1. The new models have not neck curvature, which is different from the traditional models[6].

In a sintering process, each grain keeps a constant volume and the distance between two grains decreases by expanding the grain (Fig.1(a)). The sum of surface energy and grain boundary energy decreases during sintering. In a grain growth process the larger grain grows and the smaller grain shrinks due to mass transport while maintaining a constant grain boundary area (Fig.1(b)). The sum of surface energy decreases during grain growth. The geometry factor such as x_1, r_1 and etc. are explained in the figure caption of Fig.1. In the formulation of sintering and grain growth rates, the ratio of boundary energy ε_{gb} to surface energy ε_s, and non dimensional parameters, which are defined as follows, were used.

$$R_0=\frac{r_{02}}{r_{01}},\ R_{1,2}=\frac{r_{1,2}}{r_{01,02}},\ X_{1,2}=\frac{x_{1,2}}{r_{1,2}},\ \alpha=\frac{\varepsilon_{gb}}{\varepsilon_s}$$

$$\text{and } R_{1,2}=\left\{\frac{1}{4}\left(1+X_{1,2}\right)^2\left(2-X_{1,2}\right)\right\}^{-1/3} \tag{2}$$

where R_0 (≤ 1) is the grain size ratio and α ($0\leq\alpha<1$) is the ratio of grain boundary energy to surface energy.

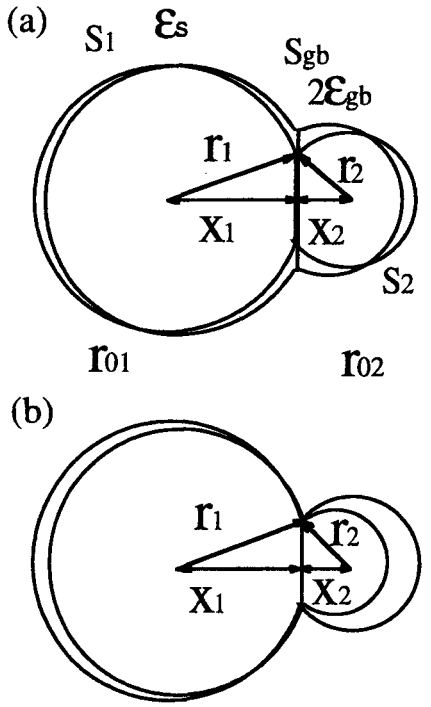

Fig.1 Models for sintering(a) and grain growth(b). Two spherical grains with different size of radii r_{01} and r_{02} ($r_{01}\geq r_{02}$), initially (time t=0) in contact at a point, join together after time t forming the grain boundary. r_1 and r_2 are the radii of grains 1 and 2, x_1 and x_2 are the distances between the grain centers and the boundary, S_1, S_2 and S_{gb} are the surfaces of grains 1, 2 and the boundary, respectively.

2. 2 Free energy that drives sintering, ΔG_{sint}

During sintering surface of grains is converted into grain boundary, and the sum of surface and grain boundary energy decreases. In the model, the system of two grains has the energy, $E_{sys}=\varepsilon_s(S_1+S_2)+2\varepsilon_{gb}S_{gb}$. The normalize free energy of the system is then;

$$\Psi=\frac{\left\{\varepsilon_s\left(S_1+S_2\right)+2\varepsilon_{gb}S_{gb}\right\}}{4\pi\varepsilon_s\left(r_{01}^2+r_{02}^2\right)}=\frac{R_1^2\left(1+X_1\right)+R_0^2R_2^2\left(1+X_2\right)+\alpha R_1^2\left(1-X_1^2\right)}{2\left(1+R_0^2\right)} \tag{3}$$

X_1 and X_2 are equal to 1 when the two grains are initially in contact at a point, and decrease from 1 as sintering proceeds and the grain boundary area expands.

