A Free Energy Approach for Deriving Rate Equations for Diffusion-controlled Sintering

Susumu ONAKA\(^1\) and Masaharu KATO\(^2\)

\(^1\) Department of Engineering Science, Faculty of Engineering, Kyoto University, Yoshida-honmachi, Sakyo-ku, Kyoto, Kyoto-fu, 606 Japan.
\(^2\) Department of Materials Science and Engineering, Tokyo Institute of Technology, Nagatsuta, Midori-ku, Yokohama, Kanagawa-ken, 227 Japan.

(Received on November 30, 1988; accepted in the final form on May 19, 1989)

Diffusion-controlled sintering is discussed from thermodynamic and kinetic points of view and sintering rate equations are derived by regarding the overall change in the free energy of a material being sintered as driving force of diffusion. This new approach is much simpler than the conventional one and it enables us to derive the rate equations without knowing local chemical potential fields. The kinetics of the diffusional shape change of pores in the sintering aggregate is also formulated. On the basis of the derived rate equations, new criteria are proposed for the change in sintering stages. The results of the present theoretical analyses are compared with previous experimental results. Reasonable agreement between them is found.

KEY WORDS: sintering; diffusion; grain boundary; rate equations; free energy.

1. Introduction

One of the classical and important problems in the theories of sintering is to find rate equations for such basic processes as neck growth and densification. Since diffusion plays an important role in sintering, efforts to relate sintering rates to sintering conditions and material constants for several different diffusion-controlled processes have been made by a number of investigators.\(^1\)\(^-\)\(^8\) The common method to derive diffusion-controlled sintering rate equations in these previous studies is to formulate diffusion equations by finding the local gradient of the chemical potential of an atom as a function of the geometry of an aggregate being sintered.

Upon examining diffusion-controlled high-temperature deformation and fracture mechanisms,\(^9\)\(^-\)\(^11\) we naturally noticed that very similar formulations can apply to the problem of diffusion-controlled sintering.\(^12\) Thermodynamically speaking, the neck growth and densification occur since these processes decrease the overall free energy of the sintering aggregate. Therefore, the sintering rate equations can be derived directly by considering the overall change in the free energy of the material as the driving force of the diffusive flow of matter. Because sintering temperatures are usually kept constant, it is adequate to consider the change in the Helmholtz free energy for pressureless sintering.

In this paper, we will use this concept to study the diffusion-controlled sintering and will derive fundamental sintering rate equations for initial, intermediate and final stages of sintering. It should be reminded that the purpose of the present study is not to construct the whole spectrum of a new sintering theory but rather to reexamine and clarify the physics involved in the diffusion-controlled sintering processes. Therefore, such processes as vapor evaporation-condensation or grain growth,\(^12\)\(^-\)\(^18\)\(^,\)\(^17\) which can be important under certain range of sintering stages and conditions, will not be treated in the present study.

We will also formulate quantitative criteria to separate the stages of sintering. In this formulation, the relative contribution of so-called densifying and shape-changing mechanisms to each stage of sintering will be discussed under a given set of sintering conditions. Finally, the present theoretical study will be compared with other theoretical and experimental studies available in the literature.

2. Stages of Sintering and Diffusion-controlled Mechanisms

In order to clarify the concept of the present approach, we will only consider the isothermal sintering of a close-packed aggregate of parallel wires of radius \(R\), as shown in Fig. 1(a). Sintering under other geometrical conditions, such as the sintering of spherical particles, can be treated in a similar manner. Depending on the shapes of pores between wires, the sintering processes have been conventionally divided into three sequential stages, i.e., Stages 0, 1 and 2.\(^5\)\(^,\)\(^13\) As Stages 1 and 2, where the diffusion-controlled mechanisms become operative, are the essential processes of the sintering phenomena,\(^5\)\(^,\)\(^13\) we will focus on these two stages in the rest of the present study.

We assume that grain boundaries in the sintering aggregate are formed only at the contact areas of the wires during the sintering. Just for the purpose of simplicity, we will also neglect the grain-boundary
energy so that the cylindrical pores between wires should have an equilibrium circular cross section in Stage 2. Figs. 1(b) and 1(c) show the shapes of the pores and the location of the grain boundaries during each stage of sintering. The inclusion of the grain-boundary energy contribution results in the change in the equilibrium pore shape. However, except for the appearance of some geometrical factors, the following argument remains valid.

As shown by previous studies, four kinds of matter transport listed in Table 1 play important roles in the diffusion-controlled neck growth and densification during sintering. We classify these mechanisms into the following two groups:

I) Densifying mechanisms (Mechanisms 1 and 2); these cause the volume change of the pores by the flow of atoms from grain boundaries to neck surfaces.

II) Shape-changing mechanisms (Mechanisms 3 and 4); these cause only the shape change of the pores from their unequilibrium shapes towards the equilibrium shape.

Using appropriate models, we will first derive the sintering rate equations for each mechanism in the two groups.

3. Fundamental Equations

As shown in Fig. 2(a), let us consider a regular-triangular region of side length 2c and unit depth (measured perpendicularly to the sheet) in which the amount of matter is conserved during sintering of the wire aggregate. The assignment of a specific sintering mechanism enables us to evaluate the change in the overall Helmholtz free energy, $\partial F$, associate with the diffusive movement of $\partial n$ atoms. Since $\partial F$ is considered to drive diffusion, the average thermodynamic force acting on an atom, $f_p$, is expressed as

$$ f_p = -\frac{\partial F}{\partial n}/l, \quad \text{(1)} $$

where, $l$: the average diffusion distance of atoms.

From Einstein's equation, the average drift velocity of atoms, $v$, can then be written as

$$ v = (f_p D)/(kT), \quad \text{(2)} $$

where, $D$: a characteristic diffusion coefficient

$k$: the Boltzmann constant

$T$: absolute temperature.

