Analysis of Sintering of Two Cylindrical Particles by Lattice or Grain Boundary Diffusion at the Initial Stage

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Sintering of two cylindrical particles by lattice or grain boundary diffusion at the initial stage is analysed by a variational principle and use of the continuity equation. The expression for the growth rate by lattice or grain boundary diffusion indicates that the length of the neck increases as a power of time.

§ 1. Introduction

Many analytical investigations have been made into the growth rate of two sintering particles at the initial stage (Kingery and Berg 1955; Nichols and Mullins 1965; Johnson 1969; Coblenz et al. 1980). Their analytical solutions have been derived by considerable approximations applied to the geometry of sintering particles and the diffusion field of vacancies. Consequently there have been discrepancies that a gradient of the vacancy concentration at the neck does not occur or no volume conservation is satisfied. Recently a self-consistent treatment of sintering by surface diffusion has been proposed using a variational principle and the continuity equation (Saitou, 1999). The analytical solution for the growth rate by surface diffusion is found by use of the shape profile function of sintering particles represented by $r^2=b^2-4a^2\sin^2\theta$. The profile function is chosen mainly because it becomes a circle at the initial time and a circle-like figure with the neck profile at the sintering time, and it has a negative surface curvature at the neck and positive one at the remaining. The growth rate by surface diffusion shows the power law($r_1^n \propto t$ where r_1 is the neck length and t is time) and the exponent n=5.

However the treatment proposed has not yet been applied to the case of sintering by lattice diffusion or grain boundary diffusion. In the lattice diffusion model, the vacancy flux represented by $\boldsymbol{j} \propto \nabla c$ where c is the vacancy concentration is transported through the internal part of the particle from the neck to the surface. However the sintering process by grain boundary diffusion has been mainly considered to be a relaxation process of stress by vacancies (Johnson 1969; Zhang and Schneibel 1995). Hence the atomic flux in the grain boundary is represented not by $\boldsymbol{j} \propto \nabla c$ but by $\boldsymbol{j} \propto \nabla \sigma$ where σ is the stress normal to the grain boundary. In this study the stress normal to the grain boundary is also considered to be the driving force for atom transport, and under the condition that the geometrical symmetry of sintering particles holds during sintering, the growth rate of sintering particles by grain boundary diffusion is derived.

The purpose of this paper is to analyse the growth of two cylindrical particles occurring by lattice diffusion or grain boundary diffusion. Making use of a variational principle and the continuity equation of vacancies, we show expressions for the growth of the neck with time.

§ 2. Theory

First, we need to find an expression for the pressure p. In the lattice diffusion model, the pressure is related to the vacancy concentration c given by $c= C_0 \exp(-p\Omega/kT)$ where C_0 indicates a constant value, Ω the atom volume, k the Boltzmann constant and T the temperature. The Gibbs-Thompson equation has often been employed to describe the pressure, that is given as $p=\gamma[(1/r_a)+(1/r_b)]$ where γ is the surface tension, and r_a and r_b are the principal radii of curvature. However, under a fixed volume of two particles (volume conservation) 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.

2.1 Lattice Diffusion

Fig.1 shows the sintering geometry of the two cylindrical particles in two dimensions. The Helmholtz free energy F and the area A are given by

$$F=\int p\, dA+\int \gamma\, dl, \tag{1}$$

$$A=\int (r^2/2)\, d\theta, \tag{2}$$

where the line element along the particle surface dl is given by $dl=[r^2+(r')^2]^{1/2}d\theta$ where r' indicates $dr/d\theta$. The procedure of the principle of variation leads to

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

where $f = pr^2/2+\gamma[r^2+(r')^2]^{1/2}+\lambda r^2/2$ and λ is a constant. The solution has been already reported using the shape profile of the sintering particle represented by $r^2=b^2-4a^2\sin^2\theta$ (Saitou 1999). At the initial time t=0, the profile function represent a circle and at t>0 it can represent a circle-like figure with the neck as shown in Fig.2. The parameter b indicates the diameter of the sintering particle. The parameter a is related to the length of the neck r_1 by $r_1^2 = b^2-4a^2$ and gives deviations from a circle. The condition $b\geqq 2a$, is used for this study. The solution of equation (3) becomes