Ψ has a minimum, Ψ_{min}, where the system reaches a pseudo-equilibrium state. The excess energy $\Delta\Psi$ is defined, $\Delta\Psi=\Psi-\Psi_{min}$, which drives mass transport for sintering. ΔG_{sint} (in 1 mole), is:

$$\Delta G_{sint}=4\pi\varepsilon_s\left(r_{01}^2+r_{02}^2\right)\Delta\Psi\frac{V_m}{\frac{4\pi}{3}\left(r_{01}^3+r_{02}^3\right)} \tag{4}$$

where V_m is the molar volume of the material.

2. 3 Free energy that drives grain growth, ΔG_{gg},

The excess energies ϕ_1 and ϕ_2 which drive the growth of grains 1 and 2,respectively, are given by the differences in surface and boundary energies between the system and grains 1 and 2.

$$\phi_1=\frac{\left\{\varepsilon_s\left(S_1+S_2\right)+2\varepsilon_{gb}S_{gb}\right\}}{\left(r_{01}^3+r_{02}^3\right)/V_m}-\frac{\left(\varepsilon_sS_1+\varepsilon_{gb}S_{gb}\right)}{r_{01}^3/V_m}$$

$$\phi_2=-\frac{\left\{\varepsilon_s\left(S_1+S_2\right)+2\varepsilon_{gb}S_{gb}\right\}}{\left(r_{01}^3+r_{02}^3\right)/V_m}-\frac{\left(\varepsilon_sS_2+\varepsilon_{gb}S_{gb}\right)}{r_{02}^3/V_m} \tag{5}$$

and, averaging on the volume:

$$\Delta G_{gg}=\frac{r_{01}^3}{r_{01}^3+r_{02}^3}\phi_1+\frac{r_{02}^3}{r_{01}^3+r_{02}^3}\phi_2=\frac{3\varepsilon_s V_m}{r_{01}}f_g$$

$$\text{and } f_g=-\frac{1}{\left(1+R_0^3\right)}\left[-\left\{\frac{1-R_0^3}{2\left(1+R_0^3\right)}\right\}\left\{R_1^2\left(1+X_1\right)+R_0^2R_2^2\left(1+X_2\right)+\alpha R_1^2\left(1-X_1^2\right)\right\}+\frac{R_1^2}{4}\left\{2\left(1+X_1\right)+\alpha\left(1-X_1^2\right)\right\}-\frac{R_0^2R_2^2}{4}\left\{2\left(1+X_2\right)+\alpha\left(1-X_2^2\right)\right\}\right] \tag{6}$$

ΔG_{gg} is positive since grain 1 is larger than grain 2, and mass transport occurs from grain 2 to grain 1.

2.4 Diffusion path, (a_x/λ_x)

The term for the diffusion path in Eq.(1), (a_x/λ_x), is given by Eq.1. $a_m(x)$ for small volume dv, where material flows from its area, $a_x(x)$, to the outlet at the grain boundary, $a_{gb}(x_1)$, is given by $\{a_x(x)\ a_{gb}(x_1)\}^{1/2}$. Putting $a_m(x)$ and λ_x (=distance between dv and grain boundary) into Eq.(1), (a_x/λ_x) for the two-sphere model, a_x/λ_x is calculated as :

$$\left(\frac{a_x}{\lambda_x}\right)=16\pi r_{01}g_d$$

$$\text{and } g_d=\left(1+R_0^3\right)\left[\frac{R_1^2}{\left(1-X_1^2\right)^{1/2}}\left\{4\left(1-X_1^2\right)^{3/2}+6X_1^2\left(1-X_1^2\right)^{1/2}+6X_1\arcsin X_1+3\pi X_1\right\}+\frac{R_0^2R_2^2}{\left(1-X_2^2\right)^{1/2}}\left\{4\left(1-X_2^2\right)^{3/2}+6X_2^2\left(1-X_2^2\right)^{1/2}+6X_2\arcsin X_2+3\pi X_2\right\}\right]^{-1} \tag{7}$$