If $\partial n$ atoms are transported across an area $a$ per unit depth (cross-sectional area of diffusion) during the time interval $\partial t$, conservation of matter requires

$$ \partial n = \text{vol} \partial t, \quad \text{(3)} $$

where, $\text{vol}$: the atomic volume.

From Eqs. (1) to (3), we have

$$ \frac{\partial n}{\partial t} = \left(\frac{D}{kT}\right)\left(\frac{\partial F}{\partial n}\right)\left(\frac{a}{l}\right). \quad \text{(4)} $$

This basic equation will be applied to derive various sintering rate equations.

Different from the usual classical method based on the evaluation of the local chemical potential of an atom, only the overall change in the Helmholtz free energy will be considered in the energy discussion. Therefore, the adoption of the present method not only makes the derivation much simpler, but also keeps the physical background clearer. Moreover, if external stress such as hydrostatic pressure is applied during sintering, we can simply substitute the change in the Gibbs free energy, $\delta G$, for $\delta F$ to incorporate the change in the potential energy for the external stress system.

4. Derivation of Rate Equations

4.1. Densifying Mechanisms

As listed in Table 1, grain boundaries are the sources for the Group I) densifying mechanisms. The densifying mechanisms can operate both in Stages 1
and 2.

4.1.1. Stage 1 Densification Model

Here, we will derive the rate equations for the densifying mechanisms (Mechanisms 1 and 2 in Table 1) during Stage 1 under the assumption that the effects of the operation of the shape-changing mechanisms (Mechanisms 3 and 4 in Table 1) can be neglected except at the local neck-surface regions. In other words, we assume that the redistribution of atoms at the pore surfaces is very limited and the atoms flowed into the pores from the grain boundaries are accumulated at the neck-surface regions. This assumption can be justified at the early stage of the Stage 1 sintering, because the widths of the necks and the neck-surface regions are much smaller than the radius of the wire.

On the basis of the above assumption, we will consider the simple geometry of the sintering aggregate shown in Fig. 2, the Stage 1 densification model. Such a simple flat neck-surface approximation, rather than a more detailed curved neck surface, is sufficient in the present study. This is because we consistently stand on a viewpoint that it is the change in the overall Helmholtz free energy that drives diffusion. Therefore, the detailed description of the local neck-surface shape is not needed. From simple geometrical consideration, we find the relationship among $R$, $x$ (one half of the neck width), $y$ (one half of the interpenetration between two wires), $z$ (one half of the width of the neck surface region between two wires) and $\theta$ in Fig. 2(b) as

\[ x = R \sin \theta, \]
\[ y = R(2 - \theta) \sin \theta - \cos \theta]/2, \]
\[ z = R(\theta) \sin \theta - \cos \theta]/2. \]

Even if Stage 1 proceeds according to the Stage 1 densification model, the shape of the cross section of the pores eventually becomes equiaxed, as approximated by a regular hexagon in Fig. 2(c). In the present study, this stage is identified as the end of Stage 1 controlled solely by the densifying mechanisms. At this critical stage, the following equation is satisfied.

\[ z = R(\pi/6 - \theta) \]

which, with Eq. (5), leads to

\[ \theta = 0.455 \]

for the critical (maximum) value of $\theta$ at the end of Stage 1. Therefore, the maximum neck size for Stage 1 controlled by the densifying mechanisms is $x/R = 0.439$. Swinkels and Ashby\(^{13}\) approximated the neck surface region to have the radius of curvature $\rho$ defined as $\rho = x^2/2(R-x)$ and derived the critical value $x/R = 0.443$ at the start of Stage 2 after the operation of only the densifying mechanisms in Stage 1. The good agreement between the two critical values indicates that the present much simpler geometry of the sintering aggregate can give almost the same geometrical characteristics, such as the cross-sectional area of the pores and the width of the necks, as those considered previously.\(^{13}\)

Instead of Eqs. (5), however, it is more convenient to adopt the following approximate equations:

\[ x \approx R \theta, \]
\[ y \approx R^2/2, \]
\[ z \approx R^2/3. \]

For $0 \leq \theta \leq 0.455$, the differences between Eqs. (6) and the corresponding Eqs. (5) are at most 4%. Therefore, we will use the simpler Eqs. (6) in the following analysis.

As mentioned in the previous section, all calculations below will be performed for one rectangular-triangular region of side length $2C$ and unit depth (Fig. 2(a)). $C$ can be expressed in terms of $R$ and $x$ as

\[ C = R - y = R(1 - x^2/6R^2). \]

If $C$ decreases as the necks grow and, thereby, the densification occurs.

When the diffusive flow of atoms causes the neck growth by $2\Delta x$ ($=2Ra\theta$) during an infinitesimal time interval $\Delta t$, the reduction in the surface area of the pore leads to the change in the Helmholz free energy of the material, $\Delta F$, as

\[ \Delta F = -6R(\Delta \theta + 6\Delta x) = -6R(1 - 2\theta)/3\Delta \theta, \]

where, $F$: the surface energy per unit area.

The volume of the transported matter, $\Delta V$, to cause the neck growth by $2\Delta x$ and the number of atoms transported from the grain boundaries to the neck, $\Delta n$, are related as

\[ \Delta V = \Delta n, \]

where,

\[ \Delta V = \frac{3}{2}(4\Delta x\rho) = 2R\rho^2 \Delta \theta. \]

is obtained for the geometry shown in Fig. 2.

The diffusion distance of atoms is approximated as a quarter of the neck width $2x$ or

\[ \Delta l = x/2 \]

for both Mechanisms 1 and 2. When diffusion occurs only along grain boundaries (Mechanism 1), we have

\[ D = D_b \]

where, $D_b$: the grain-boundary self diffusion coefficient.

\[ W_b: \] the effective thickness.

