Analysis of the Initial Stage of Sintering in Pure Materials by Surface Diffusion

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The growth of two sintering particles by surface diffusion at the initial stage is analytically solved by a variational principle and use of the continuity equation. The solution satisfies the conservation of mass and is rigorously found using no approximations, unlike past studies. The expression for the growth of the two cylindrical particles shows that the length of the neck increases with the fifth power of time.

§ 1. Introduction

Many investigations have been made into the rate of the contact area between two particles at the initial sintering stage (see, for example, Coblenz et al. 1980; Zhang and Schneibel 1995). The rate depends on the mechanism of material transport such as evaporation-condensation, surface diffusion, grain boundary diffusion and lattice diffusion. From the viewpoint of analytical simplicity, a single mechanism is normally chosen and in particular the case of the sintering by the surface diffusion of vacancies has been treated theoretically. However, the analytical solution by surface diffusion has been found by making the following considerable approximations to the geometry of the sintering particles and the diffusion field of vacancies (Kingery and Berg 1955; Nichols and Mullins 1965; Johnson 1969; Coblenz et al. 1980): (1) the volume of the neck increases during the initial sintering process but the remaining portion is unchanged; (2) the neck has a fixed radius of curvature ρ; (3) the vacancy concentration c in pure materials is given by $C_o \exp(-p\Omega/kT)$ where C_o indicates a constant, Ω the atomic volume and k the Boltzmann constant, and the pressure (normal stress) p is approximately equal to $-\gamma/\rho$ where γ is the surface tension ; (4) the relationship between the flux vector of vacancies $\boldsymbol{j}$ and the radius of curvature ρ is approximately represented by $|\boldsymbol{j}| \sim -D_v \Delta c/\rho$ where D_v is the surface diffusion coefficient of vacancies and Δc is the difference between the vacancy concentration at the neck and the remaining portion.

The approximation (1) indicates that the conservation of mass is ignored. Hence the undercutting of the sintering particles which Nichols and Mullins (1965) reported never appears in the model. According to the approximations (2) and (3), the difference between the vacancy concentration at the neck and the remainder causes atom transport to the neck. However, a gradient of the vacancy concentration at the neck does not occur because there is no change of the radius of curvature ρ there. Hence the model under these assumptions is not self-consistent. It is very crude to take $-D_v \Delta c/\rho$ as the approximate form of $\boldsymbol{j} = -D_v \nabla c$. As a consequence, each model predicts its own behaviour of neck growth and it is desirable to find a rigorous solution using none of the assumptions.

Many numerical calculations of sintering particles by surface diffusion have been made. The results by German and Lathrop(1978) are in substantial disagreement with those of Zhang and Schneibel(1995). Hence the importance of finding a physically satisfactory analytical solution should be emphasized.

The purpose of this study is to analyse the growth of two cylindrical particles occurring only by surface diffusion at the initial stage. We make use of a variational principle and the continuity equation of vacancies. The solution of the sintering model by surface diffusion satisfies the conservation of mass and is rigorously found using no approximations and an expression for the growth of the neck with time is given.

§ 2. Theory

We first need to find an expression for the pressure p that is related to the vacancy concentration as stated in § 1. The Gibbs-Thompson equation has often been employed to describe the pressure, which is derived as follows. From $\triangle F = -p\triangle V + \gamma\triangle A$ and $\triangle A/\triangle V = (1/r_a) + (1/r_b)$, the formula $p = \gamma[(1/r_a)+(1/r_b)]$ is obtained where F indicates the Helmholtz free energy, p is the pressure at any point of the surface, V is the volume, γ is the surface tension, A is the surface area, and 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. Fig.1 shows the sintering geometry of the two cylindrical particles in two dimensions. Using $\triangle F = -p\triangle V + \gamma\triangle A$, F and A are given by

$$F = \int (pr^2/2)\, d\theta + \int \gamma[r^2+(r')^2]^{1/2} d\theta, \qquad (1)$$

$$A = \int (r^2/2)\, d\theta, \qquad (2)$$

where r' indicates $dr/d\theta$. The procedure of the principle of variation leads to

$$\partial f/\partial r - d(\partial f/\partial r')/d\theta = 0, \qquad (3)$$

where $f = pr^2/2 + \gamma[r^2+(r')^2]^{1/2} + \lambda r^2/2$ and λ is a constant. Consequently equation (3) becomes

$$dp/dr + 2p/r = -2\lambda/r - 2\gamma/(r\rho), \qquad (4)$$

$$\rho = [(r')^2 + r^2]^{3/2} / [2(r')^2 + r^2 - rr''], \qquad (5)$$

where ρ is the radius of curvature at r and r'' indicates $d^2r/d\theta^2$.