2.5 Rate equation for sintering

In this study the rate of sintering is the shrinkage of the distance between two grains, $dX_{1,2}/dt$. As the sintering process was defined in Fig.1(a), the mass needed for the expansion of the grain boundary is $dv=\pi(r_1^2-x_2^2)(dx_1+dx_2)$, and the condition for constant volume of each grain is $(\pi/3)(r_{1,2}+x_{1,2})^2(2r_{1,2}-x_{1,2}) = (4\pi/3)\, r_{01,02}^3$, then;

$$\frac{dv}{dt} = -\frac{2\pi r_{01}^3 R_1^2\left\{R_1(1-X_1)+R_0R_2(1-X_2)\right\}}{(2-X_1)}\frac{dX_1}{dt} \tag{8}$$

From eqs.(1), (3),(7) and (8), the sintering rate is expressed as follows.

$$\frac{dX_1}{dt} = -\left(\frac{3\varepsilon_s D_x V_m}{\pi RT}\right)\frac{8\pi}{r_{01}^3} \times \frac{\left(1+R_0^2\right)(2-X_2)\,\Delta\Psi\, g_d}{\left(1+R_0^3\right)R_1^2\left\{R_1(1-X_1)+R_0R_2(1-X_2)\right\}} \tag{9}$$

2.6 Rate equations for grain growth

In the grain growth process(Fig.1(b)), the grain boundary area is held constant, $r_1^2-x_1^2=r_2^2-x_2^2$, and the amount of mass transport in the system is:

$$\frac{dv}{dt} = 2\times 4\, r_{01,02}^2\frac{dr_{01,02}}{dt} \tag{10}$$

From Eqs.(1), (6), (7) and (10), the rate equation for grain growth in grain 1 is formulated as follows.

$$\frac{1}{r_{01}}\frac{dr_{01}}{dt} = \left(\frac{3\varepsilon_s D_x V_m}{\pi RT}\right)\frac{2\pi}{r_{01}^3} f_g\, g_d \tag{11}$$

dX_2/dt and $(1/r_{02})(dr_{02}/dt)$ can be obtained by exchanging $r_{01}\leftrightarrow r_{02}$, $X_1\leftrightarrow X_2$, $R_1\leftrightarrow R_2$ and $R_0\leftrightarrow 1/R_0$ in eq.(9) and (11).

3. CALCULATIONS AND DISCUSSION

3.1 Calculations of sintering behavior

As noted in Fig.1 sintering and grain growth are not separated and simultaneously proceed. In order to simulate sintering behavior of two grains, the increments in X_1, X_2 and R_0 for small range of time Δt were calculated and these values at at time $t+\Delta t$ were obtained. These calculations were started with $r_{01}=1$ and the given $R_0=0.1$ to 1, the given $\alpha=0$ to 1 and from $X_{1,2}=1$ at $t=0$, and repeated until X_2 became 0. The results are shown in Figs.2(a) to (d).

3.2 Effects of grain boundary energy and grain size on sintering behavior

From the results in Fig.2, the sintering behavior of two grains is illustrated in Fig.3. Two grains in the figure initially in contact at a point began to sinter and expanded their grain boundary. The centers of the two grains moved closer and the larger grain grew and the smaller grain shrank. The rates of sintering or the grain boundary expansion, and the rate of grain growth of large grain or the rate of grain shrinkage of small grain largely depended on the initial grain radius and grain boundary energy.

When the ratio of grain boundary to surface energy was small, the expansion of the grain boundary, i.e., sintering, was fast(see Fig.2 (a), and Fig.3(b) to (d)). If $\alpha=1$ where grain boundary relax no surface energy, nothing happened in grains.