The factor three in front of $W_b$ arises since three grain boundaries meet a pore in the present model. Substituting Eqs. (6) and (8) to (12) into Eq. (4), we have the neck growth rate for Mechanism 1:

\[ \frac{\Delta x}{\Delta t} = 9W_bD_b \left( \frac{1 - 2\Delta x}{3K} \right) \frac{R^2}{x^2} \]

(Grain-boundary diffusion).\(^{13}\)

On the other hand, when volume diffusion (Mechanism 2) occurs solely, $D$ and $a$ in Eq. (4) become

\[ D = D_a \]

where, $D_a$: the self-diffusion coefficient.
where, $D_c$: the volume self diffusion coefficient. Here, $a$=3x is assigned since $x$ can be considered as the area of the sources of matter on a grain boundary per unit depth. Then, substitution of Eqs. (6), (8) to (11) and (14) into Eq. (4) leads to

$$\frac{\partial x}{\partial t} = \frac{9}{kT} \frac{D_s}{1 + \frac{2x}{3D_c}} \left(1 - \frac{2x}{3R} \right) R^2$$

(Volume diffusion). ......................(15)

When the grain-boundary diffusion and volume diffusion cooperate, the total changes in $F$, $V$ and $x$ are regarded to be the sum of the contributions by the two mechanisms. Then, we obtain the neck growth rate:

$$\left( \frac{\partial x}{\partial t} \right)_L = \frac{9}{kT} \left(1 + \frac{W_s D_b}{x D_c} \right) \Omega \Gamma' \left(1 - \frac{2x}{3R} \right) R^2$$

(Stage 1 densification model), ......................(16)

where the subscript 1 in the left-hand side represents the Stage 1 densification model. From Eq. (16), it is found that when $W_s D_b > x D_c$, Mechanism 1 is dominant and when $W_s D_b < x D_c$, Mechanism 2 is dominant.

4.1.2. Stage 2 Densification Model

At the end of Stage 1, the pores become equiaxed (rounded) and small. Then, since the diffusion distance for the shape-changing mechanisms becomes small, these mechanisms can operate rapidly. In other words, we can define Stage 2 as the stage where the pores shrink keeping their equilibrium circular cross section and sintering is controlled by the densifying mechanisms. In the following, by considering the geometry of the sintering aggregate shown in Fig. 3, rate equations for the Stage 2 sintering will be derived.

The infinitesimal change in the pore radius by $d \rho$, during $d t$ introduces the change in the Helmholtz free energy, $\delta F$, as much as

$$\delta F = 2\pi r d\rho.$$ ..............................(17)

Calculations to derive the rate equations will again be performed for the regular-triangular region of side length 2C and a unit depth.

The volume of the transported matter, $\delta V$, to shrink the pores by $d \rho$ is expressed by the pore radius, $r$, and its change, $d \rho$, as*

$$\delta V = -2\pi r d\rho.$$ ..............................(18)

Since $\delta V$ is related to $d \rho$ through Eq. (9), we have a pore shrinkage rate equation from Eqs. (4), (17) and (18):

$$\frac{d \rho}{d t} = \frac{1}{2\pi} \frac{D_s}{kT} \frac{1}{r^2} \frac{\Omega \Gamma'}{R^2}$$

(Stage 2 densification model). ......................(19)

The diffusion distance, $l$, for the grain-boundary and volume diffusions is again estimated to be $x/2$. From the conservation of matter, we obtain a geometrical relationship:

$$\sqrt{3} C^2 - \pi \rho^2 = \pi R^2/2.$$ ..............................(20)

Then, $l$ and $x$ can be expressed in terms of $R$ and $r$ as

$$2l = x = \left(\sqrt{3} \pi/18\right)(R^2 + 2r^2)^{1/2} - r.$$ ..............................(21)

Because $r$ is at most 0.227R (in the case of C=R in Eq. (20) in the present model and it is much less than $R$ during the most period of the Stage 2 sintering, Eq. (21) can be approximately rewritten as

$$2l = x \approx (\sqrt{3} \pi/18)^{1/2} R - r = 0.5500 R - r.$$ ..............................(22)

$D$ and $a$ in Eq. (19) for the grain-boundary diffusion (Mechanism 1) and volume diffusion (Mechanism 2) are given by Eqs. (12) and (14), respectively. From Eqs. (12) and (19), and noting $(\partial x/\partial t)_L = -(\partial \rho/\partial t)$ from Eq. (22), we obtain the neck growth rate controlled by Mechanism 1 as

$$\frac{\partial x}{\partial t} = \frac{3}{\pi} \frac{W_s D_b}{kT} \frac{\Omega \Gamma'}{r^2}$$

(Grain-boundary diffusion). ..............................(23)

When the neck growth is controlled by the volume diffusion (Mechanism 2), the neck growth rate is obtained from Eqs. (14), (19) and (22) as

$$\frac{\partial x}{\partial t} = \frac{3}{\pi} \frac{1}{kT} \frac{W_s D_b}{x D_c} \frac{\Omega \Gamma'}{r^2}$$

(Volume diffusion). ..............................(24)

The neck growth rate for the simultaneous operation of Mechanisms 1 and 2 becomes from Eqs. (23) and (24):

$$\left( \frac{\partial x}{\partial t} \right)_L = \frac{3}{\pi} \frac{W_s D_b}{kT} \frac{\Omega \Gamma'}{r^2}$$

(Stage 2 densification model), ..............................(25)

where the subscript 2 in the left-hand side denotes the Stage 2 densification model.

4.2. Shape-changing Mechanisms

In Stage 2, the shape-changing mechanisms to maintain an equilibrium pore shape occur very rapidly. Therefore, the present Stage 2 densification model is regarded to satisfactorily represent the later stage of sintering. On the other hand, the Stage 1 densification model in the initial stage of sintering neglected the long-range operation of the shape-changing mechanisms, which is not necessarily justified. In reality, both the densifying mechanisms and the shape-chang-

* Strictly speaking, $\delta V$ is slightly less than $-2\pi r d\rho$. However, this effect is negligibly small.
ing mechanisms may cooperate at any point in Stage 1 to cause the overall shape change of the pores. In this section, on the basis of the present method of analysis shown in Chap. 3, we will extract the contribution of the two possible shape-changing mechanisms in Stage 1.

