Initial Sintering of Cylindrical Particles of Different Sizes by Surface Diffusion

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Sintering of two cylindrical particles of different sizes by surface diffusion at the early stage is theoretically analysed. Formulae for the neck growth rate are derived using a variational principle and the continuity equation of vacancies. The size difference between two particles is found to influence the growth rate of the neck only when the difference is large.

§ 1 Introduction

Many theoretical investigations have been made into sintering of two particles of the same size at the initial stage (Kingery and Berg 1955, Nichols and Mullins 1965, Johnson 1969, German and Lathdrop 1978, Coblenz et al. 1980). From the viewpoint of analytical simplicity, particles of the same size have normally been chosen, whereas powders for sintering actually comprise particles with a range of sizes. However there have been very few analytical studies on sintering of particles of different sizes. Only Coble (1973) analysed sintering models for particles with size distributions by lattice or grain-boundary diffusion, making considerable approximations to the geometry of the sintering particles and the diffusion field of vacancies. He showed that the driving force for the neck growth was related to $\gamma\,(R_1^{-1} + R_2^{-1})^{-n}$ where γ is the surface tension, R_1 and R_2 indicate the initial radii of two particles, and n is 1 for lattice diffusion and 2 for grain-boundary diffusion.

This Letter focuses on the growth of sintering particles by surface diffusion which is considered to be a dominant mechanism at the early stage of sintering (Pan et al. 1998). Recently instead of Coble's approximations, self-consistent solutions (Saitou 1999) for the growth rate of sintering particles of a single size have been derived from a variational principle, the continuity equation of vacancies and a shape profile function. The present paper extends the study to the growth of two cylindrical particles of different sizes by surface diffusion at the early stage and presents expressions for the neck growth.

§ 2 Theory

One first needs to find an expression for the pressure p that is related to the vacancy concentration (Kingery and Berg 1955, Nichols and Mullins 1965). The Gibbs-Thompson equation (Johnson 1969) has often been employed to describe the pressure at any point of the surface, $p = \gamma\,[(1/r_a) + (1/r_b)]$ where r_a and r_b are the principal radii of curvature. However, under a fixed volume of two particles it is appropriate to derive the pressure from a variational principle. Hence the problem in this study is to find the smallest free energy under a given area A_c. Fig.1 shows the sintering geometry of the two cylindrical particles that satisfy $a_1 > a_2$ and $b_1 > b_2$. The free energy F and cross-sectional area A_c in this model are given by

$$F = \sum_{i=1}^{2} \Big(\int_{A_i} p_i \,\mathrm{d}A_i + \int_{l_i} \gamma \;\mathrm{d}l_i \Big), \tag{1}$$

$$A_C = \sum_{i=1}^{2} \int_0^{\pi/2} (r_i^2 / 2) \mathrm{d}\theta, \tag{2}$$

where $\mathrm{d}A_i$ indicates the cross-sectional area element for the particle i, $\mathrm{d}l_i$ the line element expressed by $\mathrm{d}l_i = [(r_i')^2 + r_i^2]^{1/2}\mathrm{d}\theta$ for the particle i, r_i' the derivative $\mathrm{d}r_i/\mathrm{d}\theta$, and the radius is represented by a profile function $r_i^2 = b_i^2 - 4a_i^2 \sin^2\theta$ (Saitou 1999). For $b_i = 2a_i$, the profile function becomes a circle of $2a_i$ in diameter. For $b_i > 2a_i$, the profile function represents the shape profile of a sintering particle that is similar to a circle but has a neck region as shown in Fig.1. The parameter b_i indicates the diameter of sintering particles. The neck length r_3 at $\theta = \pi/2$ is equal to $(b_i^2 - 4a_i^2)^{1/2}$. Hence the parameter a_i determines the neck length and the deviation from a circle. The condition $b_i \geq 2a_i$, is used for this study.

Since the problem is to find $\delta(F + \lambda A_C) = 0$ under the mass conservation condition, i.e., a given area A_C where λ is a constant Lagrange multiplier, the procedure of the principle of variation leads to

$$\partial f / \partial r_i - \mathrm{d}(\partial f / \partial r_i') / \mathrm{d}\theta = 0, (i = 1,2), \tag{3}$$

where $f = \sum_{i=1}^{2} (p_i r_i^2 / 2 + \gamma\sqrt{r_i^2 + r_i'^2} + \lambda\ r_i^2 / 2)$. Consequently equation (3) becomes