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

where $d=(b^2-4a^2)/[2(b^2-2a^2)]$. We can easily make sure that p becomes $2\gamma/b$ for r=b. The value $2\gamma/b$ is consistent with that obtained from the Gibbs-Thompson equation. On the other hand, the mass (volume) conservation requires

$$\int_0^{\pi/2} (r^2/2)\, d\theta=\pi r_o^2/2, \tag{5}$$

where r_o is an initial radius of the sintering particle. Consequently, equation (5) becomes

$$2r_o^2=b^2-2a^2. \tag{6}$$

From equation (6), 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 $\theta=\pi/4$ divide 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.

Next, consider the growth rate of the neck by surface diffusion from the continuity equation of vacancies. The continuity equation of vacancies is given by

$$d(\int \Omega c\, dV)/dt=-\Omega \int \boldsymbol{j}\cdot \boldsymbol{n}\, dS, \tag{7}$$

where t indicates time, $\boldsymbol{j}$ the flux vector of vacancies, $\boldsymbol{n}$ the unit vector normal to the particle surface and dS the small surface area on the side. 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 $dS=dl$ x 1 where the thickness in the z-axis direction is taken as a unit length, equation (7) reduces to

$$dV^2/dt=2\Omega \int \boldsymbol{j}\cdot \boldsymbol{n}\, dl. \tag{8}$$

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

$$\boldsymbol{j}=-D_v\nabla c=-D_v\, (dc/dr)(\boldsymbol{r}/r), \tag{9}$$

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

$$(\boldsymbol{r}/r)\cdot\boldsymbol{n} = r/[(r')^2+r^2]^{1/2}, \tag{10}$$

Hence equation (8) becomes

$$dV^2/dt=2\Omega D_v \int (dc/dr) r\, d\theta . \tag{11}$$

From the Appendix, equation (11) becomes

$$dV^2/dt=-2E(r_o^2-a^2)/a^2. \tag{12}$$

On the other hand, the increasing volume is given by

$$V=A_c x 1=\int_{\pi/4}^{\pi/2} (r^2/2)d\theta , \tag{13}$$

where A_c 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 (13) becomes

$$V=(r_o^2-a^2)/2. \tag{14}$$

Hence equation (12) becomes

$$a^2 d(r_o^2-a^2)/dt=-4E\Omega D_v. \tag{15}$$

Integrating equation (15) and applying the initial condition to the result, we have

$$(r_1^2-r_o^2)^2=r_o^4-8E\Omega D_v t. \tag{16}$$

This equation represents the growth of the neck when the atom transport occurs only by lattice diffusion.

Other solutions not for two cylindrical particles but for two spherical particles have been reported before. Hence we here derive a solution for cylindrical particles using the same geometrical assumptions as the past studies (Kingery and Berg 1955, Coble 1958, Coblenz 1980). The geometrical expressions of two cylindrical sintering particles by lattice diffusion are the neck radius $\rho_n=r_1/2r_o$, the area of the neck surface $S_n=\pi\rho_n/2$ and the neck volume $V_n=r_1\rho_n$. According to the Coble's study (1958), the continuous equation of vacancy is

$$dV_n/dt=j_c S_n \Omega, \tag{17}$$

where the vacancy flux is given by $j_c=D_v\Delta c$ and the difference between the vacancy concentration at the neck and that at the remaining portion is expressed by $\Delta c=\gamma\Omega C_o/(kT\rho_n)$. Substituting the geometrical expressions into equation (17) and integrating the result, we have