As described in Chap. 2, the shape-changing mechanisms (Mechanisms 3 and 4) cause the diffusion-controlled shape change of the pores without introducing their volume change. In Stage 1, the surface of the pores has periodic irregularities with the three-fold symmetry as shown in Fig. 2(a). The shape-changing mechanisms may occur in order to reduce such surface irregularities and the shape change of the pores continues till the pores have an equilibrium circular shape. Therefore, the problem to derive the rate equations for the shape-changing mechanisms is reduced to the problem to obtain rate equations for the diffusion-controlled diminution of the periodic irregularities of the pore surface.

In Appendix, the rate equations for the diffusion-controlled diminution of periodic irregularities on a surface of a semi-infinite material are derived. These results will be used to derive the rate equation for the shape-changing mechanisms.

Since three grain boundaries meet a pore, the three-fold symmetry of the pore shape is always maintained. Therefore, the wavelength of the periodic irregularities of the pore surface, \( \lambda_p \), can be assigned as

\[
\lambda_p = \left(2\pi \sqrt{r_e^3}\right)/3, \quad \ldots \quad \ldots \quad (26)
\]

where, \( r_e \): the radius of a cylinder having the same cross-sectional area as the pore (an equivalent pore).

From the conservation of matter in one regular-triangular region in Fig. 2(a), we have

\[
\sqrt{3}/(2\pi) R^2 = \pi r_e^2, \quad \ldots \quad \ldots \quad (27)
\]

Using this equation and Eq. (7), \( r_e \) can be approximately expressed in terms of \( x/R \) as

\[
r_e \approx \sqrt{\frac{2}{3}} \frac{\sqrt{R}}{2\pi} \left\{ R \sqrt{1 - \left(2\sqrt{3}/(6\sqrt{3}-3\pi)\right)(x/R)^2}\right\} \approx 0.227 R \sqrt{1 - 3.58(x/R)^2}, \quad \ldots \quad \ldots \quad (28)
\]

To apply the results in Appendix, the shape of the pore surface is approximated using a polar coordinate system (\( r_p, \theta_p \)) with its origin at the center of the pore (Fig. 4) as

\[
\theta_p = \theta_e + A \cos(3\theta_p), \quad \ldots \quad \ldots \quad (29)
\]

where, \( A \): the average amplitude of the periodic irregularities of the pore.

Then, from Eqs. (26), (A-10) and (A-16), the shape-changing rate, \( \partial A/\partial t \), and the relaxation time, \( \tau_p \), can be written as

\[
\frac{\partial A}{\partial t} = -\frac{A}{\tau_p}, \quad \ldots \quad \ldots \quad (30)
\]

and

\[
\tau_p = \frac{2kT_0}{27\pi D_r \left(1 + 6W/D_r \right) \Omega^*}, \quad \ldots \quad \ldots \quad (31)
\]

Since \( \tau_p \) is proportional to the third or fourth power of \( r_e \), \( \tau_p \) becomes small as \( r_e \) becomes small. Therefore, even when Stage 1 is initially controlled by the densifying mechanisms, the long-range operation of the shape-changing mechanisms can become progressively important. At some point in Stage 1, because of the onset of the long-range operation of the shape-changing mechanisms, the rate equations obtained by the Stage 1 densification model, i.e., Eqs. (13), (15) and (16), may become inadequate to describe the actual process of the Stage 1 sintering. This will be discussed in Chap. 6.

5. Comparison with Previous Studies

As mentioned in Introduction, the sintering rate equations for initial, intermediate and final stages of sintering have been discussed in many studies. For pressureless sintering, the following forms of the rate equations for Mechanism 1 are often quoted for the Stage 1 sintering\(^{5,10}\):

\[
\frac{\partial x}{\partial t} = k_1 W_e D_e \frac{\Omega^*}{kT} \frac{R^e}{x^e} \quad \text{(Stage 1)}, \quad \ldots \quad \ldots \quad (32)
\]

and for the Stage 2 sintering\(^{5,10}\)

\[
\frac{\partial x}{\partial t} = k_2 W_e D_e \frac{\Omega^*}{kT} \frac{1 + r/x}{x^2} \quad \text{(Stage 2)}, \quad \ldots \quad \ldots \quad (33)
\]

where, \( k_1, k_2 \): numerical constants.

Comparison of these equations with Eqs. (13) and (23) reveals that they differ only by terms \((1-2x/3R)\) and \((1+r/x)\), respectively. However, since both \( x/R \) and \( r/x \) are always smaller than one, our derived Eqs. (13) and (23) are essentially the same as the above equations.

In the present study, the cross-sectional area of the volume diffusion is assigned as \( a = 3x \) (Eq. (14)). This assignment enables us to relate the volume diffusion contribution to the solution for the grain-boundary diffusion by a commonly used geometric scaling factor, \( x D_e/W_e D_e \)\(^{5,8,10}\). As a natural result, the rate equations for Mechanism 2 obtained by the present analysis also becomes essentially the same as most of those in the previous literature. On the other hand, some studies assigned \( a \) as the area of the neck surface region\(^{3,4,6,7,9,13}\). According to the previous study\(^{11}\), the former assignment gives the upper limit of the
volume diffusion contribution and the latter assignment gives the lower limit.

Swinkels and Ashby modified Eq. (32) taking into account the local curvature of the pore. For example, their approximate solution, Eq. (2.8) in their paper, for the densifying mechanism controlled by the grain-boundary diffusion in Stage 1 is

\[ \dot{V}_i = -3 \frac{W_i D_{ij}}{kT} \frac{R_{ij}^2}{x} \Omega \frac{K_i}{x} \], \hspace{1cm} (34)

where, \( \dot{V}_i \) is the local curvature of the pore at the base of the neck.