$$\mathrm{d}p_i / \mathrm{d}r_i + 2p_i / r_i = -2\lambda / r_i - 2\gamma\ (2r_i'^2 + r_i^2 - r_i r_i'') / [r_i (r_i'^2 + r_i^2)^{3/2}], \tag{4}$$

where r_i'' indicates $\mathrm{d}^2 r_i / \mathrm{d}^2\theta$. The solutions of equation (4) have already been reported (Saitou 1999), which have the forms

$$\begin{aligned} p_1 &= -\lambda + g(r_2)/r_1^2 - \gamma\ r_1 / \sqrt{8(b_1^2 - 2a_1^2)(r_1^2 - b_1^2 d_1)}, \\ p_2 &= -\lambda + h(r_1)/r_2^2 - \gamma\ r_2 / \sqrt{8(b_2^2 - 2a_2^2)(r_2^2 - b_2^2 d_2)}, \end{aligned} \tag{5}$$

where $g(r_2)$ and $h(r_1)$ are a function of r_2 and that of r_1, and $d_i = (b_i^2 - 4a_i^2)/[2(b_i^2 - 2a_i^2)]$. The term d_i becomes zero for $b_i = 2a_i$, that is, the cross-sections of the two particles are circles. The boundary condition for equation (5) is $p_i = \gamma / a_i$ for $b_i = 2a_i$, which gives, noting that $d_i = 0$ for $b_i = 2a_i$,

$$-\lambda + g(r_2)/r_1^{\,2} = 5\gamma/(4a_1), -\lambda + h(r_1)/r_2^{\,2} = 5\gamma/(4a_2). \tag{6}$$

Taking the differentials of Eq.(6) with respect to θ , we have $[\mathrm{d}g(r_2)/\mathrm{d}r_2](\mathrm{d}r_2/\mathrm{d}\theta) = 2g(r_2)(\mathrm{d}r_1/\mathrm{d}\theta)/r_1$ and $[\mathrm{d}h(r_1)/\mathrm{d}r_1](\mathrm{d}r_1/\mathrm{d}\theta) = 2h(r_1)(\mathrm{d}r_2/\mathrm{d}\theta)/r_2$. Hence one promptly obtains

$$[\mathrm{d}g(r_2)/\mathrm{d}r_2][\mathrm{d}h(r_1)/\mathrm{d}r_1] = 4g(r_2)h(r_1)/(r_1r_2). \tag{7}$$

The solutions of Eq.(7) become

$$g(r_2) = Mr_2^{\,2},\ h(r_1) = Mr_1^{\,2}, \tag{8}$$

where M is a constant that represents the effect of the size difference. Combining Eqs. (6) and (8) yields for $\theta = 0$,

$$\begin{aligned} M &= (5\gamma/4)\ (1/a_1 - 1/a_2)/[(b_2/b_1)^2 - (b_1/b_2)^2], \\ \lambda &= (5\gamma/4)\ [(b_1/b_2)^2/a_1 - (b_2/b_1)^2/a_2]/[(b_2/b_1)^2 - (b_1/b_2)^2]. \end{aligned} \tag{9}$$

The constant M is a term that results from connection of two particles and may be called a coupling constant.

Next, consider the growth rate of the neck by surface diffusion from the continuity equation of vacancies. According to Kingery and Berg(1955), and Johnson(1969), the vacancy concentration c is given everywhere as $c = C_o\exp(-p\Omega/k_BT)$ where C_o is a constant, Ω the atomic volume, k_B the Boltzmann constant and T the temperature. Using the flux vector of vacancies given by $\boldsymbol{j} = -D_V\nabla c = -D_V(\mathrm{d}c/\mathrm{d}r)(\boldsymbol{r}/r)$ where D_V is the surface diffusion coefficient of vacancies, $\boldsymbol{r}$ the position vector of an arbitrary point on the surface and $\boldsymbol{r}/r$ the unit vector, the continuity equation of vacancies is given by

$$\mathrm{d}\left(\int_{V_O}^{V} \Omega c\,\mathrm{d}V\right)/\mathrm{d}t = -\Omega\int_{S_1+S_2} \boldsymbol{j}\cdot\boldsymbol{t}\,\mathrm{d}S, \tag{10}$$