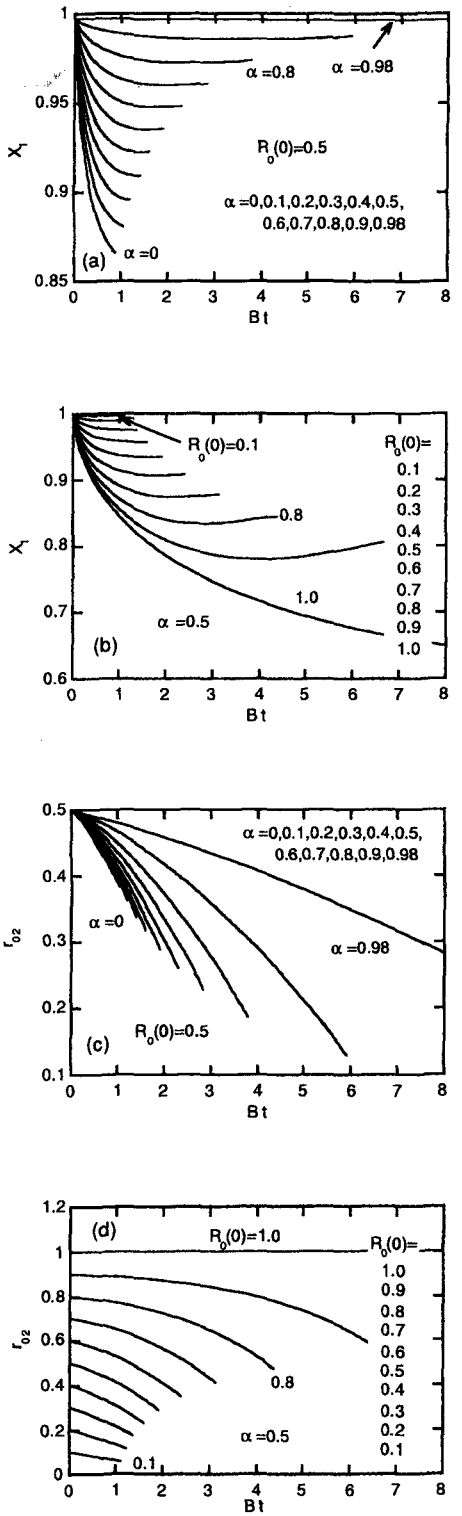

Fig.2 Changes in distance between grain center and grain boundary, $X_{1,2}$, and in grain radii, $r_{01,02}$, with sintering time Bt. B is normalizing factor, $\varepsilon_s D_x V_m/RTr_u^3$, where r_u is unit of radius.