On the other hand, since \( 6 \dot{V}_i = \dot{V} \Omega t = 2(x/R)(\partial x/\partial t) \) from Eq. (10) with \( x = R \theta \), our Eq. (13) can be rewritten approximately by regarding the term \( 2x/3R \) being much smaller compared to one as

\[ \dot{V}_i = 2 \frac{W_i D_{ij}}{kT} \frac{R}{x^3} \Omega \], \hspace{1cm} (35)

Then, if \( -R K_i = 1/(x/R)^2 \), Eqs. (34) and (35) become identical. It is interesting to find from Fig. 3 in the paper by Swinkels and Ashby that such a relationship between \( -R K_i \) and \( x/R \) is in fact approximately satisfied. Therefore, although the present analyses are based on the much simpler geometry of the pore shape, the derived rate equations are in reasonable agreement with those by Swinkels and Ashby.

The above comparison with other studies indicates that the present analyses, based on the change in the overall Helmholtz free energy, can give adequate sintering rate equations for the densifying mechanisms in a much simpler manner without knowing the detailed chemical potential fields while keeping the physics involved clear.

Nicholls and Mullins and Rockland considered the morphological changes of a pore and derived rate equations assuming the operation of only the shape-changing mechanisms. However, since their analytical equations were expressed in terms of the neck width, they can not be compared with Eqs. (30) and (31) in a meaningful manner. Therefore, the applicability of these equations will be examined later by comparing with an experimental study. At this moment, however, we feel it worthwhile to discuss further implications of the role of the shape-changing mechanisms in Stage 1.

6. Rate-controlling Mechanisms in Stage 1

In the Stage 1 densification model, the pore is considered to have the periodic surface irregularities as shown in Fig. 2(a). Using Eqs. (6), the surface area of the pore per unit depth is expressed as

\[ S_p = R (\pi - 6x/R) + 2(x/R)^2 \]. \hspace{1cm} (36)

The equilibrium shape of the pore is a cylinder having a circular cross section of radius \( r_{se} \). Using Eq. (28), the excess surface area of the pore, \( \Delta S \), compared with its equilibrium shape is given by

\[ \Delta S = S_p - 2 \pi r_{se} = R (\pi - 6x/R) + 2(x/R)^2 - 1.42 \sqrt{1 - 3.56(x/R)^2} \]. \hspace{1cm} (37)

From Eqs. (26) and (A-3), the average amplitude of the pore surface irregularities, \( A \), can be regarded as

\[ A = (2 \pi r_{se} / \Delta S)^{1/2} \]. \hspace{1cm} (38)

When only the densifying mechanisms operate according to the Stage 1 densification model, it is found from Eq. (38), that \( A \) decreases with the rate given by

\[ \frac{\Delta A}{\Delta t} = \frac{1}{9 \pi A} \left( \frac{\partial}{\partial t} \frac{\partial (\Delta S)}{\partial t} + \Delta S \frac{\partial r_{se}}{\partial t} \right) \]. \hspace{1cm} (39)

where, \( \frac{\partial (\Delta S)}{\partial t} = \left[ \frac{2}{2 \pi} \frac{2x}{R - 3} + 1.15 \frac{x}{r_{se}} \right] \frac{\partial x}{\partial t} \). \hspace{1cm} (40)

from Eq. (37), and

\[ \frac{\partial r_{se}}{\partial t} = -\frac{0.184 x}{r_{se}} \frac{\partial x}{\partial t} \]. \hspace{1cm} (41)

from Eq. (28).

The superscript "\( d \)" in Eq. (39) means that decrease in \( A \) is due to the operation of the densifying mechanisms according to the Stage 1 densification model.

On the other hand, provided that only the long-range shape-changing mechanisms operate for the geometry shown in Fig. 2(a), Eq. (30) is valid:

\[ \frac{\partial A}{\partial t} = -\frac{A}{\tau_b} \]. \hspace{1cm} (42)

The superscript "\( s \)" means that the decrease in \( A \) is due to the long-range operation of the shape-changing mechanisms.

Here, we introduce a following parameter \( \Sigma \):

\[ \Sigma = [\partial A / \partial t]^s / (\partial A / \partial t)^d \]. \hspace{1cm} (43)

This parameter is a measure of the relative importance of the densifying mechanisms and the shape-changing mechanisms for the diminution of the surface irregularities during Stage 1. When \( \Sigma > 1 \), the contribution of the long-range operation of the shape-changing mechanisms is small. On the other hand, when \( \Sigma < 1 \), it can be expected that the surface irregularities of the pore diminish mainly by the long-range operation of the shape-changing mechanisms. Therefore, a criterion \( \Sigma = 1 \) determines whether the densifying mechanisms (Stage 1 densification model) or the shape-changing mechanisms are dominantly operative in Stage 1.

From Eqs. (38) to (42), we have

\[ \Sigma = \tau_b \left( \frac{1}{2} \frac{\partial (\Delta S)}{\partial t} + \frac{1}{r_{se}} \frac{\partial r_{se}}{\partial t} \right) \]. \hspace{1cm} (44)

Using Eqs. (28), (37), (40) and (41), Eq. (44) can be written as

\[ \Sigma = 1.75 \frac{\tau_b}{R} \left( \frac{\partial x}{\partial t} / 1 + 3.00 (x/R) \right) \]. \hspace{1cm} (45)
where \((\delta s/\delta t)_{i}\) and \(\tau_{p}\) are given in Eqs. (16) and (31), respectively. Eq. (45) can be expressed explicitly as

\[
\Sigma = 0.194 \frac{RD_{b}(1+W_{1}D_{o}/xD_{o})}{W_{1}D_{o}(1+\pi R_{0}D_{o}/6W_{1}D_{o})} \left(\frac{7x}{3R}\right)^{1/4}.
\]

(46)

Let us evaluate the values of \(\Sigma\) using the material data for copper listed in Table 2. Fig. 5(a) shows the calculated relationship between \(\Sigma\) and \(x/R\) for various radii of copper wires at 0.95 \(T_{w}\). It is found that \(\Sigma\) decreases rapidly with increase in \(x/R\). \(\Sigma > 1\) when \(x/R < 0.1\) and \(\Sigma \ll 1\) when \(x/R > 0.35\) are the common characteristics for any wire radius. It is also found that the value of \(\Sigma\) at a certain value of \(x/R\) increases as \(R\) increases. This shows that when \(R\) increases, the Stage 1 densification model becomes applicable for the larger value of \(x/R\).