$$r_1^5=20r_o^2 D\gamma\Omega t/(3kT), \tag{18}$$

where the diffusion coefficient of atoms is defined by $D=D_V C_o\Omega$ (Kingery and Berg 1955, Coble 1958). The neck length increases as a fifth power of time. To see the time-dependent behavior of the neck length in equations (16) and (18), we choose as a typical example copper wires 200μm in diameter (Matsumura 1968). Using the thermo-physical data of copper at 1273K (Swinkels and Ashby,1981), $B\approx Co$, $D(cm^2/sec)=1.89\times10^{-9}$ and $\gamma\Omega/kT(cm)=1.16\times10^{-7}$ are obtained. Consequently we have

$$[1-(r_1/r_o)^2]^2=1-2.18\times10^{-6}t, \tag{19}$$

$$(r_1/r_o)^5=1.46\times10^{-9}t, \tag{20}$$

which are plotted in Fig.3. It can been seen that in addition to the exponent there is considerable difference between the values of r_1 in equations (19) and (20).

2.2 Grain Boundary Diffusion

In a similar way, we first consider a solution that gives the minimum free energy. As shown in Fig.1, the grain boundary defined in this study is the joint plane of the two cylindrical particles. The vacancy diffusion paths from the neck to the grain boundary are illustrated in Fig.2. In the case of sintering by grain boundary diffusion, the free energy has the form,

$$F=\int p\,dA+\int \gamma\, dl+(2/\pi)\int \gamma_G\, r_1 d\theta. \tag{21}$$

where γ_G indicates the grain boundary energy. The procedure of the principle of variation formally leads to

$$\partial f/\partial r-d(\partial f/\partial r')/d\theta=0, \tag{22}$$

$$\partial f/\partial r_1 - d(\partial f/\partial r_1')/d\theta = 0, \tag{23}$$

where $f = pr^2/2 + \gamma[r^2 + (r')^2]^{1/2} + 2\gamma_G r_1/\pi + \lambda r^2/2$, r_1' is $dr_1/d\theta$ and λ is a constant. If the grain boundary is not perpendicular to the x-axis, the function f should become $f(r, r', r_1, r_1')$. But in this study the grain boundary is assumed to be always normal to the x-axis. Consequently equations (22) and (23) become

$$dp/dr + 2p/r = -2\lambda/r - 2\gamma/(r\rho), \tag{24}$$

$$dp/dr_1 = 0, \tag{25}$$

$$\rho = [(r')^2 + r^2]^{3/2} / [2(r')^2 + r^2 - rr''], \tag{26}$$

where ρ is the radius of curvature at r and r'' indicates $d^2r/d\theta^2$. The solution of equation (24) is given by the same form as the case of lattice diffusion,

$$p = -\lambda + C_o/r^2 - \gamma r/[4r_o(r^2 - b^2 d)], \tag{27}$$

where $C_o = C_o(r_1)$. From equations (25) and (27), we have $C_o = -4r_1\gamma_G/\pi + C_1$ where C_1 is a constant. Hence p is given as

$$p = -\lambda - \gamma r/[4r_o(r^2 - b^2 d)] - 4\gamma_G r_1/(\pi r^2) - C_1/r^2. \tag{28}$$

The boundary conditions for equation (24) are

$$r_1 = 0,\ p = \gamma/a, \quad \text{for } b = 2a. \tag{29}$$

Hence we have $C_1 = 0$ and $\lambda = -5\gamma/(4r_o)$.

In general, the atomic flux is represented by $\boldsymbol{j} = -D(\nabla c - c\boldsymbol{F}/kT)$ where $\boldsymbol{F}$ is the force vector (De Groot and Mazur1984). If the system is in a stress field, the force is equal to $-\nabla(\Omega\sigma)$ (Allnatt and Lidiard 1993). The driving force for atom transport in the grain boundary is considered to be the stress gradient rather than the vacancy concentration gradient(Johnson 1969, and Zhang and Schneibel 1995). We assume that the geometrical symmetry of sintering particles holds during sintering. Hence the grain boundary remains straight. The atomic flux equation for grain boundary diffusion (Johnson 1969, and Zhang and Schneibel 1995) is