where V_o is an initial volume of the two cylindrical particles, t indicates the time, S_i the surface area for the cylindrical particle i, $\boldsymbol{t}$ the unit vector tangent to the particle surface which satisfies $(\boldsymbol{r}/r)\cdot\boldsymbol{t} = r'/\sqrt{r'^2 + r^2}$ and $\mathrm{d}S$ the small surface area. Equation (10) indicates that only the tangential component of the vacancy flux on the surface contributes to the neck growth. Moreover it is noted that the left-hand side in this equation represents an integration over the increasing volume at the neck. This is because the sum of the vacancy volume eliminated at the surface is thought to be equal to the increase in the neck volume. Since $\mathrm{d}V_i = -\Omega \mathrm{d}c_i$ for the particle i and $\mathrm{d}S_i = \mathrm{d}l_i \mathrm{x}1$ where the thickness in the z-axis direction is taken as a unit length, Eq.(10) reduces to

$$\sum_{i=1}^{2} \mathrm{d}V_i^{\,2} / \mathrm{d}t = (2\Omega^2 D_V / k_B T)\left(\int_{p_A}^{p_C} c\mathrm{d}p + \int_{p_B}^{p_C} c\mathrm{d}p\right), \tag{11}$$

where p_i is the pressure at the position i (i =A,B, and C) as shown in Fig.1. On the other hand, the increasing volume satisfies using $b_1^2 - 4a_1^2 = b_2^2 - 4a_2^2$,

$$V = \sum_{i=1}^{2} (r_{oi}^{\;2} - a_i^{\;2})/2 = r_3^{\;2}/2, \tag{12}$$

where r_{01} and r_{02} are the initial radii of the particle 1 and 2. Substituting Eq.(12) into Eq.(11) yields

$$r_3^{\;3}\mathrm{d}r_3/\mathrm{d}t = 4\Omega D_v C_O[2\exp(-\Omega p_C/k_B T) - \exp(-\Omega p_A/k_B T) - \exp(-\Omega p_B/k_B T)], \tag{13-a}$$

$$\begin{gathered} p_A = -\lambda + M(b_2/b_1)^2 - \gamma/(2b_1),\; p_B = -\lambda + M(b_1/b_2)^2 - \gamma/(2b_2), \\ p_C = -\lambda + M - \gamma/2r_3,\; \lambda + M = (5\gamma/4)(b_1^{\;2}/a_1 + b_2^{\;2}/a_2)/(b_1^{\;2} + b_2^{\;2}), \end{gathered} \tag{13-b}$$

where the relation $b_1^2 - 4a_1^2 = b_2^2 - 4a_2^2$ is used, and λ and M are given in Eq.(9). Generally the cylindrical particles used for the experiments (Matsumura 1968) have an initial radius 100 to 200 μm. Expanding the exponential terms in Eq.(13-a) since $\Omega p_i / k_B T < 10^{-3}$ (referred to the data of Swinkels and Ashby 1981), and substituting Eqs. (9) and (13-b) into the result, one obtains

$$(k_B T / 4\Omega^2 D_V C_O) r_3^{\,3} \mathrm{d}r_3 / \mathrm{d}t = \gamma\ [(5b_2^{\,2}/4)(1/a_2 - 1/a_1)/(b_1^{\,2} + b_2^{\,2}) + (5b_1^{\,2}/4)(1/a_2 - 1/a_1)/(b_1^{\,2} + b_2^{\,2}) - 1/(2b_2) - 1/(2b_1) + 1/r_3]. \tag{14}$$

The right-hand side in Eq.(14) represents a force per unit area on the surface of the two particles. The first and second terms are ones that result from connection of the two particles by sintering. The force, related to the curvature radius drives the movement of atoms toward the neck.

Here one introduces k and h defined by $k = r_{02}/r_{01}$, $h = r_3/r_{02}$ and $hk = r_3/r_{01}$. Since the non-dimensional length r_3/r_{02} at the initial stage of sintering (Jonson and Cutler 1963, Coblenz et al. 1980) is generally put within a range 10^{-2} to 0.2, one can set k <1 and h<0.2. In order to simplify Eq.(14) and render it soluble, the magnitudes of the terms on the right-hand side can be evaluated as follows:

$$\begin{aligned} &2b_1^{-1}/r_3^{-1} \le 1/\{2[1+4/(hk)^2]^{1/2}\} \cong 0.05,\ 2b_2^{-1}/r_3^{-1} \le 1/\{2[1+4/h^2]^{1/2}\} \cong 0.05, \\ &[(5b_2^{\,2}/4)(a_2^{-1} - a_1^{-1})/(b_1^{\,2} + b_2^{\,2})]/r_3^{-1} \le (5/4)k^2 h(1-k)/(1+k^2) \cong 0.025, \\ &[(5b_1^{\,2}/4)(a_2^{-1} - a_1^{-1})/(b_1^{\,2} + b_2^{\,2})]/r_3^{-1} \le (5/4)h(1-k)/(1+k^2) \cong 0.25. \end{aligned} \tag{15}$$