For the limiting case of \(R \to \infty\), while keeping \(x/R\) and \(\tau_{p}/R\) finite, Eq. (46) reduces to

\[
\Sigma \approx 0.371 \left(\frac{\tau_{p}}{R}\right)^{3/2} \left(\frac{7x}{3R}\right).
\]

(47)

This case corresponds to the case where Mechanisms 2 and 4 are dominant compared respectively with Mechanisms 1 and 3. Eq. (47) shows that \(\Sigma\) does not depend either on sintering temperature or on the absolute magnitude of \(R\), but it depends only on \(x/R\). For the other limiting case of \(R \to 0\), \(\Sigma\) reduces to

\[
\Sigma = 0.194 \left(\frac{W_{1}D_{o}}{W_{1}D_{o}}\right) \left(\frac{1}{x/R}\right)^{1/4} \left(\frac{7x}{3R}\right)^{1/4}.
\]

(48)

Table 2. Material data of copper.13)

\[\begin{array}{ll}
T_{w} & 1356 K \\
\rho & 1.18 \times 10^{-9} m^{3} \\
\pi & 1.72 J/m^{3} \\
\rho_{s} & 6.20 \times 10^{-9} \exp \left(-3.44 \times 10^{-9} \left[J/kT\right]\right) (m^{3}/s) \\
W_{1}D_{o} & 5.12 \times 10^{-9} \exp \left(-1.74 \times 10^{-9} J/kT\right) (m^{3}/s) \\
W_{1}D_{o} & 6.00 \times 10^{-9} \exp \left(-3.41 \times 10^{-9} J/kT\right) (m^{3}/s)
\end{array}\]

where, \(r\): the radius of the pore which has a circular cross section

\[\frac{\partial r}{\partial t}\]: the pore shrinkage rate.

If \(\Sigma \ll 1\) is satisfied, Condition (49) is found to be fulfilled automatically from Eq. (44). Therefore, within the framework of the present theoretical analysis, the criterion of \(\Sigma \ll 1\) not only means the dominant roles of the shape-changing mechanisms in Stage 1, but also it constitutes the sufficient condition for the occurrence of Stage 2.

7. Comparison with Experimental Results by Alexander and Ballufi

Alexander and Ballufi sintered a close-packed bundle of wires and measured the change in the size of the pores.20) They used copper wires of radius 64 \(\mu m\) and sintered these wires at temperatures between 1.173 and 1.348 K (0.865–0.994 \(T_{w}\)).

For the comparison with the present analysis, it is convenient to convert the neck-growth rate equations into the densification rate equations. This conversion can be done as follows.

From simple geometry, we have

\[
\sqrt{3} \cdot \pi \cdot d = \pi R^{2} d/2,
\]

(50)

where, \(d\): the apparent density of the wire aggregate containing pores

\(d_{i}\): the true density of the material (wire).

Using Eq. (7), Eq. (50) can be rewritten as

\[
J = (\pi/2 \sqrt{3}) d_{i} (1-x^{2}/R^{2})^{2}
\]

\[
\approx (\pi/2 \sqrt{3}) d_{i} (1-(x/R)^{2})^{2}.
\]

(51)

Therefore, \(x\) can be expressed by \(R\) and the relative density of the sintering aggregate \(f(=d/d_{i})\) as

![Fig. 5. The relationship between \(\Sigma\) and \(x/R\) for copper wire sintering.](image-url)
\[ x = R \sqrt{3 - \sqrt{3} \frac{\pi}{2f}} \]
\[ = 1.73 R \sqrt{1 - 0.907/f}. \tag{32} \]

Since we consider the close-packed bundle of wires, \( f \) is 0.907 at the beginning of the sintering. Using Eqs. (51) and (52), Eq. (16) can be rewritten as
\[
\frac{1}{D_x} \frac{\partial D_x}{\partial t} = 1.05 \frac{N}{R^2} \frac{[1 - 1.15(1 - 0.907/f)]^{1/2}}{(1 - 0.907/f)^{1/2}}
\]
(Stage 1 densification model), \tag{53}
where \( N \) is given as follows:
\[
N = \frac{D_x}{kT} \left( \frac{1 + W_x}{x D_x} \right) \Omega. \tag{54} \]

Since Eq. (50) holds for Stage 2 as well as Stage 1, from Eq. (20), we obtain,
\[
J = J_0 (1 + 2f^2/R^2). \tag{55} \]
Therefore, \( r \) can be expressed by \( R \) and \( f \) as
\[
J = R \sqrt{(1/f - 1/2)^2}. \tag{56} \]
Then, from Eqs. (55) and (56), Eq. (25) can be also rewritten as
\[
\frac{1}{D_x} \frac{\partial D_x}{\partial t} = 3.82 \frac{N}{R^2} \left( \frac{1}{f - 1/2} \right)^{1/2}
\]
(Stage 2 densification model), \tag{57}
where \( N \) is given in Eq. (54).

From Fig. 5, it is found that the values of \( x/R \) giving \( \Sigma = 1 \) for \( R = 64 \mu \text{m} \) are almost the same for the above temperature range and they are about 0.22. This value gives \( f = 0.922 \) from Eq. (51). Therefore, for the values of \( f \) from 0.907 to 0.922, the Stage 1 densification model is conceived to be valid under their experimental conditions.