$$\boldsymbol{j}=-\mu\nabla\sigma(y), \tag{30}$$

where $\mu=D/kT$ and $\sigma(y)$ indicate the atom mobility and the stress normal to the grain boundary at y. The assumption that geometrical symmetry of sintering particles keeps unchanged during sintering requires

$$\nabla\boldsymbol{j}=-\mu\nabla^2\sigma(y)=\text{constant}. \tag{31}$$

This equation holds at any points along the grain boundary. The boundary conditions for $\sigma(y)$ are

$$\sigma(y)=p, \qquad \text{at } y=r_1, \tag{32}$$

$$d\sigma(y)/dy=0, \quad \text{at } y=0, \tag{33}$$

$$\int_{-r_1}^{r_1}\sigma(y)\,dy=2\gamma\sin(\delta/2), \tag{34}$$

where δ is the dihedral angle and in the case of using $r^2=b^2-4a^2\sin^2\theta$ the angle δ becomes π. The symmetry of $\sigma(y)$ in the x-axis is represented in equation (33). Equation (34) indicates the force balance exerted on the particle. Since the stress distribution $\sigma(y)$ is known as a quadratic polynomial (Zhang and Schneibel 1995), equation (32) and the boundary conditions give

$$\nabla^2\sigma(y)=-(9\gamma/2+12\gamma_G/\pi)/r_1^3+15\gamma/(4r_o r_1^2). \tag{35}$$

The non-dimensional length r_1/r_o and r_1/a in the experiments is put in a range 10^{-2} to 0.1. Hence equation (35) becomes approximately

$$\nabla\boldsymbol{j}\approx D(9\gamma/2+12\gamma_G/\pi)/(r_1^3\,kT), \tag{36}$$

From equation (8), the continuity equation is

$$d(V^2/2)/dt=\Omega\int\nabla\boldsymbol{j}\,dV. \tag{37}$$

If equation (31) holds constant in a range of ε where ε is the thickness of the region of enhanced diffusion at the grain boundary (Coble 1958,Johnson 1969), integration of equation (37) is immediately made,

$$d(V^2/2)/dt= \varepsilon \Omega D(9 \gamma /2 +12 \gamma_G / \pi) /(r_1^2kT) . \quad (38)$$

Consequently we have the solution

$$r_1^6=72 \varepsilon \Omega D(3\gamma +8\gamma_G/\pi) t/(kT). \quad (39)$$

This equation represents the growth of the neck when the atom transport occurs only by grain boundary diffusion. Equation (39) shows a sixth power relationship between r_1 and t.

As stated in 2.1 Lattice Diffusion, a solution for cylindrical particles using the same geometrical assumptions as past studies is needed to compare. From $\sigma(r_1)=-\gamma/\rho_n$ used in the past studies(Johnson 1969), and equations (33) and (34), the atomic flux at the neck is given by

$$j_n=3D\gamma/(kTr_1\rho_n), \quad (40)$$

where $\rho_n=r_1^2/(4r_o)$ (Coble 1958). Substituting $S_n=\varepsilon x1$ and equation (40) into equation (17) and integrating the result, we have

$$r_1^6=96D\gamma\Omega r_o^2\varepsilon t/(kT). \quad (41)$$

In comparison with equation (39), equation (41) includes the term r_o^2 as well as other solutions for spherical particles. In view of the diffusion path of atoms, the motion of atoms will be influenced only by the grain-boundary except the point $r= r_1$ (see the second term in the right hand side of equation (35)). Hence it seems that the neck growth has no relation to the initial size of sintering particles. The ratio of r_1 in equation (39) to that in equation (41) is

$$R= \{3[3 +8\gamma_G/(\gamma\pi)]/(4 r_o^2)\}^{1/6}. \quad (43)$$

From the data of copper, $\gamma_G/\gamma=0.349$ (Koda 1976) and a typical wire radius r_o(cm) $=1x10^{-2}$ (Matsumura 1968), we obtain a very great value R=5.5 owing to the term r_o^2, which implies that equation (41) underestimates at the effect of grain boundary diffusion on the particle growth.