Then instead of a fixed radius of curvature at the neck, as in past studies in which the neck is assumed to be circular, (Kingery and Berg 1955; Nichols and Mullins 1965; Johnson 1969; Coblenz et al. 1980), we assume that the shape profile of the sintering particle is represented by the following equation,

$$r^2=b^2-4a^2\sin^2\theta . \tag{6}$$

For b=2a, equation (6) represents a circle of 2a in diameter. For b>2a, equation (6) represents the shape profile of a sintering particle that is similar to a circle but has a neck region as shown in Fig.2. The parameter b indicates the diameter of sintering particles. The neck length r_1 at $\theta=\pi/2$ is given as $(b^2-4a^2)^{1/2}$. Hence the parameter a determines the neck length and the deviation from a circle. The condition $b\geqq 2a$, is used for this study. As the sintering process proceeds, the growth rate of the neck increases with a decrease in the parameter a. Thus the two parameters a and b enable us to treat the changing shape profile of the particle with time. In summary, equation (6) is chosen because: (1) for the initial time t=0, it indicates a circle and for t>0, it can represent the shape profile of a sintering particle that is similar to the circle but has a neck region; (2) it has a negative surface curvature at the neck and a positive one at the remaining as shown in Fig.2. Such a property of the surface curvature causes surface diffusion and was also used in past studies; (3) it can give a geometrical expression for mass conservation (volume conservation). Substituting equation (6) into equation (4), we have

$$dp/dr+2p/r=-2\lambda/r-2^{3/2}\gamma(r^2-3b^2d/2)/[(b^2-2a^2)(r^2-b^2d)^3]^{1/2}, \tag{7}$$

where $d=(b^2-4a^2)/[2(b^2-2a^2)]$ becomes zero when b=2a, that is, the particles are circles. The first differential equation (7) can be easily solved,

$$p=-\lambda+C_o/r^2-\gamma r/[8(b^2-2a^2)(r^2-b^2d)]^{1/2}, \tag{8}$$

where C_o is a constant of integration. The boundary condition for equation (8) is

$$p=\gamma/a \qquad \text{when } b=2a. \tag{9}$$

For equation (9), we have

$$\lambda=-5\gamma/2b, \tag{10}$$

$C_o = 0$. (11)

Equation (11) is found from the condition that the stress p should be independent of r when b=2a. On the other hand, the conservation of mass (volume) conservation requires

$$A_o = \int_0^{\pi/2} (r^2/2)\, d\theta = \pi r_o^2/2, \quad (12)$$

where r_o is the initial radius of the particle at time t=0. Consequently, equation (12) becomes

$$2r_o^2 = b^2 - 2a^2. \quad (13)$$

From equations (6) and (13), it is found that the shape profile always passes through a fixed point (r_o, r_o). The x-y coordinates (r_o, r_o) at $\theta = \pi/4$ divides the particle into an increasing and decreasing area. The decreasing area, for $0 \leqq \theta \leqq \pi/4$, is called the undercutting area, named by Nichols and Mullins (1965). The occurrence of the undercutting indicates that mass conservation is satisfied during the sintering process. The shape profile of the particle in this study is similar to the numerical result by Zhang and Schneibel (1995). From equations (10) to (13), the solution is given by

$$p = 5\gamma/2b - \gamma r/[4r_o(r^2 - b^2d)^{1/2}]. \quad (14)$$

We can easily make sure that p becomes $2\gamma/b$ when r=b. The value $2\gamma/b$ is consistent with that obtained from the Gibbs-Thompson equation.