On the other hand, as discussed in the previous chapter, the Stage 2 densification model is valid when \( \Sigma < 1 \). According to the present model, the validity of the Stage 2 model is assured at \( x/R = 0.439 \), as analyzed in Chap. 4. Fig. 5(b) indicates that even for \( R \rightarrow \infty \), this value of \( x/R \) indeed gives a small value of \( \Sigma = 4.08 \times 10^{-8} \). Therefore, although rather arbitrarily, we assume that \( \Sigma = 4 \times 10^{-2} \) is small enough compared to one for the validity of the Stage 2 model. For \( R = 64 \mu \text{m} \) and \( 0.865 T_a \leq T \leq 0.994 T_a \), this value of \( \Sigma \) gives the values of \( x/R \) around 0.39 from Fig. 5(b) or the values of \( f \) around 0.955 from Eq. (52). Therefore, by using Eqs. (53) and (57), we can obtain the theoretical densifying rate as a function of \( f \). Since Mechanism 2 is dominant under the experimental conditions of Alexander and Balluffi, \( N \) defined in Eq. (54) can be approximated as \( D_x \Omega / kT \).

Then, we can normalize the densification rate by \( N \) and \( R^2 \). Fig. 6 shows the relationship between the normalized theoretical densification rate by the Stage 1 and Stage 2 densification models, \((\partial J/\partial t)(R^2)_x(N)\) and \((\partial J/\partial t)(R^2)_x(N)\), and the relative density, \( f \). For the values of \( f \) from 0.922 to 0.955, the Stage 1 densification model gives the upper limit and the Stage 2 densification model gives the lower limit. For this region of \( f \), we connect the two curves for the Stage 1 and Stage 2 densification models by a broken line as shown in Fig. 6.

In Fig. 6, we also plotted the experimental data by Alexander and Balluffi at various temperatures, by using Table 1 in their paper. The data points shown in Fig. 6 are restricted to the ones obtained before the disappearance of some grain boundaries by grain growth. Although these show considerable scatter, they appear to lie along the theoretical curve derived from the present theory. We think that this agreement indicates the important role of the shape-changing mechanisms in Stage 1 as discussed in the present study.

8. Conclusions

By considering the change in the free energy as the driving force for the diffusive flow of matter, the thermodynamics and kinetics of the diffusion-controlled sintering were examined.

(1) Various sintering rate equations for wires such as neck-growth, or densifying rate equations for the Stage 1 (initial stage) and Stage 2 (intermediate and final stage) sintering were derived.

(2) Our method of analysis is much simpler than the conventional one based on the evaluation of the local chemical potential field, and yet the derived sintering rate equations for densifying mechanisms were essentially the same as those derived previously for all practical purposes.

(3) Rate equations for the diffusional shape change of pores in the sintering aggregate were newly derived. New criteria for the change in the sintering stages from Stage 1 to Stage 2 were proposed.

(4) Various experimental results on the variation of the densifying rate during sintering obtained by Alexander and Balluffi were well explained by the present theory.
Acknowledgments

We would like to express our thanks to Professors S. Miura and S. Hashimoto for their encouragement during the course of the preparation of the manuscript. We would also appreciate valuable discussions given by Professor K. T. Aust.

REFERENCES

1) G. C. Kuczynski: *Trans. Am. Inst. Min. Metall. Pet. Eng.*, 185 (1949), 169.
2) W. D. Kingery and M. Berg: *J. Appl. Phys.*, 26 (1955), 1205.
3) R. L. Coble: *J. Am. Ceram. Soc.*, 41 (1958), 55.
4) D. L. Johnson and J. B. Cutler: *J. Am. Ceram. Soc.*, 46 (1963), 541.
5) T. L. Wilson and P. G. Shevonon: *Trans. Metall. Soc. AIME*, 236 (1966), 48.
6) D. L. Johnson: *J. Appl. Phys.*, 40 (1969), 192.
7) D. L. Johnson: *J. Am. Ceram. Soc.*, 53 (1970), 574.
8) M. F. Ashby: *Acta metall.*, 22 (1974), 275.
9) R. L. Eadie, D. S. Wilkinson and G. C. Weatherly: *Acta metall.*, 22 (1974), 1185.
10) R. L. Eadie and G. C. Weatherly: *Scr. metall.*, 9 (1975), 283.
11) R. L. Eadie, G. C. Weatherly and K. T. Aust: *Acta metall.*, 26 (1978), 759.
12) W. K. Lee, R. L. Eadie, G. C. Weatherly and K. T. Aust: *Acta metall.*, 26 (1978), 1837.
13) F. B. Swinkels and M. F. Ashby: *Acta metall.*, 29 (1981), 259.
14) S. Onaka, M. Kato and T. Mori: *Metall. Trans. A*, 17A (1986), 1949.
15) S. Onaka, M. Kato, S. Soeta and T. Mori: *Trans. Jpn. Inst. Met.*, 29 (1988), 284.
16) S. Onaka, M. Kato and T. Mori: Sintering '87, Proc. of the ISS Symp., ed. by S. Somiya, M. Shimada, M. Yoshimura and R. Watanabe, Elsevier Appl. Sci., London, 1988, 334.
17) C. H. Hsu and A. G. Evans: *Acta metall.*, 31 (1983), 189.
18) R. Raj and M. F. Ashby: *Acta metall.*, 23 (1975), 653.
19) M. V. Speight and W. Beere: *Metal Sci.*, 9 (1975), 190.
20) F. A. Nichols and W. W. Mullins: *J. Appl. Phys.*, 36 (1965), 1826.
21) J.G.R. Rockland: *Acta metall.*, 14 (1966), 1273.
22) T.-J. Chuang, K. I. Kagawa, J. R. Rice and L. B. Sills: *Acta metall.*, 27 (1979), 265.
23) B. H. Alexander and R. W. Balluffi: *Acta metall.*, 5 (1957), 666.