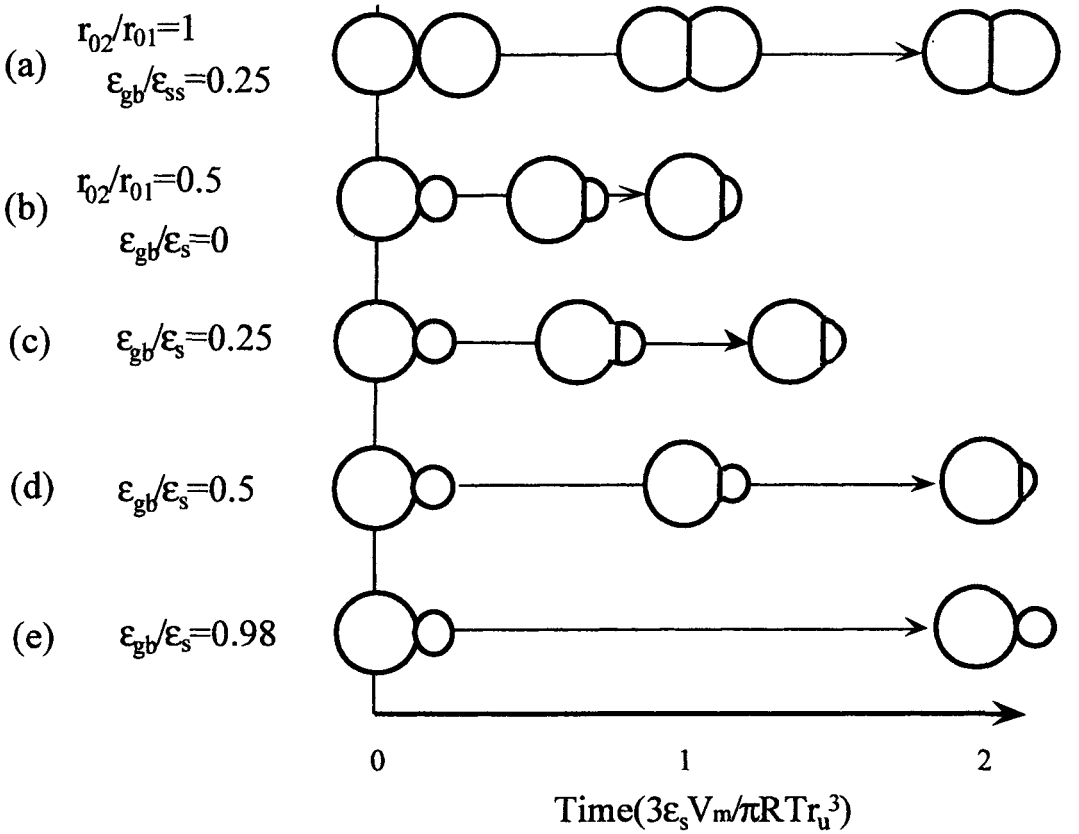

Fig.3 Sintering and grain growth behaviors of two grains as a function of grain size ratio $r_{02}/r_{01}(=R_0)$ and ratio of grain boundary energy to surface energy, $\alpha=\varepsilon_{gb}/\varepsilon_s$.

When the size ratio of two grains (R_0) became smaller, grain growth proceeded more faster, but grain boundary did not expand so much(see Fig .2 (b) and (d)).

The results obtained by the calculations suggest that the smaller the grain boundary energy and the smaller the difference in grain size, the faster the sintering occurs. It is further suggested that ceramic powders, such as Si_3N_4 and SiC, hardly sinter because these materials have a highly covalent bonding nature and grain boundary energy is high ($\alpha\approx1$), and that the additives, such as Al_2O_3 for Si_3N_4 and B and C for SiC, are needed to decrease grain boundary energy. It is also shown that fine powders with uniform grain distribution easily sinter if grains contact uniformly during the sintering process.

4. SUMMARY

Rate equations for sintering and grain growth were derived from the new models and the new rate equation of material transport, i.e. free energy theory for material transport. In the model, it was postulated that sintering and grain growth simultaneously took place and that the excess free energy on the surface and the grain boundary in grains directly drove mass transport for sintering and grain growth by the rate equations that were formulated by Y. Inomata and H. Tanaka.

The sintering and grain growth equations included parameters such as the ratio of grain boundary energy to surface energy, the size ratio and grain distance. From the calculation using the rate equations, it was found that sintering occurred rapidly when the ratio of grain boundary energy to surface energy was small and that with large differences in the size of the two grains grain boundary expanded slowly.

REFERENCES

[1] W. D. Kingery, H. K. Bowen and D. R. Uhlmann, " Introduction to Ceramics", John Wiley and Sons, New York, (1976) pp. 448-515.

[2] Y. M. Chiang, D. P. Birnie and W. D. Kingery, "Physical Ceramics", John Wily and Sons, Inc., New York,(1976) pp.351-429.

[3] J. E. Burke, "Ceramic Microstructures", Ed. by R.M.Fulrath et al., John Wiley & Sons, New York, (1968) pp.681-700.

[4] Y. Inomata, in "Pro. Int. Symp. Ceram. Components for Engine", Ed. by S. Somiya et al., KTK Science, Tokyo, (1983) pp. 753-761.

[5] Y. Inomata, *J. Ceram. Soc. Japan*, **90**, 527-531 (1982).

[6] H. Tanaka, *J. Ceram. Soc. Japan*, **103**, 138-143 (1995), **104**, 253-258 (1996) and **105**, 294-298 (1997).

(Received January 18, 2002; Accepted April 30, 2002)