Thus we have the formulae for the growth rate of sintering cylindrical particles. However it is not so easy to determine the exponent n ($r_1^n \propto t$) from experimental data. For defects and impurities in the real system, taken into no consideration in this study, will influence atom transport. Especially thin oxide layers formed on the surface of metal particles even in a low vacuum pressure will have a great effect on the growth of necks. Moreover what condition determines the dominant mechanism is not clear at present. Hence it is thought that these problems are next subjects to be treated in experimental and analytical ways.

§ 3. Conclusion

An investigation has been made into the growth of the two cylindrical particles by lattice or grain boundary diffusion at the initial stage from the principle of variation and the continuity equation reported before. The solution satisfies the conservation of mass and is rigorously obtained using no geometrical approximations as in past studies. Thus the growth of the neck by lattice or grain boundary diffusion is found to increase as a power of time.

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Appendix

In an range of θ in equation(12), the following relation consists,

$$\{2/[1+(a/r_o)^2]\}^{1/2} \leqq r/(r^2-b^2d)^{1/2} \leqq \{2/[1+(a/r_o)^4]\}^{1/2}. \tag{A.1}$$

Generally speaking, the wires used for the experiments (Matsumura 1968) have an initial diameter 100 to 200 μm. The non-dimensional length r_1/r_o in the experiments is put in a range 10^{-2} to 0.1. Hence we have

$$0.995 \leqq (a/ r_o)^2 \leqq 0.99995. \tag{A.2}$$

From equations (A.1) and (A.2), $r/(r^2-b^2d)^{1/2}$ has almost no change over the range of θ in comparison with $(r^2-b^2d)^{-1}$. Hence we have

$$\int (dc/dr)r\, d\theta = -C_o\Omega\gamma b^2d/(4r_okT) \int r(r^2-b^2d)^{-3/2}\exp(-\Omega p/kT)\, d\theta$$

$$\approx -B\Omega\gamma db^2r/[4r_okT(r^2-b^2d)^{1/2}] \int (r^2-b^2d)^{-1}\, d\theta, \tag{A.3}$$

where $B= C_o\exp[-5\Omega\gamma/(2bkT)]\exp\{\Omega\gamma r/[4r_okT(r^2-b^2d)^{1/2}]\}$ becomes nearly constant over the range of θ since $\Omega\gamma/kT \approx 10^{-6}-10^{-7}$ cm and $b \approx 5\times10^{-3}$ cm (referred to the data of Swinkels and Ashby(1981), and Kingery and Berg(1955)). Using (A.2), we obtain

$$(r^2-b^2d) \approx 2a^2(1+\cos 2\theta), \tag{A.4}$$

$$b^2rd/(r^2-b^2d)^{1/2} \approx 2(r_o^2-a^2). \tag{A.5}$$

In the end, substituting (A.4) and (A.5) into (A.3) and integrating the result over θ, we have

$$\int (dc/dr)r\, d\theta = -E(r_o^2-a^2)/a^2, \tag{A.6}$$

where $E= B\Omega\gamma/(8r_okT)$.

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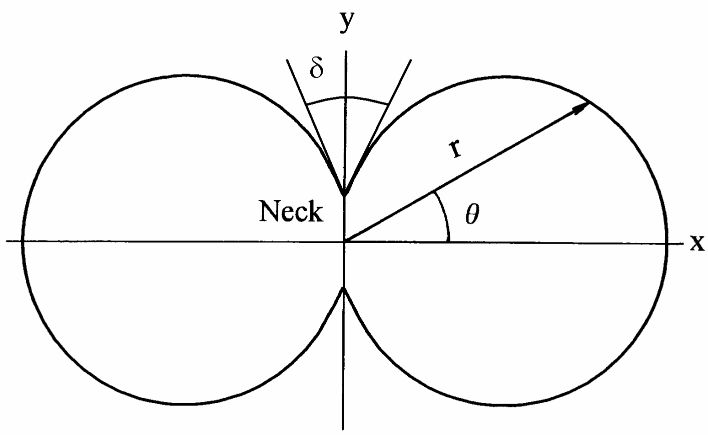
Figure Captions

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

Fig.2 Geometry of the sintering particle. The arrows near the grain boundary indicates the diffusion paths of atoms.
$\boldsymbol{r}$ / r is the unit vector, $\boldsymbol{n}$ is the unit vector normal to the shape profile, and $\tan\alpha = r/r'$ where $r' = dr/d\theta$.