Appendix

Matter Transport at a Surface of a Semi-infinite Material

When a semi-infinite material has periodic irregularities at its surface, diffusion-controlled mechanisms flatten the surface. The relaxation times for the surface flattening can be calculated by considering the change in the Helmholtz free energy.

We examine two-dimensional periodic surface irregularities of the surface along the \( x_1 \) direction (see Fig. A-1) and approximate it as a cosine function:

\[
x_2 = A(t) \cos (2\pi x_1 / \lambda), \quad \text{.........(A-1)}
\]

where, \( A(t) \): the amplitude of the irregularities and a function of time

\[
\lambda: \text{the wavelength of the irregularities}.
\]

The area, \( S_0 \), of the surface per \( \lambda \) and unit depth (measured perpendicular to the sheet in Fig. A-1) is expressed as

\[
S_0 = 4 \int_0^{2/4} \sqrt{1 + [2\pi A(t) / \lambda]^2 \sin^2 (2\pi x_1 / \lambda)} \, dx_1.
\quad \text{.........(A-2)}
\]

When \( A(t) \) is much smaller than \( \lambda \), \( S_0 \) can be approximated by the function \( S \):

\[
S = [\pi^2 A(t) / \lambda^2 + \lambda]. \quad \text{.........(A-3)}
\]

This approximation is reasonable for a rather wide range of \( A(t) / \lambda \). Even if \( A(t) / \lambda \) is 0.55, \( S \) differs from \( S_0 \) by only 15%.

The change in the Helmholtz free energy of the material during the surface flattening consists entirely of the change in the surface energy. Then, the excess Helmholtz free energy of the material having the periodically irregular surface as compared with the equilibrium state (the completely flat surface), \( \Delta F \), per \( \lambda \) and unit depth is expressed as:

\[
\Delta F = \Gamma (S - S_0) = [\pi^2 \Gamma A(t) / \lambda^3].\quad \text{.........(A-4)}
\]

When the diffusive flow of atoms causes the change in the amplitude by \( \delta A(t) \) during an infinitesimal time interval, \( \delta t \), the change in the Helmholtz free energy, \( \delta(\Delta F) \), is given by Eq. (A-4):

\[
\delta(\Delta F) = [2\pi^2 \Gamma A(t) / \lambda^3].\quad \text{.........(A-5)}
\]

Since the total volume of matter per \( \lambda \) and unit depth that must be transported to realize the flat surface is calculated as

\[
2 \int_0^{2/4} A(t) \cos (2\pi x_1 / \lambda) \, dx_1 = [\pi A(t) / \lambda^2],\quad \text{.........(A-6)}
\]

the volume of the matter transported by diffusion, \( \delta V \), and the number of transported atoms, \( \delta n \), during the time interval \( \delta t \) are related as,

\[
\delta V = -[\delta \delta A(t) / \pi] = \Omega \delta n. \quad \text{.........(A-7)}
\]

Using Eqs. (A-5) and (A-7) and the basic equation to derive rate equations for diffusion-controlled mechanisms, Eq. (4), we obtain

\[
\frac{\delta A(t)}{\delta t} = -2\pi^2 \frac{DG}{kT} \frac{\Gamma}{\lambda^3} A(t). \quad \text{.........(A-8)}
\]

Boundary conditions to solve Eq. (A-8) are chosen as

\[
A(0) = A_0 \quad \text{when} \; t = 0, \quad \text{and} \; A(\infty) = 0 \quad \text{when} \; t = \infty. \quad \text{.........(A-9)}
\]
Then, we obtain $A(t)$ as a function of time, $t$:

$$A(t) = A_0 \exp \left( -\frac{t}{\tau} \right), \quad \text{...........(A-10)}$$

where,

$$\tau = \frac{kT}{2\pi^4 D \Omega \rho} \left( \frac{\rho}{\alpha} \right) \quad \text{...........(A-11)}$$

is the relaxation time for the flattening of the surface.

Two different diffusion mechanisms; (1) surface diffusion, and (2) volume diffusion, are considered to occur. The diffusion distance, $l$, for both diffusion mechanisms is approximately estimated to be $\lambda/4$.

When the surface diffusion is dominant, $D$ and $\alpha$ in Eq. (A-11) become

$$D = D_s \quad \text{and} \quad \alpha = 2W_s, \quad \text{...........(A-12)}$$

where, $D_s$: the surface diffusion coefficient

$W_s$: the effective surface diffusion thickness.

On the other hand, when the volume diffusion is dominant, we have

$$D = D_v \quad \text{and} \quad \alpha = 2(\lambda/4), \quad \text{...........(A-13)}$$

From Eqs. (A-11) and (A-12), the relaxation time, $\tau_s$, for the surface diffusion is obtained as follows:

$$\tau_s = \frac{kT}{16\pi^4 W_s D_s \Omega \rho} \lambda^3. \quad \text{...........(A-14)}$$

When the surface flattening is governed by the volume diffusion, Eq. (A-11) becomes:

$$\tau_s = \frac{kT}{4\pi^4 D_s \Omega \rho} \lambda^3. \quad \text{...........(A-15)}$$

from Eq. (A-13).

When both the surface diffusion and volume diffusion cooperate, the combined relaxation time becomes:

$$\tau = \frac{kT \lambda^3}{4\pi^4 D_s \Omega \rho \left( 1 + \frac{4W_s D_s}{\lambda^2 D_v} \right)^3} \quad \text{...........(A-16)}$$

from Eqs. (A-14) and (A-15).

The relaxation times given by Eqs. (A-14) and (A-15) are essentially the same as those previously obtained by Chuang et al. by considering, as usual, the gradient of the chemical potential of an atom at the surface of a material.21