Numerous authors (Kingery and Berg 1955; Nichols and Mullins 1965; Johnson 1969; Coblenz et al. 1980) have assumed that p is $2\gamma/b$ at ρ_1 away from the centre as shown in Fig.2. Using equation (14), we examine the validity of the assumption. First, we define r_1 and ρ_1 at $\theta = \pi/2$ from equations (5) and (6),

$$r_1^2 = b^2 - 4a^2, \quad (15)$$

$$|\rho_1| = (b^2 - 4a^2)^{3/2}/(b^2 - 12a^2), \quad (16)$$

where r_1 is the length of the neck and ρ_1 is the radius of curvature at $\theta=\pi/2$. Secondly, we calculate the stress p at $r= r_1+|\rho_1|$ which is a bit larger than $(r_1^2+|\rho_1|^2)^{1/2}$. For $|\rho_1|<<r_1$, as assumed in past studies , we have

$$(r_1+|\rho_1|)^2\sim r^{12}(8r_o^2-3r_1^2)/(8r_o^2-5r_1^2), \tag{17}$$

$$bd^2=r_1^2(4r_o^2-r_1^2)/4r_o^2. \tag{18}$$

Using equations (17) and (18), for $r_1<<r_o$, p at $r= r_1+|\rho_1|$ becomes

$$p\sim 5\gamma/2b-2^{1/2}r_o/r_1. \tag{19}$$

Hence we conclude that p at $r=r_1+|\rho_1|$ is quite different from $2\gamma/b$.

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(1968), the vacancy concentration c is given everywhere as $c= C_o \exp(-p\Omega/kT)$. The continuity equation of vacancies is given by

$$d(\int \Omega c\, dV)/dt=-\Omega\int_G^H \boldsymbol{j}\cdot\boldsymbol{t}\ dS, \tag{20}$$

where c indicates the vacancy concentration, t the time, j the flux vector of vacancies, $\boldsymbol{t}$ the unit vector tangent to the particle surface and dS the small surface area. Equation (20) 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 $dV=-\Omega dc$ and $dS=ds \times 1$ where ds is the line element along the particle surface and the thickness in the z-axis direction is taken as a unit length, equation (20) reduces to

$$dV^2/dt=2\Omega\int_G^H \boldsymbol{j}\cdot\boldsymbol{t}\, ds. \tag{21}$$

The flux vector $\boldsymbol{j}$ is rewritten as

$$\boldsymbol{j} = -D_v \nabla c = -D_v\,(dc/dr)(\boldsymbol{r}/r), \tag{22}$$

where D_v is the surface diffusion coefficient of vacancies, $\boldsymbol{r}$ is the position vector of an arbitrary point on the surface and $\boldsymbol{r}/r$ is the unit vector. Moreover, from the geometry of the particle shown in Fig.2, we have

$$(\boldsymbol{r}/r)\cdot\boldsymbol{t} = r'/[(r')^2+r^2]^{1/2}, \tag{23}$$

$$ds=[(r')^2+r^2]^{1/2}\, d\theta, \tag{24}$$

Hence equation (21) becomes

$$dV^2/dt=(2\Omega^2 D_v/kT)\int_{p_o}^{p_1} c\, dp, \tag{25}$$

where p_o and p_1 are the stress at G and H. On the other hand, the increasing volume is given by

$$V=Ax1=\int_{\pi/4}^{\pi/2} (r^2/2)\, d\theta, \tag{26}$$

where A is the cross-section of the increasing volume for $\pi/4 \leqq \theta \leqq \pi/2$ and the thickness in the z-axis direction is taken as a unit length. Consequently equation (26) becomes

$$V=(r_o^2-a^2)/2. \tag{27}$$

In result, equation (25) becomes

$$d(r_o^2-a^2)^4/dt=-8\Omega D_v C_o[\exp(-\Omega p_1/kT)-\exp(-\Omega p_o/kT)], \tag{28}$$

where $p_o=[2/(r_o^2+a^2)]^{1/2}\gamma$ and $p_1=[2/(r_o^2+a^2)]^{1/2}\gamma+\gamma/\{8[(r_o^2+a^2)^{1/2}-(r_o^2-a^2)^{1/2}]\}$. Equation (28) is derived using no approximations.