Fig.3 Numerical comparison of two kinds of the neck growth equations for copper wires by lattice diffusion.



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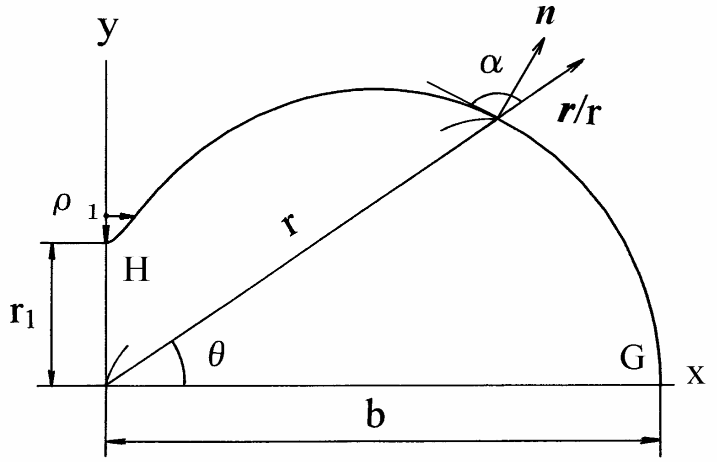

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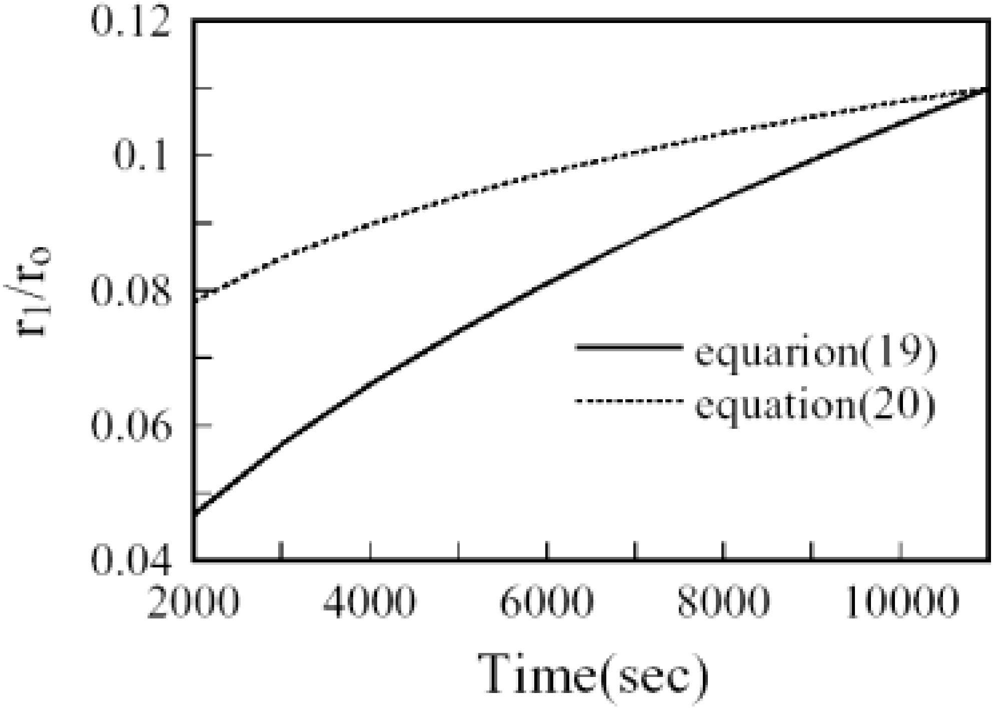

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