Therefore at least the following condition is required to neglect the second term on the right-hand side in Eq.(14),

$$(5/4)h(1-k)/(1+k^2) \le 0.05. \tag{16}$$

The value 0.05 is chosen because of the result in Eq.(15). Eq.(16) is plotted in Fig.2 that defines the two areas P and Q. It can be seen from Fig.2 that the size difference k characterized by the radii of the initial particles in the area P has no effect on the neck growth. Fig.2 shows that as long as the size ratio k greater than 0.7, the difference has no effect on the neck growth. Consequently the equations to be solved are

$$r_3^{\,4} \mathrm{d}r_3 / \mathrm{d}t = 4\Omega^2 D_V C_O \gamma\ /(k_B T), \text{ for area P}, \tag{17}$$

$$r_3^{\,4} \mathrm{d}r_3/\mathrm{d}t = [4\Omega^2 D_V C_O \gamma\ /(k_B T)][1 + (5/4) r_3 b_1^{\,2} (a_2^{-1} - a_1^{-1})/(b_1^{\,2} + b_2^{\,2})], \text{for area Q}. \tag{18}$$

If k <1 and h<0.2, one has

$$r_3 b_1^{\ 2}(a_2^{\ -1} - a_1^{\ -1})/(b_1^{\ 2} + b_2^{\ 2}) \approx r_3(r_{02}^{\ -1} - r_{01}^{\ -1})/(1+k^2). \tag{19}$$

Eq. (18) can be rewritten as

$$r_3^{\ 4}\mathrm{d}r_3 / \mathrm{d}t = [4\Omega^2 D_V C_O \gamma \ /(k_B T)][1+(5/4)r_3(r_{02}^{\ -1} - r_{01}^{\ -1})/(1+k^2)]. \tag{20}$$

Hence one has the solutions

$$r_3^{\ 5} = 20\Omega^2 D_V C_O \gamma \ t/(k_B T), \quad \text{for area P,} \tag{21}$$

and

$$\sum_{i=5}^{\infty}(-1)^{i-1}(r_3/B)^i / i = 4\Omega^2 D_V C_O \gamma \ t/(B^5 k_B T), \ \text{ for area Q,} \tag{22}$$

where $B = (5/4)(1+k^2)r_{02}/(1-k)$. Eq.(21) is the same formula as one for two cylindrical particles of the same sizes (Saitou 1999). The sintering experiments of copper wires each of a fixed radius by Alexander and Balluffi (1957), and Ichinose and Kuczynski (1962) showed that the neck growth rate increases as the fifth root of time.

The size difference has no effect on the neck growth as long as the size ratio $k = r_{02}/r_{01}$ greater than 0.7 as shown in Fig.2. This result roughly agrees with the numerical results by Pan et al. (1998) that the neck growth is not affected by the size difference greater than 0.5. However the second term on the right-hand side in Eq.(14) cannot be ignored for the area Q in comparison with r_3^{-1}. This implies that a change of the surface energy of the smaller particle with the sintering time is similar to that at the neck. Hence the force to which the two terms contribute promotes the neck growth by surface diffusion, which results in the greater reduction of the surface area. This well agrees the fact that a greater difference of particle sizes promotes the initial sintering.

Here let us consider roughly evaluating the effect of the particle size difference. From Eqs.(17) and (19), letting G be the growth rate of the neck, one has G (for $r_{01} \neq r_{02}$)/G (for $r_{01} = r_{02}$)=1+(5/4) $h(1-k)/(1+k^2)$. Particles of the different sizes have at most a 1.25 times greater growth rate than those of the same sizes. This well explains the experimental results that, in the initial sintering stage, the size distribution does not change significantly until the neck is completely formed between the particles.

§ 3 Conclusions

The growth rate of the two cylindrical particles of the different sizes by surface diffusion has been derived using the variational principle and continuity equation of vacancies. The solutions indicate that a greater difference between two particle sizes influences the growth rate of the neck.

References

Alexander, B.H., and Balluffi, R.W., Acta Metall.,**5**,666(1957).

Coble, R. L., J. Amer. Ceram. Soc.,**56**,461(1973).

Coblenz, W. S., Dynys, J. M., Cannon, R. M., and Coble, R. L., Mater. Sci. Res.,**13**,141(1980).

German, R. M., and Lathdrop, J. F., J. Mat. Sci.,**1**,921(1978).

Ichinose, H. and Kuczynski, G.C., Acta Mater.,**10**,209(1962).