Generally speaking, the particles used for the experiments (Kingery and Berg 1955; Johnson 1969) have an initial radius of over 10 μm. The non-dimensional length r_1/r_o in the experiments is put in a range 10^{-2} to 0.2. Since $\Omega p_o/kT<10^{-2}$

(referred to the data of Swinkels and Ashby(1981)) and $(r_o^2-a^2)^{-1/2} >> (r_o^2+a^2)^{-1/2}$, equation (28) becomes

$$d(r_o^2-a^2)^2/dt \sim 4\Omega^2 D_v C_o \gamma/\{kT[2(r_o^2-a^2)]^{1/2}\}. \tag{29}$$

Therefore we have the solution

$$r_1^5=(20\Omega^2\gamma D_v C_o/kT)t. \tag{30}$$

This equation represents the growth of the neck when the atom transport occurs only by surface diffusion. We compare this result with other solutions reported earlier. Equation (30) shows a fifth power relationship between r_1 and t. The theoretical approximate solution by Coblenz et al. (1980) shows the same fifth power relation as ours. But they derived the expression for the rate by making the considerable approximations described in §1. Hence the coefficient in equation (30) is much different from theirs. On the other hand, the numerical calculations by Nichols and Mullins(1965), and Zhang and Schneibel (1995) show a sixth power relation, where German and Lathrop(1978) predict a seventh power relation. The difference between numerical and theoretical solutions is not clear at moment.

In this study, the two-dimensional sintering model is analytically treated. In the three dimensional case, consider whether the exponent n of the power law $r_1^n \propto t$ changes or not. From equations (27) and (29), we obtain $dV/dt \propto -\gamma K$ where K is the surface curvature at $\theta=\pi/2 (K=1/r_a)$, where r_a is the principal radius of the curvature given by $r_a^{-1} \sim -4a^2/r_1^3$ in this study. In three dimensions, we will have $dV/dt \propto -\gamma(1/r_a+1/r_b)$ where r_b is the principal radius of the curvature. Hence if $|r_a| \ll |r_b|$, the exponent n will not change in the three dimensional case. This indicates that the surface tension γ acts as a line force.

§3. Conclusion

An investigation has been made into the growth of the two cylindrical particles by surface diffusion at the initial stage from the principle of variation and the continuity equation. The solution satisfies the conservation of mass and is rigorously obtained using no geometrical approximations as in past studies. The growth of the neck is found to be proportional to the fifth power of time.

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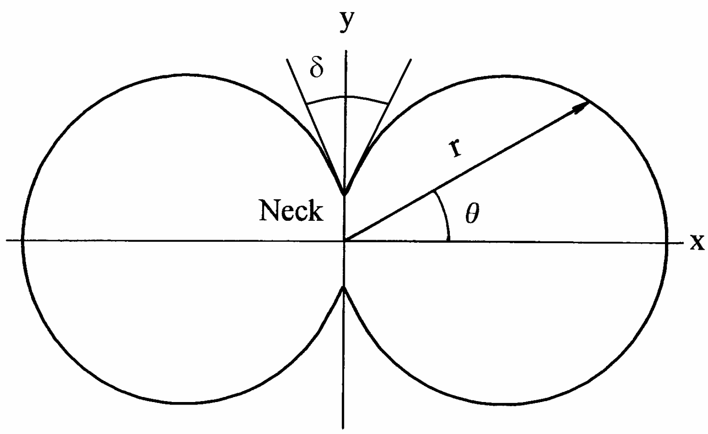
Figure Captions

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

Fig.2 Geometry of the sintering particle.

$\boldsymbol{r}$ / r is the unit vector, t is the unit vector tangent to the shape profile, and $\tan\alpha = r/r'$ where $r' = dr/d\theta$.



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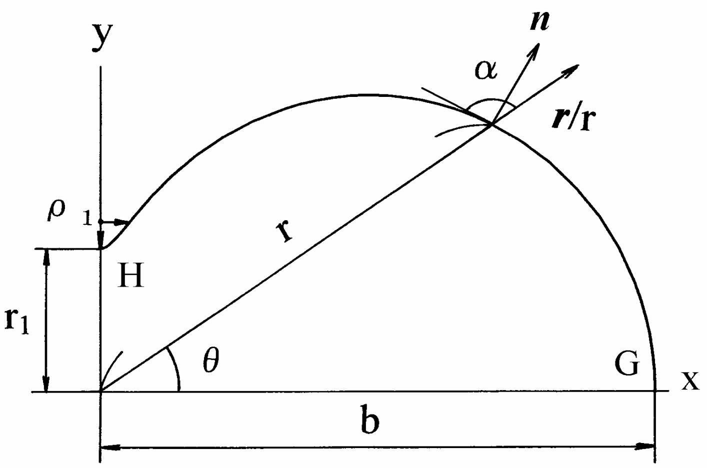

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