Johnson, D.L., J. Appl. Phys.,**40**,192(1969).

Johnson, D.L., and Cutler I.B., J. Amer. Ceram. Soc.,**46**,541(1963).

Kingery, W. D., and M. Berg, M., J. Apply. Phys.**26**,1205(1955).

Matsumura, G., Bull. Jpn. Inst. Metals, **7**,448(1968).

Nichols, F.A., and Mullins, W. W., J. Apply. Phys.**36**,1826(1965).

Pan, J., Le, H., Kucherenko, S. and Yeomans, J. A., Acta Mater., **13**,4671(1998).

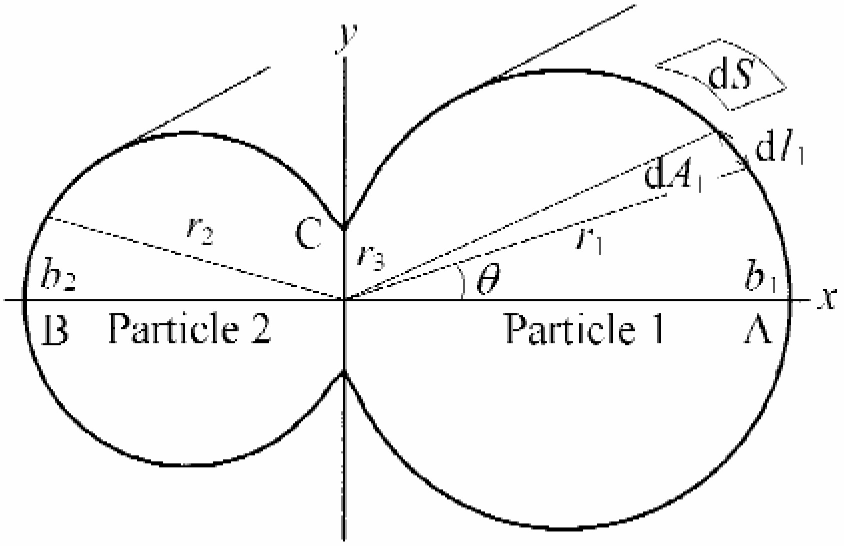
Saitou, M., Phil. Mag. Lett. **79**, 257(1999), **79**,877(1999).

Swinkels, F. B., and Ashby, M. F., Acta Metall., **29**,259(1981).

Figure Captions

Fig. 1 Illustration of the geometry of the two cylindrical particles.

Fig.2 Diagram of the size difference effect on the neck growth rate. The line indicates $h(1-k)/(1+k^2)=0.04$. P : area that has no effect on the growth rate, Q: area that has effect on the growth rate.



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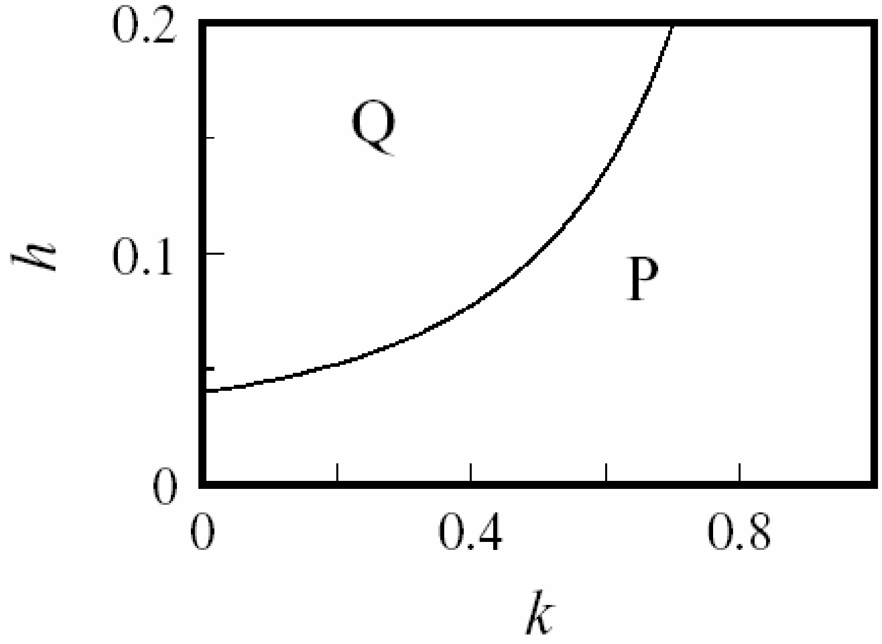

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